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Statistical-Mechanical Theory of Transport in Fluids*

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A statistical-mechanical theory of transport processes in fluids of g components is presented on the assumption that the macroscopic state of the system can be described by one velocity, one temperature, and g mass-density fields. The formulation is based on the explicit recognition of the fact that there are two relaxation processes in fluids: one is the macroscopic process of attaining spatial uniformity and is represented by the hydrodynamical equations, whereas the other is the microscopic process of attaining internal thermal equilibrium in small mass elements of macroscopic size and determines the transport coefficients. For instance, in dilute gases the microscopic process is the relaxation process in momentum space. The coupling of the two processes is investigated to obtain the dissipative terms in the transport equations with the aid of the correlation function method outlined in a previous paper. The hydrodynamical equations, the equation of entropy balance, and the linear relations between the thermodynamic fluxes and affinities are thus derived with explicit expressions for the coefficients of viscosity, thermal conductivity, and diffusion, which are valid for liquids as well as for gases. The classical limits of these expressions, $\hbar \to 0$, are somewhat different from those obtained by Green for classical mechanical systems.

1. INTRODUCTION

STATISTICAL-MECHANICAL theories of transport processes in liquids have been investigated in a number of papers,[1-6] with the purposes of deriving the hydrodynamical equations from molecular dynamics and of obtaining the transport coefficients in terms of molecular quantities. There seem to be two fundamental approaches to these problems; one, the distribution function method, is concerned with the explicit determination of nonequilibrium phase-space distribution functions used in the formulation of averages of dynamical quantities which correspond to macroscopic properties such as the pressure tensor and the heat flow. The other approach, the correlation function method, is concerned with the direct determination of the change in time of the state variables and the transport coefficients are expressed in terms of the correlation functions of equilibrium fluctuations of the appropriate dynamical quantities. The explicit introduction of nonequilibrium distribution functions is not necessary. The above investigations, except that of Green, belong to the first approach. The possibility of the second approach can be seen in Onsager's work on the reciprocity theorem[7] and a further development of it.[8]

In the present paper we discuss a statistical-mechanical description of transport processes in the framework of the correlation function method outlined in a previous paper,[9] and we derive the hydrodynamical equations with explicit expressions for the coefficients of viscosity, thermal conductivity, and diffusion in

[1] N. N. Bogoliubov, *Problems of Dynamical Theory in Statistical Physics* (Technical Press, Moscow, 1946).

[2] J. G. Kirkwood, J. Chem. Phys. 14, 180 (1946); Zwanzig, Kirkwood, Stripp, and Oppenheim, J. Chem. Phys. 21, 2050 (1953).

[3] M. Born and H. S. Green, *A General Kinetic Theory of Liquids* (Cambridge University Press, Cambridge, 1949).

[4] K. P. Gurov, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 110 (1948); 20, 279 (1950).

[5] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950); R. J. Bearman and J. G. Kirkwood, J. Chem. Phys. 28, 136 (1958).

[6] M. S. Green, J. Chem. Phys. 22, 398 (1954).

[7] L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931).

[8] Kubo, Yokota, and Nakajima, J. Phys. Soc. Japan 12, 1205 (1957).

[9] H. Mori, J. Phys. Soc. Japan 11, 1029 (1956). This will be referred to hereafter as (I).

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fluids of g components without chemical reactions. Furthermore we attempt to provide a statistical-mechanical foundation of the thermodynamics of irreversible processes in continuous systems.[10] The derivations are developed with the aid of quantum statistics, but the classical formulation can be deduced easily. We consider fluids whose macroscopic state can be described by one local velocity, one local temperature, and g local mass densities, and confine ourselves mainly to linear dissipative processes.

In Sec. 2, we describe the basis of the present theory, and emphasize that there are two kinds of relaxation processes in fluids; one is the hydrodynamical process of attaining uniformity in coordinate space, whereas the other is the microscopic process of attaining internal thermal equilibrium in small mass elements of macroscopic size. With the aid of the fact that the relaxation times for the two relaxation processes are, in order of magnitude, quite different from each other, we derive a macroscopic equation for the change in time of the local state variables such as the densities of molecules, momentum, and energy. In Sec. 3, we investigate the coupling of the two relaxation processes and find it to be expressed by the sum of the products of two kinds of quantities. One of these are the affinities,[10] namely the driving forces of the hydrodynamical process. The other kind are dynamical fluxes whose averages in a certain manner become the thermodynamic fluxes conjugate to the affinities, and the autocorrelation functions of equilibrium fluctuations in time of these dynamical fluxes are related to the transport coefficients. The time dependence of the autocorrelation functions represents the elementary processes which determine the attainment of internal thermal equilibrium in small mass elements.

Section 4 is concerned with a statistical-mechanical derivation of the irreversible production of entropy and of the linear relations between the thermodynamic fluxes and affinities, and with a general consideration of the asymptotic behavior of the time correlation of fluxes. In Sec. 5, the hydrodynamical equations and the equation of entropy balance are derived, and the physical pictures of the thermodynamic fluxes and the entropy flow are discussed.

In Sec. 6, the conservation laws for the local density operators of number of molecules, momentum, and energy are derived from the Heisenberg equation of motion, and the explicit expressions for the dynamical fluxes and the transport coefficients are obtained. The last section is devoted to a brief summary, in which the physical framework of the present theory is discussed, and to a brief comparison with the work of Green.[6] The application of the present theory to the problem of thermoelectricity yields the same expression for the static electrical conductivity as Kubo's theory[11]

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[10] S. R. De Groot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1952).

[11] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).

based on the linear response of thermodynamic systems to mechanical disturbances.

2. GENERAL CONSIDERATION

We consider a liquid in a nonequilibrium state and in contact with heat and mass reservoirs. The equilibrium state which the liquid approaches can be described by the grand canonical ensemble[12]

$$\rho_0 = Z_0^{-1} \exp(-\beta H_\mu), \qquad (2.1)$$

$$H_\mu = H - \sum_{k=1}^{g} \mu_0{}^k N^k, \qquad (2.2)$$

where H is the Hamiltonian of the liquid, N^k the number operator of molecules of component k, and $1/\beta$ and $\mu_0{}^k$ are, respectively, the equilibrium values of the temperature multiplied by the Boltzmann constant and the chemical potential of component k. Equation (2.2) satisfies the relation

$$\{H_\mu, H\} = 0, \qquad (2.3)$$

where the symbol $\{ \ , \ \}$ denotes the Poisson bracket in the classical case, and the commutator divided by $(i\hbar)$ in the quantum-mechanical case.[13]

The nonequilibrium state changes in time toward the equilibrium state (2.1) via, approximately, the local equilibrium states specified by the local temperatures $\beta(\mathbf{x})$ and the local chemical potentials $\mu^k(\mathbf{x})$,

$$\rho_t = Z^{-1} \exp\left\{ -\int \beta(\mathbf{x})[E(\mathbf{x}) - \sum_k \mu^k(\mathbf{x}) n^k(\mathbf{x})] d\mathbf{x} \right\}, \quad (2.4)$$

where $E(\mathbf{x})$ is the internal energy density operator and $n^k(\mathbf{x})$ the number density operator of molecules of component k. The subscript t expresses the time dependence of the macroscopic state parameters $\beta(\mathbf{x})$, $\mu^k(\mathbf{x})$, and the local velocity.[14] Integration extends over the entire coordinate space of the liquid unless otherwise indicated. The integrand is the grand canonical ensemble applied to uniform small portions of macroscopic size, the order of magnitude of whose linear extent l is very large compared to a microscopic distance l_0, for example, the mean free path of molecules in the case of dilute gases, and is small compared to the linear extent of the liquid L;

$$l_0 \ll l < L. \qquad (2.5)$$

The physical basis for the validity of (2.4) is the fact that each small mass element attains, approximately, internal thermal equilibrium very quickly, say in a short time interval τ_0, before equilibrium between mass elements is reached. Here the following situation is

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[12] D. ter Haar, *Elements of Statistical Mechanics* (Rinehart and Company, Inc., New York, 1954), Chap. VII.

[13] L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), Sec. 23.

[14] The internal energy density $E(\mathbf{x})$ contains the macroscopic local velocity as a parameter. See Eq. (3.8).

important[15]: the relaxation time, τ_r, for the macroscopic state to attain complete equilibrium becomes longer as the size of the system becomes larger, whereas τ_0 is a constant; hence we have

$$\tau_0 \ll \tau_r, \qquad (2.6)$$

since the linear extent of the liquid L is supposed to be very large. The time τ_0 can be defined, exactly, as the average relaxation time for the spatially uniform small mass elements of macroscopic size to attain complete equilibrium when the interaction with the neighboring mass elements has been cut off. In the actual fluids this microscopic relaxation, however, is disturbed by the influence of the neighboring mass elements, namely by the coupling with the hydrodynamical process of attaining equilibrium between mass elements, and forms a quasisteady state. Therefore, the complete termination of this relaxation takes place only when complete thermal equilibrium has been reached. In the case of dilute gases, the microscopic relaxation becomes the relaxation process in momentum space so that the time τ_0 is of the order of magnitude of the mean free time of molecules,[16] and the following approximate relation can be obtained[7]:

$$\tau_r / \tau_0 \sim (l/l_0)^2. \qquad (2.7)$$

The relation (2.7) leads to the fact that, when the system is close to complete equilibrium so that the measure of spatial uniformity l is of the order of the linear extent of the system L, τ_r tends to infinity in proportion to L^2 as $L \to \infty$. The local thermodynamical quantities $\beta(\mathbf{x})$ and $\mu^k(\mathbf{x})$ can thus be defined so that the macroscopic description of nonequilibrium states becomes possible. In order to be able to define one temperature for each mass element of the fluid we neglected relaxation effects such as the energy transfers between the translational and internal degrees of freedom of polyatomic molecules, and between the ion and electron systems in the gas discharge plasma.

The average value of a dynamical quantity F is given by

$$\langle F \rangle(t) = \mathrm{Tr}\, F\rho(t), \qquad (2.8)$$

where $\rho(t)$ is the density matrix of the liquid at time t. The local equilibrium distribution is determined from the precise distribution $\rho(t)$ by the fact that, in parallel to the kinetic theory of dilute gases,[17] the state parameters involved in the local equilibrium distribution (2.4), the local temperature, the local chemical potentials, and the local velocity,[14] are to be considered to be deter-

[15] L. Landau and E. Lifshitz, *Statistical Physics* (State Technical Press, Moscow, 1951), Chap. I.

[16] H. Mori, Phys. Rev. **111**, 694 (1958). This will be referred to hereafter as (II).

[17] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, Cambridge, 1939).

mined by the requirements

$$\langle E(\mathbf{x}) \rangle_t = \langle E(\mathbf{x}) \rangle(t),$$
$$\langle n^k(\mathbf{x}) \rangle_t = \langle n^k(\mathbf{x}) \rangle(t), \qquad (2.9)$$
$$\langle \mathbf{j}(\mathbf{x}) \rangle_t = \langle \mathbf{j}(\mathbf{x}) \rangle(t),$$

where the left-hand side of each equation denotes the average with the local equilibrium distribution

$$\langle F \rangle_t = \mathrm{Tr}\, F\rho_t. \qquad (2.10)$$

The quantity $\mathbf{j}(\mathbf{x})$ is the momentum density operator with which the local velocity is defined as in (3.7). The precise distribution $\rho(t)$ deviates but slightly from the local equilibrium distribution,

$$\rho(t) = \rho_t + \rho'(t), \qquad (2.11)$$

and it can be seen from (2.9) that the deviation must satisfy the relation

$$\mathrm{Tr}\, Q\rho'(t) = 0, \qquad (2.12)$$

where Q is a linear function of $E(\mathbf{x})$, $n^k(\mathbf{x})$, and $\mathbf{j}(\mathbf{x})$.

To determine the change in time of the average value, we need the equation of motion for $\rho(t)$ [or $F(t)$]. Since the liquid is supposed to be very large, the quantities of interest are the local densities, such as the densities of molecules, momentum, and energy, at points very remote from the boundary of the liquid. Therefore, we can neglect the interaction with the reservoirs in the evaluation of the time dependence of these local quantities in such short time intervals τ that

$$\tau \ll \tau_r. \qquad (2.13)$$

Thus we obtain[9]

$$\rho(t+s) = U(s)\rho(t)U^\dagger(s), \quad 0 < s < \tau, \qquad (2.14)$$

$$U(s) = \exp(-isH/\hbar) = U^\dagger(-s), \qquad (2.15)$$

where H is the Hamiltonian operator of the liquid used in (2.2) and does not include the interaction with the reservoirs. Use of (2.8) and (2.14) leads to

$$\langle F \rangle(t+s) = \mathrm{Tr}\, F(s)\rho(t), \quad 0 < s < \tau, \qquad (2.16)$$

where

$$F(s) = U^\dagger(s)FU(s) \qquad (2.17)$$

is the Heisenberg representation of F following the equation of motion

$$dF(s)/ds = \dot{F}(s) \equiv \{F(s), H\}. \qquad (2.18)$$

It is worth while to observe here that (2.16) enables us to investigate the change in time of the average value of a dynamical quantity by following its temporal development rather than the temporal development of the density matrix, so that the second approach stated at the beginning of Sec. 1 becomes possible.

As has been discussed in (I), the time differential of macroscopic state variables appearing in the hydrodynamical equations is to be interpreted, from the microscopic point of view, as a quotient of differences,

namely

$$\frac{\delta}{\delta t}\langle F\rangle(t) = \frac{1}{\tau}\int_0^\tau ds\,\frac{d}{ds}\langle F\rangle(t+s),\qquad(2.19)$$

for the corresponding dynamical quantity F. The time interval will turn out later to be such that

$$\tau_0\ll\tau\ll\tau_r.\qquad(2.20)$$

But for the present we assume only $\tau\ll\tau_r$, (2.13), as a natural requirement. Equation (2.19) can be written with the aid of (2.16) as

$$\frac{\delta}{\delta t}\langle F\rangle(t) = \mathrm{Tr}\,\dot{F}\bar{\rho}(t),\qquad(2.21)$$

where

$$\bar{\rho}(t) = \frac{1}{\tau}\int_0^\tau ds\,\rho(t+s),\qquad(2.22)$$

means the time-smoothed density matrix over the time interval τ. Let us denote the deviation of the time-smoothed density matrix from the local equilibrium distribution by $\bar{\rho}'(t)$ [18]:

$$\bar{\rho}(t) = \rho_t + \bar{\rho}'(t).\qquad(2.23)$$

Then we have

$$\frac{\delta}{\delta t}\langle F\rangle(t) = \langle\dot{F}\rangle_t + [\dot{F}],\qquad(2.24)$$

where

$$[\dot{F}] = \mathrm{Tr}\,\dot{F}\bar{\rho}'(t),\qquad(2.25)$$

namely the square bracket implies an average formed with the $\bar{\rho}'(t)$. To derive the hydrodynamical equations, we shall take as F the local densities mentioned before (2.13). Then $\dot{F}$ consists of two parts:

$$\dot{F} = Q + I,\qquad(2.26)$$

such that Q is an operator satisfying the characteristic relation of macroscopic quantities, (2.12), and I is an operator characteristic of the microscopic processes taking place in the system. By taking the time average of (2.12) over the time interval τ, we obtain [18]

$$[Q] = 0.\qquad(2.27)$$

The second term of (2.24) arises from the deviation of the density matrix from the local equilibrium distribution, and will be shown to yield the dissipative terms describing the phenomena of viscosity, thermal conduction, and diffusion. We calculate this term with the approximation of linear deviation of the macroscopic state of the system from complete equilibrium, regarding the first term, namely the ideal fluid equa-

tions [19] as the zeroth approximation. Use of (2.23) and (2.14) leads to

$$\bar{\rho}'(t) = \frac{1}{\tau}\int_0^\tau \rho(t+s)ds - \rho_t,$$

$$= \int_0^\tau\left(1-\frac{s}{\tau}\right)U(s)\{H,\rho(t)\}U^\dagger(s)ds$$
$$+[\rho(t)-\rho_t].\qquad(2.28)$$

For further reduction of this equation we introduce the following approximation. If one neglects the deviation of the precise distribution from the local equilibrium distribution, $\rho'(t+s)$, throughout the time interval $s=0$ to $s=\tau$, then the $\bar{\rho}'(t)$ vanishes [18] so that (2.24) leads to the ideal fluid equations without any dissipative terms. [19] Therefore we neglect the deviation at only the initial time of that time interval,

$$[\rho(t+s)]_{s=0} = \rho_t,\qquad(2.29)$$

and calculate contributions from the deviation developed, thereafter, according to the equation $\rho(t+s) = U(s)\rho_t U^\dagger(s)$. From (2.12) we see that $\rho(t)$ and ρ_t describe equivalently the macroscopic state of the system. Therefore it is physically clear that our distribution which starts from the frozen state ρ_t approaches the precise distribution rapidly as a result of the excitation of the microscopic processes with decay time τ_0 due to the interaction between mass elements. In fact we can consider that the difference vanishes after a lapse of time of the order of τ_0. This follows from the fact that the difference in the corresponding microscopic states is removed by the spontaneous decay of the previously-excited microscopic processes. In the calculation of the over-all contribution during the time interval τ, therefore, the error due to the approximation (2.29) can be estimated to be at most of the order of magnitude of $(\tau_0/\tau)|\rho(t)-\rho_t|$ and hence can be neglected if $\tau\gg\tau_0$ as in the present case. This is the physical basis for the validity of the coarse-graining approximation (2.29). Insertion of (2.29) into (2.28) leads to

$$\bar{\rho}'(t) = \int_0^\tau ds\left(1-\frac{s}{\tau}\right)U(s)\int_0^\beta d\lambda\,\exp[-\lambda(H_\mu+R)]$$
$$\times\dot{R}\,\exp[\lambda(H_\mu+R)]\rho_t U^\dagger(s),\qquad(2.30)$$

where we have rewritten the local equilibrium distribution (2.4) as

$$\rho_t = Z^{-1}\exp[-\beta(H_\mu+R)],\qquad(2.31)$$

and made use of the identity [11]

$$\{H,e^{-\beta A}\} = \int_0^\beta d\lambda\,e^{-\lambda A}\{A,H\}e^{\lambda A}e^{-\beta A}.\qquad(2.32)$$

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[18] Since the macroscopic state parameters do not change appreciably in the time interval τ, the time average of the local equilibrium distribution over the τ, $\bar{\rho}_t$, satisfies the relation $\bar{\rho}_t\simeq\rho_t$. Therefore to this approximation $\bar{\rho}'(t)$ can be considered from (2.11) to be the time average of $\rho'(t)$ over the τ.

[19] The first term leads to $\delta\langle F\rangle(t)/\delta t = \langle Q\rangle_t$ with the aid of the relation $\langle I\rangle_t=0$, which results from (3.42). This equation will be seen to lead to the ideal fluid equations without the dissipative terms.

Equation (2.30) is of the order of the deviation of the macroscopic state from complete equilibrium, R, so that we can neglect the R factors in the exponentials if we limit the analysis to linear dissipative systems close to complete equilibrium. Thus use of (2.25), (2.26), (2.27), and (2.30) leads to

$$[\dot{F}] = [I] = \int_0^\tau ds \left(1 - \frac{s}{\tau}\right) \Phi(I,\dot{R};s), \quad (2.33)$$

where we have defined the function

$$\Phi(I,J;s) = \int_0^\beta d\lambda \langle \exp(\lambda H_\mu) I(s) \exp(-\lambda H_\mu) J \rangle^0$$

$$= \Phi(J,I;-s), \quad (2.34)$$

with the symbol

$$\langle G \rangle^0 = \operatorname{Tr} G\rho_0. \quad (2.35)$$

In the classical limit, (2.34) becomes the correlation function

$$\Phi(I,J;s) = \beta \langle I(s)J \rangle^0. \quad (2.36)$$

The asymptotic property of the correlation function at $s \to \infty$ has been investigated by Kubo.[11] In accordance with (I), we simply assume here that $\Phi(I,\dot{R};s)$ vanishes in a time interval τ_c much shorter than τ. Then (2.33) becomes

$$[I] = L(I,\dot{R}) \equiv \int_0^{\tau_c} \Phi(I,\dot{R};s)ds. \quad (2.37)$$

This assumption will be considered in Sec. 4. Equation (2.37) is fundamental for the derivation of molecular expressions for the transport coefficients of linear dissipative systems.

The integrand of (2.37) can be reduced to the auto-correlation functions of the dynamical fluxes defined by (4.13). These correlations functions, as has been shown in (II), express in the case of dilute gases the relaxation processes in momentum space associated with the fluxes, and decay approximately exponentially to zero in times comparable to the mean free time of molecules. The time interval τ_0 defined just after (2.6) can thus be in this case identified with τ_c. From the following sections, this identification seems to be possible also in the case of liquids. The integration in (2.37) can be extended formally to infinity:

$$L(I,\dot{R}) = \int_0^\infty \Phi(I,\dot{R};s)ds, \quad (2.38)$$

which is guaranteed, in general,[8] by the fact that the relaxation time τ_r becomes infinity by extending the volume of the system to infinity.

The physical meaning of (2.37) will be investigated in detail in the last section, but it may be worth while to note some points here. The integrand may be con-

sidered to express the microscopic relaxation in isolated and spatially uniform mass elements discussed after (2.6) and we shall refer to this as an unperturbed relaxation. Let us now suppose a macroscopic process described by the ideal fluid equations.[19] This process couples with the unperturbed relaxation in the actual fluids, and the mechanism in the dilute gas for instance is the collisions between molecules from different mass elements. This coupling can be described by the quantity $\dot{R}$ in our formulation and produces the deviation of the density matrix from the local equilibrium distribution which introduces the dissipative terms in the hydrodynamical equations.[20] The relaxation of the macroscopic state to complete equilibrium is thus a consequence of this coupling. A further physical consequence of the coupling is the continual excitation of the modes of unperturbed relaxation in the small mass elements which gives rise to a quasi-steady process of attaining internal equilibrium in each mass element in the fluid. The decomposition of this quasi-steady process into a superposition of elementary processes, each one represented by the time-correlation function of the corresponding dynamical flux, corresponds to the mathematical approximation of restricting the deviation from complete equilibrium to linear terms.

3. CALCULATION OF $\dot{R}$

The quantity $\dot{R}$ appearing in (2.37), as pointed out in the preceding section, expresses the coupling between the microscopic relaxation process in mass elements and the hydrodynamical process. This quantity can be written from the definition of R, (2.31), as

$$\dot{R} = \{R,H\} = \int \dot{Y}(\mathbf{x})d\mathbf{x}, \quad (3.1)$$

where

$$Y(\mathbf{x}) = [T_0/T(\mathbf{x})]\{E(\mathbf{x}) - \sum_k \mu^k(\mathbf{x})n^k(\mathbf{x})\}, \quad (3.2)$$

where $T(\mathbf{x})$ is the local temperature and T_0 its equilibrium value.

Equation (3.1) is expressed in terms of the rate of change in time of the local densities due to H. For simplicity, let us confine ourselves to the fluids in which no chemical reaction is taking place so that the N^k's are constants of motion with respect to H. Let $\mathbf{x}_i$ and $\mathbf{p}_i$ be the coordinates and momenta of the center-of-mass of molecule i. The molecular expression for $n^k(\mathbf{x})$ is given by

$$\rho^k(\mathbf{x}) = m^k n^k(\mathbf{x}) = \sum_{i\epsilon(k)} m_i \delta(\mathbf{x}_i - \mathbf{x}), \quad (3.3)$$

$$N^k = \int n^k(\mathbf{x})d\mathbf{x}, \quad (3.4)$$

[20] Note that we set up the initial condition (2.29) for the ensemble of the system and calculated contributions from the deviation developed thereafter to obtain (2.30) and (2.37).

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where m_i is the mass of molecule i, and the summation runs over all molecules of component k. The local momentum density is given by

$$\mathbf{j}^k(\mathbf{x}) = \sum_{i\epsilon(k)} \tfrac{1}{2}\{\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})+\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i\}, \quad (3.5)$$

where the symmetrized product has been taken due to the noncommutativity of $\mathbf{p}_i$ and the δ function in the quantum-mechanical case.[13] The densities of mass and momentum of the entire fluid are given by

$$\rho(\mathbf{x})=\sum_k\rho^k(\mathbf{x}), \quad \mathbf{j}(\mathbf{x})=\sum_k\mathbf{j}^k(\mathbf{x}). \quad (3.6)$$

Let us consider the case in which the macroscopic motion of fluids can be described by one velocity field. (The discussion of liquid He II may not be possible with this limitation.) Then, the macroscopic local mass velocity is defined by

$$\mathbf{v}(\mathbf{x},t)=\langle\mathbf{j}(\mathbf{x})\rangle(t)/\langle\rho(\mathbf{x})\rangle(t),$$
$$=\langle\mathbf{j}(\mathbf{x})\rangle_t/\langle\rho(\mathbf{x})\rangle_t, \quad (3.7)$$

where the second expression is obtained from (2.9). The internal energy density is defined by

$$E(\mathbf{x})=H(\mathbf{x})-\mathbf{j}(\mathbf{x})\cdot\mathbf{v}(\mathbf{x})+\tfrac{1}{2}\rho(\mathbf{x})v^2(\mathbf{x}), \quad (3.8)$$

where $H(\mathbf{x})$ is the local Hamiltonian density satisfying

$$H=\int H(\mathbf{x})d\mathbf{x}. \quad (3.9)$$

The molecular expression for $H(\mathbf{x})$ depends on the details of the Hamiltonian. We take the form

$$H=\sum_{i=1}^N (p_i^2/2m_i+\epsilon_i(s_i))+\sum_{i<j}^N\sum^N u_{ij}(\mathbf{x}_i,s_i;\mathbf{x}_j,s_j), \quad (3.10)$$

where s_i is a set of coordinates and momenta of the internal motion of molecule i. Then we have

$$E(\mathbf{x})=\sum_{i=1}^N\left\{(\mathbf{p}_i-m_i\mathbf{v})^2/2m_i+\epsilon_i+\tfrac{1}{2}\sum_{j(\neq i)}^N u_{ij}\right\}$$
$$\times\delta(\mathbf{x}_i-\mathbf{x}), \quad (3.11)$$

$$H(\mathbf{x})=[E(\mathbf{x})]_{\mathbf{v}=0}, \quad (3.12)$$

which leads to (3.8). The translational kinetic part should be read as an abbreviation of the symmetrized product

$$(1/8m_i)\{p_i^2\delta(\mathbf{x}_i-\mathbf{x})+2\mathbf{p}_i\cdot\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i$$
$$+\delta(\mathbf{x}_i-\mathbf{x})p_i^2\}, \quad (3.13)$$

in which $\mathbf{p}_i$ is, in (3.11), replaced by the thermal momentum $\mathbf{p}_i-m_i\mathbf{v}$.

The macroscopic state parameters $T(\mathbf{x})$, $\mathbf{v}(\mathbf{x})$, and $\mu^k(\mathbf{x})$ have only macroscopic spatial nonuniformity so that the associated local densities in (3.2) have only the same macroscopic spatial dependence. This can be seen easily from the fact that, if $1/T(\mathbf{x})$ and $H(\mathbf{x})$ are expanded in Fourier series, then the components of $H(\mathbf{x})$ other than those with the same wave vectors as the components of $1/T(\mathbf{x})$ vanish on integration in (2.4) and (3.1). Therefore the δ function appearing in the local densities should be understood to be the "coarse-grained" one; namely[6]

$$\delta(\mathbf{x}_i-\mathbf{x})=(1/L^3)\sum_k\exp[i\mathbf{k}\cdot(\mathbf{x}_i-\mathbf{x})], \quad (3.14)$$

$$|k_x|,|k_y|,|k_z|\leq 2\pi/l, \quad (3.15)$$

where l is the average linear extent of uniform mass elements defined in (2.5), and the components of $\mathbf{k}$ are integers multiplied by $2\pi/L$ subject to (3.15).

As will be shown in Sec. 6, we have the conservation laws for the local densities

$$\dot\rho^k(\mathbf{x})=-\nabla\cdot\mathbf{j}^k(\mathbf{x}), \quad (3.16)$$

$$\dot\rho(\mathbf{x})=-\nabla\cdot\mathbf{j}(\mathbf{x}), \quad (3.17)$$

$$\dot H(\mathbf{x})=-\nabla\cdot\mathbf{J}_H(\mathbf{x}), \quad (3.18)$$

$$d\mathbf{j}(\mathbf{x})/ds=-\nabla\cdot\mathbf{J}_j(\mathbf{x}). \quad (3.19)$$

Therefore, use of (3.2) and (3.8) leads to

$$\dot Y(\mathbf{x})=-(T_0/T(\mathbf{x}))\{\nabla\cdot\mathbf{J}_H-\mathbf{v}\cdot(\nabla\cdot\mathbf{J}_j)$$
$$+\tfrac{1}{2}v^2\nabla\cdot\mathbf{j}-\sum_k(\mu^k/m^k)\nabla\cdot\mathbf{j}^k\}, \quad (3.20)$$

where the time rate of the macroscopic state parameters does not enter according to the definition of $\dot Y(\mathbf{x})$. The second term, $\mathbf{v}\cdot(\nabla\cdot\mathbf{J}_j)$, can be written as

$$\mathbf{v}\cdot\nabla p+\nabla\cdot[(\mathbf{J}_j-p\mathbf{1})\cdot\mathbf{v}]-(\mathbf{J}_j^*-p\mathbf{1}):\nabla\mathbf{v},$$

where $p(\mathbf{x})$ is the local pressure and $\mathbf{J}_j^*$ is the transpose of the tensor $\mathbf{J}_j$. Equation (3.20) can thus be written as

$$\dot Y(\mathbf{x})=-\nabla\cdot\mathbf{J}_Y(\mathbf{x})+Z(\mathbf{x})+\nu(\mathbf{x}), \quad (3.21)$$

where

$$Z(\mathbf{x})=\mathbf{J}_v:\mathbf{X}_v+\mathbf{J}_T\cdot\mathbf{X}_T+\sum_k\mathbf{J}_d^k\cdot\mathbf{X}_d^k, \quad (3.22)$$

$$\mathbf{J}_Y(\mathbf{x})=\frac{T_0}{T}\left\{\mathbf{J}_H-(\mathbf{J}_j-p\mathbf{1})\cdot\mathbf{v}+\tfrac{1}{2}v^2\mathbf{j}-\sum_k\frac{\mu^k}{m^k}\mathbf{j}^k\right\},$$

$$=\frac{T_0}{T}\left\{\mathbf{J}_T+T\sum_k\frac{s^k}{m^k}\mathbf{J}_d^k+\mathbf{v}T\sum_k n^k s^k\right. \quad (3.23)$$
$$\left.-\mathbf{v}(p'-p)\right\},$$

$$\nu(\mathbf{x})=\mathbf{v}\cdot\left\{(p-p')\mathbf{X}_T+\frac{T_0}{T}\nabla p+\sum_k\rho^k\mathbf{X}_d^k\right\}$$
$$+\mathbf{j}\cdot\frac{T_0}{T}\nabla\tfrac{1}{2}v^2+(\mathbf{j}\mathbf{v}+\mathbf{v}\mathbf{j}-\rho\mathbf{v}\mathbf{v}):\mathbf{X}_v. \quad (3.24)$$

Here we have defined the quantities

$$\mathbf{J}_v=\mathbf{J}_j^*-p\mathbf{1}-\mathbf{j}\mathbf{v}-\mathbf{v}\mathbf{j}+\rho\mathbf{v}\mathbf{v},$$
$$\mathbf{X}_v=-(T_0/T)\nabla\mathbf{v}\simeq-\nabla\mathbf{v}, \quad (3.25)$$

$$\mathbf{J}_T=\mathbf{J}_H-(\mathbf{J}_j-p'\mathbf{1})\cdot\mathbf{v}+\tfrac{1}{2}v^2\mathbf{j}-\sum_k (h^k/m^k)\mathbf{j}^k,$$
$$\mathbf{X}_T=\nabla(T_0/T)\simeq-\nabla\ln T, \tag{3.26}$$

$$\mathbf{J}_d{}^k=\mathbf{j}^k-\rho^k\mathbf{v},$$
$$\mathbf{X}_d{}^k=-(T_0/T)(\nabla\mu^k+s^k\nabla T)/m^k, \tag{3.27}$$

where $h^k(\mathbf{x})$ and $s^k(\mathbf{x})$ are the local values of the enthalpy and entropy per molecule of component k, satisfying the relation

$$h^k=\mu^k+Ts^k. \tag{3.28}$$

The quantity p' appearing in (3.26) and (3.24) can be an arbitrary function since it cancels identically. It is taken, however, to be

$$p'(\mathbf{x})=-E(\mathbf{x})+\sum_k n^k(\mathbf{x})h^k(\mathbf{x}), \tag{3.29}$$

so that the $\mathbf{J}_T$ can be written, as will be shown in Sec. 6, as

$$\mathbf{J}_T=\mathbf{q}-\sum_k (h^k/m^k)\mathbf{J}_d{}^k, \tag{3.30}$$

where

$$\mathbf{q}=[\mathbf{J}_H]_{\mathbf{p}_i\to\mathbf{p}_i-m_i\mathbf{v}} \tag{3.31}$$

means the quantity obtained by replacing $\mathbf{p}_i$ by the thermal momentum $\mathbf{p}_i-m_i\mathbf{v}$ in the molecular expression for $\mathbf{J}_H$. The $\mathbf{J}_v$ and $\mathbf{J}_d{}^k$ can also be expressed in terms of the thermal momentum, being invariant to Galilei's transformation. The X's are the affinities in the thermodynamics of irreversible processes.[10,21] The averages of $\mathbf{J}_v$, $\mathbf{J}_T$, and $\mathbf{J}_d{}^k$ with the time-smoothed density matrix become the conjugate thermodynamic fluxes [see reference 24 and (4.11)]; hence these dynamical quantities will be called the dynamical fluxes conjugate to the affinities. For simplicity, let us denote the dynamical fluxes by $\{J_\alpha(\mathbf{x})\}$ and the conjugate affinities by $\{X_\alpha(\mathbf{x})\}$; then (3.22) can be written as

$$Z(\mathbf{x})=\sum_\alpha J_\alpha(\mathbf{x})X_\alpha(\mathbf{x}). \tag{3.32}$$

The quantity $\dot{Y}(\mathbf{x})$ or $\dot{R}$ will turn out to be the most important quantity in the investigation of the microscopic processes associated with the hydrodynamical motion of the system.

Equation (3.24) can be written as

$$\nu(\mathbf{x})=\mathbf{v}\cdot\{(p-p')\mathbf{X}_T+\sum_k (\rho^k-\langle\rho^k\rangle)\mathbf{X}_d{}^k\}$$
$$+(\mathbf{j}-\rho\mathbf{v})\cdot(T_0/T)\nabla\tfrac{1}{2}v^2+(\mathbf{j}\mathbf{v}+\mathbf{v}\mathbf{j}-2\rho\mathbf{v}\mathbf{v}):\mathbf{X}_v, \tag{3.33}$$

where use has been made of the relations

$$\nabla p=\sum_k \langle n^k\rangle(\nabla\mu^k+s^k\nabla T),$$
$$\mathbf{v}\cdot\nabla\tfrac{1}{2}v^2=\mathbf{v}\mathbf{v}:\nabla\mathbf{v}. \tag{3.34}$$

We notice that the quantity p' defined by (3.29) satisfies the characteristic relation of macroscopic quantities (2.12) and its average value yields the local pressure:

$$p(\mathbf{x})=\langle p'(\mathbf{x})\rangle_t=\langle p'(\mathbf{x})\rangle(t). \tag{3.35}$$

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[21] Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley and Sons, Inc., New York, 1954), Chap. 11.

Therefore we obtain

$$\langle\nu(\mathbf{x})\rangle(t)=\langle\nu(\mathbf{x})\rangle_t=0, \tag{3.36}$$
$$[\nu(\mathbf{x})]=0, \tag{3.37}$$

where, in deriving the second equation, (2.27) has been employed.

Insertion of (3.21) into (3.1) leads to

$$\dot{R}=\int \{Z(\mathbf{x})+\nu(\mathbf{x})\}d\mathbf{x}, \tag{3.38}$$

since the surface integral of $\mathbf{J}_Y(\mathbf{x})$ at the boundary vanishes because $\mathbf{J}_Y(\mathbf{x})$ is a flow due to H. Therefore use of (3.36) and (3.37) leads to

$$\langle\dot{R}\rangle=\int \langle Z(\mathbf{x})\rangle d\mathbf{x}, \tag{3.39}$$

$$[\dot{R}]=\int [Z(\mathbf{x})]d\mathbf{x}. \tag{3.40}$$

We note here an important theorem which is characteristic of the local equilibrium distribution. By taking the trace of both sides of the identity (2.32), we obtain

$$\langle\dot{R}\rangle_t=0, \tag{3.41}$$

which is combined with (3.39) and (3.22) to yield

$$\langle\mathbf{J}_v(\mathbf{x})\rangle_t=0,$$
$$\langle\mathbf{J}_T(\mathbf{x})\rangle_t=0, \tag{3.42}$$
$$\langle\mathbf{J}_d{}^k(\mathbf{x})\rangle_t=0.$$

These equations mean that the local equilibrium distribution cannot express any transport flows.

4. IRREVERSIBLE PRODUCTION OF ENTROPY

To see the physical significance of the quantities $\mathbf{J}_v$, $\mathbf{J}_T$, and $\mathbf{J}_d{}^k$, we derive the irreversible production of the total entropy, which will lead to a statistical-mechanical derivation of the linear relations between the thermodynamic fluxes and affinities for linear dissipative systems.

As has been discussed in (I), a statistical-mechanical expression for the total entropy of the system is given by

$$S(t)=-k\operatorname{Tr}\rho(t)\ln\rho_t. \tag{4.1}$$

Let us write its change in a short time as

$$\delta S(t)=\delta_1 S(t)+\delta_2 S(t), \tag{4.2}$$

where

$$\delta_1 S(t)=-k\operatorname{Tr}\{\rho(t+\tau)-\rho(t)\}\ln\rho_t, \tag{4.3}$$

$$\delta_2 S(t)=-k\operatorname{Tr}\rho(t+\tau)\{\ln\rho_{t+\tau}-\ln\rho_t\}. \tag{4.4}$$

Then insertion of the local equilibrium distribution

(2.4) leads to

$$\delta_1 S(t) = \int d\mathbf{x}\{\delta'\langle E(\mathbf{x})\rangle - \sum_k \mu^k(\mathbf{x})\delta\langle n^k(\mathbf{x})\rangle\}/T(\mathbf{x}), \quad (4.5)$$

$$\delta_2 S(t) = O(\delta^2), \quad (4.6)$$

where

$$\delta'\langle E(\mathbf{x})\rangle = \mathrm{Tr}\{\rho(t+\tau) - \rho(t)\}E(\mathbf{x}),$$
$$= \delta(\langle H(\mathbf{x})\rangle - \tfrac{1}{2}\langle\rho\rangle v^2) + O(\delta^2), \quad (4.7)$$

and δ^2 means the quantities of second order in the increments of T, μ^k, $\mathbf{v}$, $\langle H\rangle$, and $\langle n^k\rangle$ in the time interval τ. Equation (4.6) will be shown in the appendix. $\delta_2 S(t)$ can thus be neglected in (4.2). Equations (4.5) and (4.7) show that the entropy (4.1) is a state function and, if one knows the hydrodynamical equations, then the entropy production can be readily obtained. It is worth while, however, to perform the direct calculation of (4.3) without any recourse to the hydrodynamical equations, because of the fact, in particular, that the entropy production itself shows compactly the structure of the transport processes taking place in the system.

The change in time of the entropy consists of two parts:

$$\delta S(t) = \delta^{(e)} S(t) + \delta^{(i)} S(t), \quad (4.8)$$

such that $\delta^{(e)} S(t)$ is the entropy supplied to the fluid by the reservoirs and $\delta^{(i)} S(t)$ is the entropy produced inside the fluid by the transport processes. Such additive separation is possible when the time interval under consideration is subject to (2.13), namely $\tau \ll \tau_r$. Therefore, we can neglect the interaction with the reservoirs in the calculation of the irreversible production of entropy, and use of (4.3), (2.14), and (2.31) leads to

$$\delta^{(i)} S(t) = (1/T_0)\,\mathrm{Tr}\rho(t)\{U^\dagger(\tau)RU(\tau) - R\}. \quad (4.9)$$

Comparison of (4.9) with (2.16) permits us to employ the results from (2.19) to (2.24), to obtain the following equation for the entropy production:

$$\left(\frac{\delta S}{\delta t}\right)_{\mathrm{irr}} = \frac{1}{T_0}[\dot{R}], \quad (4.10)$$

where (3.41) has been used. Application of (3.40) and (3.32) thus leads to

$$\left(\frac{\delta S}{\delta t}\right)_{\mathrm{irr}} = \frac{1}{T_0}\int d\mathbf{x} \sum_\alpha [J_\alpha(\mathbf{x})]X_\alpha(\mathbf{x}). \quad (4.11)$$

This shows that the quantity $[J_\alpha(\mathbf{x})]$ is the thermodynamic flux conjugate to the affinity $X_\alpha(\mathbf{x})$.

We next consider the relation between the thermodynamic fluxes and affinities in a linear dissipative system. With the approximation of neglecting the deviation of the precise distribution from the local equilibrium distribution at the initial time of the time

interval τ, (2.29), and the linear approximation, the fluxes $[J_\alpha(\mathbf{x})]$ are given by (2.33). Since the term $\nu(\mathbf{x})$ appearing in the expression for $\dot{R}$, (3.38), is of second order with respect to the parameters expressing the deviation of the macroscopic state from complete equilibrium, such as the local velocity and the affinities, it can be neglected in the linear approximation. Therefore, with the use of (2.37), we obtain

$$[J_\alpha(\mathbf{x})] = \sum_{\alpha'} \int L(J_\alpha{}^0(\mathbf{x}), J_{\alpha'}{}^0(\mathbf{x}'))X_{\alpha'}(\mathbf{x}')d\mathbf{x}', \quad (4.12)$$

where $J_\alpha{}^0(\mathbf{x})$ denote those obtained by putting $\mathbf{v}=0$ in $J_\alpha(\mathbf{x})$;

$$\mathbf{J}_v{}^0(\mathbf{x}) = \mathbf{J}_j{}^*(\mathbf{x}) - p_0\mathbf{1},$$
$$\mathbf{J}_T{}^0(\mathbf{x}) = \mathbf{J}_H(\mathbf{x}) - \sum_k (h_0{}^k/m^k)\mathbf{j}^k(\mathbf{x}), \quad (4.13)$$
$$\mathbf{J}_d{}^{k0}(\mathbf{x}) = \mathbf{j}^k(\mathbf{x}),$$

p_0 and $h_0{}^k$ being the equilibrium values. Here we have assumed that $\Phi(J_\alpha{}^0(\mathbf{x}), J_{\alpha'}{}^0(\mathbf{x}'); s)$ vanishes in a microscopic time τ_c. Thus the phenomenological coefficients have been expressed in terms of the Φ functions of the time fluctuations of the dynamical fluxes $J_\alpha{}^0(\mathbf{x})$ in the equilibrium state. These expressions satisfy Onsager's reciprocal relations.[9]

The phenomenological coefficients have many symmetry relations other than Onsager's reciprocal relations, such as Curie's law and other isotropic relations, according to the symmetry of the system. We discuss these now briefly. To remove the influence of the boundary, let us suppose the linear extent of the fluid to be infinity. Let us now assume that there is no correlation between different small portions of macroscopic size in the equilibrium state in the sense that

$$L(J_\alpha{}^0(\mathbf{x}), J_{\alpha'}{}^0(\mathbf{x}')) = \delta(\mathbf{x} - \mathbf{x}')V^{-1}L(\mathfrak{F}_\alpha, \mathfrak{F}_{\alpha'}), \quad (4.14)$$

where the δ function is defined by (3.14). V is the volume of a portion, in the equilibrium fluid, very large (but still very small compared to the total volume of the fluid) and the quantity $\mathfrak{F}_\alpha$ is defined by integration of $J_\alpha{}^0(\mathbf{x})$ over this portion:

$$\mathfrak{F}_\alpha = \int_V J_\alpha{}^0(\mathbf{x})d\mathbf{x}. \quad (4.15)$$

Then the linear relations (4.12) become

$$[J_\alpha(\mathbf{x})] = \sum_{\alpha'} V^{-1}L(\mathfrak{F}_\alpha, \mathfrak{F}_{\alpha'})X_{\alpha'}(\mathbf{x}). \quad (4.16)$$

Therefore, applying Curie's law,[10] we obtain

$$[\mathbf{J}_v(\mathbf{x})] = V^{-1}L(\mathfrak{F}_v, \mathfrak{F}_v): \mathbf{X}_v(\mathbf{x}),$$
$$[\mathbf{J}_T(\mathbf{x})] = V^{-1}\{L(\mathfrak{F}_T, \mathfrak{F}_T)\cdot\mathbf{X}_T(\mathbf{x}) + \sum_j L(\mathfrak{F}_T, \mathfrak{F}_{d^j})\cdot\mathbf{X}_{d^j}(\mathbf{x})\}, \quad (4.17)$$
$$[\mathbf{J}_d{}^k(\mathbf{x})] = V^{-1}\{L(\mathfrak{F}_{d^k}, \mathfrak{F}_T)\cdot\mathbf{X}_T(\mathbf{x}) + \sum_j L(\mathfrak{F}_{d^k}, \mathfrak{F}_{d^j})\cdot\mathbf{X}_{d^j}(\mathbf{x})\}.$$

For isotropic fluids, the phenomenological coefficients

can be expressed in terms of a few parameters[21];

$$V^{-1}L(\mathfrak{J}_v{}^{xy},\mathfrak{J}_v{}^{y'x'})=\eta(\delta_{xx'}\delta_{yy'}+\delta_{xy'}\delta_{yx'})$$
$$+(\varphi-\tfrac{2}{3}\eta)\delta_{xy}\delta_{x'y'},$$
$$V^{-1}L(\mathfrak{J}_T,\mathfrak{J}_T)=\kappa T_0 1, \qquad (4.18)$$
$$V^{-1}L(\mathfrak{J}_d{}^k,\mathfrak{J}_T)=V^{-1}L(\mathfrak{J}_T,\mathfrak{J}_d{}^k)^*=D_k 1,$$
$$V^{-1}L(\mathfrak{J}_d{}^k,\mathfrak{J}_d{}^j)=V^{-1}L(\mathfrak{J}_d{}^j,\mathfrak{J}_d{}^k)^*=D_{kj}' 1,$$

where $\mathfrak{J}_v{}^{xy}$ denotes the x, y component of the tensor $\mathfrak{J}_v$. The symbol η denotes the shear viscosity, φ the bulk viscosity, κ the thermal conductivity, D_k the thermal diffusion coefficients, and D_{kj}' the constants related to the diffusion coefficients.

To investigate the asymptotic behavior of the Φ functions, we consider the time fluctuations of the local quantities $J_\alpha{}^0(\mathbf{x})$ and $\mathfrak{J}_\alpha$ in the equilibrium state. Let us here represent these local quantities by the symbols I and J. Since the fluid is infinite, we can take

$$T\ll\tau_r, \quad T\to\infty, \qquad (4.19)$$

which permits the consideration of the following limit process;

$$\tilde{J}\equiv\lim_{T\to\infty}\frac{1}{T}\int_0^T J(s)ds, \qquad (4.20)$$

which is the invariant part of $J(s)$ and satisfies the relation

$$\{\tilde{J},H\}=0. \qquad (4.21)$$

If $\Phi(J,I;s)$ approaches a definite value as $s\to\infty$, it must be[11]

$$\lim_{s\to\infty}\Phi(J,I;s)=\beta\langle\tilde{J}I\rangle^0. \qquad (4.22)$$

According to the statistical mechanics of equilibrium systems,[15] we can expect, because of the interaction between small portions in the fluid, that the small portion passes through the neighborhood of each microscopic state many times in a time interval T long compared to τ_0 but short compared to τ_r, so that in the classical case

$$\tilde{J}=\langle J\rangle^0=0, \qquad (4.23)$$

where the second equality is obtained from (3.42). This leads to

$$\langle\tilde{J}I\rangle^0=\langle J\rangle^0\langle I\rangle^0=0. \qquad (4.24)$$

Equation (4.24) is assumed to hold also in the quantum-mechanical case. Then (4.22) leads to

$$\lim_{s\to\infty}\Phi(J,I;s)=0, \qquad (4.25)$$

which permits us to expect that the assumption made in deriving (4.12) is reasonable. It is a most essential point, however, to show that the Φ functions vanish in a short time comparable to τ_0.

5. HYDRODYNAMICAL EQUATIONS

The flows of mass, momentum, and energy can be written in terms of the dynamical fluxes defined by (3.25), (3.26), and (3.27) as

$$\mathbf{j}^k=\rho^k\mathbf{v}+\mathbf{J}_d{}^k, \qquad (5.1)$$
$$\mathbf{J}_j=\tfrac{1}{2}(\mathbf{j}\mathbf{v}+\mathbf{v}\mathbf{j})+(\mathbf{J}_v{}^*+p1)+\tfrac{1}{2}(\mathbf{j}\mathbf{v}+\mathbf{v}\mathbf{j}-2\rho\mathbf{v}\mathbf{v}), \qquad (5.2)$$
$$\mathbf{J}_H=H\mathbf{v}+\mathbf{q}+(\mathbf{J}_v{}^*+p1)\cdot\mathbf{v}+\tfrac{1}{2}v^2(\mathbf{j}-\rho\mathbf{v}), \qquad (5.3)$$

where $\mathbf{q}(\mathbf{x})$ is defined by

$$\mathbf{q}(\mathbf{x})=\mathbf{J}_T+\sum_k (h^k/m^k)\mathbf{J}_d{}^k, \qquad (5.4)$$

which expresses the flow of thermal energy relative to the local velocity. Therefore use of (3.42) leads to

$$\langle\mathbf{j}^k\rangle_t=\langle\rho^k\rangle\mathbf{v}, \qquad (5.5)$$
$$\langle\mathbf{J}_j\rangle_t=\langle\rho\rangle\mathbf{v}\mathbf{v}+p1, \qquad (5.6)$$
$$\langle\mathbf{J}_H\rangle_t=\langle H\rangle\mathbf{v}+p\mathbf{v}, \qquad (5.7)$$

and application of (2.27) leads to

$$[\mathbf{j}^k]=[\mathbf{J}_d{}^k], \qquad (5.8)$$
$$[\mathbf{J}_j]=[\mathbf{J}_v{}^*], \qquad (5.9)$$
$$[\mathbf{J}_H]=[\mathbf{q}]+[\mathbf{J}_v{}^*]\cdot\mathbf{v}. \qquad (5.10)$$

The hydrodynamical equations can be readily obtained from (2.24). With Eqs. (3.16), (5.5), and (5.8) we obtain the equation of continuity

$$\delta\langle\rho^k\rangle/\partial t+\nabla\cdot(\langle\rho^k\rangle\mathbf{v})=-\nabla\cdot[\mathbf{J}_d{}^k]. \qquad (5.11)$$

The diffusion fluxes satisfy the relation

$$\sum_k [\mathbf{J}_d{}^k]=0, \qquad (5.12)$$

as can be seen with the aid of (3.27) and (2.27), and combination of the above two equations yields the equation of continuity for the entire fluid:

$$\delta\langle\rho\rangle/\partial t+\nabla\cdot(\langle\rho\rangle\mathbf{v})=0. \qquad (5.13)$$

Similarly, use of (3.19), (5.6) and (5.9) yields the equation of motion:

$$\delta(\langle\rho\rangle\mathbf{v})/\partial t+\nabla\cdot(\langle\rho\rangle\mathbf{v}\mathbf{v})=-\nabla\cdot\mathbf{P}, \qquad (5.14)$$

where we have defined the pressure tensor

$$\mathbf{P}(\mathbf{x})=p1+[\mathbf{J}_v{}^*]. \qquad (5.15)$$

Lastly Eqs. (3.18), (5.7), and (5.10) combine to lead to the equation of energy balance:

$$\delta\langle H\rangle/\partial t+\nabla\cdot(\langle H\rangle\mathbf{v})=-\nabla\cdot([\mathbf{q}]+\mathbf{P}\cdot\mathbf{v}). \qquad (5.16)$$

If one neglects the terms containing the thermodynamic fluxes, then the above equations become the ideal-fluid equations.

For linear dissipative systems, the thermodynamic fluxes are given by Eqs. (4.12), which can be reduced to (4.17) and (4.18) for isotropic fluids. Thus insertion of (4.17) and (4.18) into the above general hydrody-

namical equations leads to the Stokes-Navier equations. It should be noted here that the derivation of the hydrodynamical equations with the linear relations (4.12) is independent of the definition of entropy (4.1).

Next we derive the equation of entropy balance, which is not only essential in the thermodynamics of irreversible processes in continuous systems, but also useful to describe the motion of fluids. In accordance with the total entropy (4.1), the local entropy per unit volume $S(\mathbf{x},t)$ is defined by

$$S(\mathbf{x},t)d\mathbf{x} = -k \operatorname{Tr} \rho(t) \ln\rho_t(\mathbf{x}), \qquad (5.17)$$

where, with the notation of (3.2),

$$\rho_t(\mathbf{x}) = Z(\mathbf{x})^{-1} \exp\{-[Y(\mathbf{x})/kT_0]d\mathbf{x}\}, \quad (5.18)$$

$$\operatorname{Tr} \rho_t(\mathbf{x}) = 1, \qquad (5.19)$$

$$S(t) = \int S(\mathbf{x},t)d\mathbf{x}. \qquad (5.20)$$

Equation (5.20) is derived on the assumption that the Boltzmann factors of different uniform small portions of macroscopic size commute with each other. In parallel to (4.3), we can obtain

$$\delta S(\mathbf{x},t)d\mathbf{x} = -k \operatorname{Tr}\{\rho(t+\tau) - \rho(t)\} \ln\rho_t(\mathbf{x}) \quad (5.21)$$

for the change in a short time subject to (2.13). Since $Y(\mathbf{x})$ is a local quantity at points remote from the boundary, this can be written as

$$\delta S(\mathbf{x},t) = (1/T_0) \operatorname{Tr}\rho(t)\{U^\dagger(\tau)YU(\tau) - Y\}. \quad (5.22)$$

Use of (2.24) thus leads to

$$\frac{\delta}{\partial t} S(\mathbf{x},t) = \frac{1}{T_0}\{\langle \dot{Y} \rangle_t + [\dot{Y}]\}. \qquad (5.23)$$

Therefore, substitution of (3.21) yields the equation of entropy balance:

$$\frac{\delta}{\partial t} S(\mathbf{x}) + \nabla \cdot (S\mathbf{v}) = -\nabla \cdot \left(\frac{\mathbf{Q}}{T}\right) + g, \qquad (5.24)$$

as can be seen with the aid of (3.42), (3.36), (2.27), and (3.37). Here we have defined the quantities

$$g(\mathbf{x}) = [Z(\mathbf{x})]/T_0, \qquad (5.25)$$

$$\mathbf{Q}(\mathbf{x}) = [\mathbf{J}_T] + T(\mathbf{x}) \sum_k [\mathbf{J}_d{}^k](s^k/m^k), \qquad (5.26)$$

$$= [\mathbf{q}] - \sum_k [\mathbf{J}_d{}^k](\mu^k/m^k). \qquad (5.27)$$

The term $g(\mathbf{x})$ is the entropy production per unit volume and agrees with the phenomenological treatments.[10] $\mathbf{Q}(\mathbf{x})$ is the flow of heat, namely the thermal energy flux other than the flow of energy associated with the diffusion processes. Equation (5.26) gives the physical picture of the flux $[\mathbf{J}_T]$; namely, it expresses the flow of heat other than the part associated with the diffusion processes.

The phenomenological derivation[10] of the entropy production is based on the application of the Gibbs thermodynamic relation,

$$T\delta s = \delta e + p\delta(1/\rho) - \sum_k (\mu^k/m^k)\delta(\rho^k/\rho), \quad (5.28)$$

to the mass elements moving with the local velocity. Here s, e, and ρ^k are the entropy and the internal energy per unit mass, and the mass density of component k. Equation (5.28) is equivalent to

$$T\delta S = \delta\langle E \rangle - \sum_k \mu^k\delta\langle n^k \rangle, \qquad (5.29)$$

which is supposed to be applied to the fixed volume elements. Equation (5.29) can be obtained from (5.21) by inserting the expression for $\rho_t(\mathbf{x})$, (5.18), in parallel to the derivation of (4.5) from (4.3).

6. EXPLICIT EXPRESSIONS FOR TRANSPORT COEFFICIENTS

The molecular expressions for the dynamical fluxes, in terms of which the transport coefficients are expressed, are obtained by deriving the conservation laws (3.16), (3.17), (3.18), and (3.19) from molecular dynamics. This is done with the calculation of the commutators of the local densities and the Hamiltonian (3.10):

$$dF/ds = \dot{F} = [F,H]/i\hbar. \qquad (6.1)$$

A. *Conservation of Mass Density.*—Since we have

$$d\mathbf{x}_i/ds = \mathbf{p}_i/m_i, \qquad (6.2)$$

$$d\mathbf{p}_i/ds = \sum_{j(\neq i)}^N \mathbf{F}_{ij}, \quad \mathbf{F}_{ij} = -\frac{\partial u_{ij}}{\partial \mathbf{x}_i} = -\mathbf{F}_{ji}, \quad (6.3)$$

$$m_i\dot{\delta}(\mathbf{x}_i - \mathbf{x}) = -\nabla \cdot \tfrac{1}{2}\{\mathbf{p}_i\delta(\mathbf{x}_i - \mathbf{x}) + \delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i\}, \quad (6.4)$$

the equations of continuity (3.16) and (3.17) can be readily derived with the expressions for the mass and momentum densities (3.3), (3.5), and (3.6).

B. *Conservation of Momentum Density.*—With the aid of (6.3), (6.4), and the dyadic relation $\mathbf{p}_i\nabla \cdot \mathbf{A} = \nabla \cdot (\mathbf{p}_i\mathbf{A})^*$ (the asterisk means the transpose of the tensor), the time derivative of the momentum density becomes

$$d\mathbf{j}(\mathbf{x})/ds = \mathbf{B}(\mathbf{x}) - \nabla \cdot \sum_i (1/4m_i)\{\mathbf{p}_i\mathbf{p}_i\delta(\mathbf{x}_i - \mathbf{x})$$
$$+ \mathbf{p}_i\delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i + [\mathbf{p}_i\delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i]^* + \delta(\mathbf{x}_i - \mathbf{x})\mathbf{p}_i\mathbf{p}_i\},$$

where

$$\mathbf{B}(\mathbf{x}) = \tfrac{1}{2} \sum_{i \neq j}\sum \mathbf{F}_{ij}\{\delta(\mathbf{x}_i - \mathbf{x}) - \delta(\mathbf{x}_j - \mathbf{x})\}. \quad (6.5)$$

Expansion of the δ functions in powers of $\mathbf{r}_{ji} = \mathbf{x}_j - \mathbf{x}_i$ leads to

$$\delta(\mathbf{x}_j - \mathbf{x}) = \delta(\mathbf{x}_i - \mathbf{x}) + \mathbf{r}_{ji} \cdot \nabla_{x_i}\delta(\mathbf{x}_i - \mathbf{x}) + O[(a/l)^2], \quad (6.6)$$

where higher terms are of the order of $(a/l)^2$. The length a corresponds to the mean range of the intermolecular forces, and the gradient of the δ function is of the order of magnitude of the reciprocal of the measure of spatial

uniformity l according to (3.14). In the limit of an infinite system, (a/l) becomes zero and the higher terms can be neglected.[6] Thus we arrive at the conservation law for the momentum density (3.19), and the molecular expression for the momentum flux is given by

$$\mathbf{J}_j(\mathbf{x}) = \sum_i^N (1/4m_i)\{\mathbf{p}_i\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})+\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i$$

$$+[\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i]^*+\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i\mathbf{p}_i\}$$

$$+\tfrac{1}{2}\sum_{i\neq j}^N\sum^N \mathbf{r}_{ij}\mathbf{F}_{ij}\delta(\mathbf{x}_i-\mathbf{x}). \quad (6.7)$$

When the intermolecular forces are spherically symmetrical with respect to the translational relative coordinate $\mathbf{r}_{ij}$, we have

$$\mathbf{F}_{ij}=-(\mathbf{r}_{ij}/r_{ij})F_{ij}, \quad (6.8)$$

so that the tensors $\mathbf{J}_j$ and $\mathbf{J}_v$ are symmetric:

$$\mathbf{J}_j=\mathbf{J}_j^*, \quad \mathbf{J}_v=\mathbf{J}_v^*. \quad (6.9)$$

C. Conservation of Energy Density.—The conservation law for the Hamiltonian density (3.18) can be obtained by calculating the commutator of the Hamiltonian density (3.12) and the total Hamiltonian. With the aid of (6.6), we thus obtain

$$\mathbf{J}_H(\mathbf{x})=\sum_i^N\left(\frac{p_i^2}{2m_i}+\epsilon_i+\tfrac{1}{2}\sum_{j(\neq i)}^N u_{ij}\right)\frac{\mathbf{p}_i}{m_i}\delta(\mathbf{x}_i-\mathbf{x})$$

$$+\tfrac{1}{4}\sum_{i\neq j}^N\sum^N \mathbf{r}_{ij}\mathbf{F}_{ij}\cdot\left(\frac{\mathbf{p}_i}{m_i}+\frac{\mathbf{p}_j}{m_j}\right)\delta(\mathbf{x}_i-\mathbf{x})$$

$$+\tfrac{1}{2}\sum_{i\neq j}^N\sum^N \mathbf{r}_{ij}\Gamma_{ij}\delta(\mathbf{x}_i-\mathbf{x}), \quad (6.10)$$

where the equation

$$\Gamma_{ij}=[\epsilon_i,u_{ij}]/i\hbar \quad (6.11)$$

expresses the rate of change in time of the internal energy of molecule i due to the interaction with molecule j. Again, to have all operators Hermitean, each term should be symmetrized; thus the first term should be read as[22]

$$(1/16m_i^2)\{p_i^2\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})+p_i^2\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i$$

$$+2\mathbf{p}_i\mathbf{p}_i\cdot\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i+2\mathbf{p}_i\cdot\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i\mathbf{p}_i+\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})p_i^2$$

$$+\delta(\mathbf{x}_i-\mathbf{x})p_i^2\mathbf{p}_i\}+\epsilon_i\tfrac{1}{2}\{\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})+\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i\}/m_i$$

$$+\tfrac{1}{2}\sum_{j(\neq i)}^N\tfrac{1}{4}\{u_{ij}\mathbf{p}_i\delta(\mathbf{x}_i-\mathbf{x})+u_{ij}\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_i$$

$$+\mathbf{p}_iu_{ij}\delta(\mathbf{x}_i-\mathbf{x})+\delta(\mathbf{x}_i-\mathbf{x})\mathbf{p}_iu_{ij}\}/m_i, \quad (6.12)$$

[22] Here we have used the relation
$$\frac{d}{ds}\{u_{ij}\delta(\mathbf{x}_i-\mathbf{x})\}=\tfrac{1}{2}\{\dot{u}_{ij}\delta(\mathbf{x}_i-\mathbf{x})+u_{ij}\dot{\delta}(\mathbf{x}_i-\mathbf{x})$$
$$+\dot{\delta}(\mathbf{x}_i-\mathbf{x})u_{ij}+\delta(\mathbf{x}_i-\mathbf{x})\dot{u}_{ij}\}.$$

and the second term as

$$\tfrac{1}{2}\left\{\mathbf{r}_{ij}\mathbf{F}_{ij}\delta(\mathbf{x}_i-\mathbf{x})\cdot\left(\frac{\mathbf{p}_i}{m_i}+\frac{\mathbf{p}_j}{m_j}\right)\right.$$

$$\left.+\left(\frac{\mathbf{p}_i}{m_i}+\frac{\mathbf{p}_j}{m_j}\right)\cdot\mathbf{F}_{ij}\mathbf{r}_{ij}\delta(\mathbf{x}_i-\mathbf{x})\right\}. \quad (6.13)$$

The molecular expressions for the dynamical fluxes $J_\alpha(\mathbf{x})$ are obtained by inserting into Eqs. (3.25), (3.26), and (3.27) the above expressions for the flows of mass, momentum, and energy. A simple rearrangement of these equations leads to

$$\mathbf{J}_v+p\mathbf{1}=[\mathbf{J}_j^*(\mathbf{x})]_{\mathbf{p}_i\to\mathbf{p}_i-m_i\mathbf{v}}, \quad (6.14)$$

$$\mathbf{q}=[\mathbf{J}_H(\mathbf{x})]_{\mathbf{p}_i\to\mathbf{p}_i-m_i\mathbf{v}}, \quad (6.15)$$

$$\mathbf{J}_d{}^k=[\mathbf{j}^k(\mathbf{x})]_{\mathbf{p}_i\to\mathbf{p}_i-m_i\mathbf{v}}, \quad (6.16)$$

where (3.29) and (5.4) have been employed, and the notation on the right-hand sides implies that $\mathbf{p}_i$ is replaced by the thermal momentum $\mathbf{p}_i-m_i\mathbf{v}$ in Eqs. (6.7), (6.10), and (3.5). These equations yield the molecular picture of the dynamical fluxes, and it can be seen that the quantities $\mathbf{J}_v$, $\mathbf{J}_T$, and $\mathbf{J}_d{}^k$ give a generalization of the dynamical fluxes obtained from the kinetic theory of dilute gases.[23]

Next we consider the coordinate-space integration of the dynamical fluxes, $\mathfrak{J}_\alpha$, defined by (4.15). The number of molecules of the very large portion V of macroscopic size may be considered to be a constant of motion as far as the short time intervals of the order of the correlation time τ_c are concerned, and is denoted by N'. Use of (3.42), (6.14), and (6.7) leads to the equation of state

$$p_0V=\tfrac{1}{3}\sum_{i=1}^{N'}\langle p_i^2\rangle^0/m_i+\tfrac{1}{6}\sum_{i\neq j}^{N'}\sum^{N'}\langle\mathbf{F}_{ij}\cdot\mathbf{r}_{ij}\rangle^0, \quad (6.17)$$

which agrees with the result of the virial theorem. We thus obtain

$$\mathfrak{J}_v=\sum_{i=1}^{N'}(\mathbf{p}_i\mathbf{p}_i-\langle\mathbf{p}_i\mathbf{p}_i\rangle^0)/m_i+\tfrac{1}{2}\sum_{i\neq j}^{N'}\sum^{N'}(\mathbf{F}_{ij}\mathbf{r}_{ij}$$

$$-\langle\mathbf{F}_{ij}\mathbf{r}_{ij}\rangle^0), \quad (6.18)$$

in terms of which the viscosity tensor appearing in (4.16) are expressed. Use of the isotropic relation (4.18) and the definition of the time integral L, (2.37) and (2.34), leads to

$$\eta=\frac{1}{V}\int_0^{\tau_c}ds\int_0^\beta\langle\mathfrak{J}_v{}^{xy}\mathfrak{J}_v{}^{xy}(s+i\hbar\lambda)\rangle^0d\lambda, \quad x\neq y,$$
$$\quad (6.19)$$

$$\varphi+\tfrac{4}{3}\eta=\frac{1}{V}\int_0^{\tau_c}ds\int_0^\beta\langle\mathfrak{J}_v{}^{xx}\mathfrak{J}_v{}^{xx}(s+i\hbar\lambda)\rangle^0d\lambda,$$

[23] We mean by these the factors associated with the affinities in the inhomogeneous term of the linearized Boltzmann equation. See, for example, Eq. (7.3–26) of reference 21.

where we have made use of the relations

$$[\mathfrak{J}_\alpha, N^k] = 0,$$
$$\exp(-\lambda H_\mu)\mathfrak{J}_\alpha \exp(\lambda H_\mu) = e^{-\lambda H}\mathfrak{J}_\alpha e^{\lambda H} = \mathfrak{J}_\alpha(i\hbar\lambda). \quad (6.20)$$

Similarly, use of (5.4), (6.15), and (6.10) leads to

$$\mathfrak{J}_T = \mathfrak{J}_H - \sum_{i=1}^{N'} h_0{}^{(i)}\frac{\mathbf{p}_i}{m_i}, \quad (6.21)$$

$$\mathfrak{J}_H = \sum_{i=1}^{N'} \left(\frac{p_i{}^2}{2m_i} + \epsilon_i\right)\frac{\mathbf{p}_i}{m_i} + \tfrac{1}{2}\sum_{i\neq j}^{N'}\sum^{N'} \tfrac{1}{2}\Big\{ (u_{ij}\mathbf{1} + \mathbf{r}_{ij}\mathbf{F}_{ij})$$

$$\cdot\frac{\mathbf{p}_i}{m_i} + \frac{\mathbf{p}_i}{m_i}\cdot(u_{ij}\mathbf{1} + \mathbf{F}_{ij}\mathbf{r}_{ij})\Big\} + \tfrac{1}{2}\sum_{i\neq j}^{N'}\sum^{N'} \mathbf{r}_{ij}\Gamma_{ij}, \quad (6.22)$$

where $h_0{}^{(i)}$ means the enthalpy per molecule of the component to which molecule i belongs. With this expression the isotropic thermal conductivity is given by

$$\kappa = \frac{1}{VT_0}\int_0^{\tau_c} ds \int_0^\beta \langle \mathfrak{J}_T{}^x \mathfrak{J}_T{}^x(s+i\hbar\lambda)\rangle^0 d\lambda. \quad (6.23)$$

It should be noted that the second term of (6.21), namely the difference of the conduction flux from the thermal energy flux does not vanish even in the case of one-component fluids and, as has been shown in (II), yields an important contribution to the thermal conductivity as a result of its fluctuations due to the interaction with the surroundings. Application of (6.19) and (6.23) to dilute gases [16] yields, in the classical limit, the Enskog-Chapman expressions for the coefficients of viscosity and thermal conductivity with the aid of a certain approximation for the correlation functions which becomes exact for the Maxwellian molecules.

In terms of the dynamical fluxes of diffusion,

$$\mathfrak{J}_d{}^k = \sum_{i\in(k)}^{N'^k} \mathbf{p}_i, \quad \langle \mathfrak{J}_d{}^k\rangle^0 = 0, \quad (6.24)$$

the diffusion and thermal diffusion coefficients are now expressed; use of the isotropic relation (4.18) leads to

$$D_{kj}' = \frac{1}{3V}\int_0^{\tau_c} ds \int_0^\beta \langle \mathfrak{J}_d{}^j\cdot\mathfrak{J}_d{}^k(s+i\hbar\lambda)\rangle^0 d\lambda = D_{jk}',$$

$$D_k = \frac{1}{3V}\int_0^{\tau_c} ds \int_0^\beta \langle \mathfrak{J}_T\cdot\mathfrak{J}_d{}^k(s+i\hbar\lambda)\rangle^0 d\lambda. \quad (6.25)$$

We note here a simplification of (6.19), (6.23), and (6.25), which is convenient for the actual evaluation of the transport coefficients.[16] The surroundings of the large portion V in the equilibrium fluid may be regarded as heat and mass reservoirs, so that the ensemble average appearing in these equations may be replaced by the grand canonical ensemble of that portion being specified by the Hamiltonian and the number operator of molecules of the portion, H' and N'^k. As far as the short time intervals of the order of τ_c are concerned, the Heisenberg time factors seem to be also replaced by those with H'. The Φ function thus obtained satisfies the symmetry relation (2.34), which is necessary for the derivation of Onsager's reciprocity theorem.[9] However, it is not immediately clear whether this satisfies the asymptotic behavior (4.25) or not, because the invariant parts of the dynamical fluxes with respect to H' are, in general, not zero. It can be shown, however, for dilute gases that the contributions of the invariant part to the time dependence of the correlation function can be neglected in the limit of $N' \to \infty$ ($V \to \infty$, but $N'/V = $ constant), so that the asymptotic behavior (4.25) is satisfied.[16]

7. SUMMARY AND SOME REMARKS

In our formulation of the quantum-statistical theory of transport processes, our particular intention was to establish the hydrodynamical equations for linear dissipative systems and to formulate the transport coefficients in terms of the time fluctuations of the dynamical fluxes in equilibrium ensemble. By dividing the nonequilibrium density matrix into the local equilibrium distribution and a deviation term, we obtained the fundamental equation (2.24). This equation led, with the aid of the properties of the local equilibrium distribution, (2.12) and (3.42), to the general hydrodynamical equations (5.11), (5.13), (5.14), and (5.16). The quantities $[J_\alpha(\mathbf{x})]$ appearing in these equations were shown, on the basis of the expression for the entropy (4.1), to be the thermodynamic fluxes conjugate to the affinities X_α. For linear dissipative systems, the thermodynamic fluxes were calculated from Eq. (2.37) which was derived with the following assumptions: coarse-graining of the density matrix, (2.29), at the initial time of each short time interval τ; validity of the linear approximation; and separation of microscopic and macroscopic relaxations, i.e., the correlation times of the dynamical fluxes $J_\alpha{}^0(\mathbf{x})$ are very small compared to the macroscopic relaxation time of the system. Thus the linear relations between the thermodynamic fluxes and affinities, (4.12), were obtained, and, with the assumption (4.14), reduced to Eqs. (4.17) and (4.18) for isotropic fluids. Insertion of these linear relations into the general hydrodynamical equations led to the Stokes-Navier equations for isotropic fluids with the molecular expressions for the transport coefficients, (6.19), (6.23), and (6.25).

To see the physical framework of the present theory, we investigate the physical significance of the quantity $\dot{R}$ which played an essential role in the present formulation. This quantity came from the deviation of the macroscopic state from complete equilibrium, R. The

structure of this quantity can be seen from the equation

$$\dot{R}=\sum_{\alpha}\int J_{\alpha}^{0}(\mathbf{x})X_{\alpha}(\mathbf{x})d\mathbf{x}, \qquad (7.1)$$

which is obtained from (3.32) and (3.38) with the use of the linear approximation. Namely, $\dot{R}$ is the sum of the products of two kinds of quantities; one are the affinities, namely the driving forces of the hydrodynamical process, and the other are the dynamical fluxes whose averages formed with the time-smoothed density matrix become the thermodynamic fluxes.[24] The dissipative terms in the hydrodynamical equations, namely the thermodynamic fluxes are the sums of the products of the affinities and the correlation functions of the dynamical fluxes, and hence express the coupling of the macroscopic process represented by the ideal-fluid equations[19] and the elementary processes represented by the time dependence of the correlation functions. The unperturbed relaxation in small mass elements discussed after (2.6) may be regarded to be a superposition of these elementary processes, and manifests itself in the acceleration of the state variables; if we take for simplicity the case of the average velocity $\mathbf{v}=0$, then we have

$$\frac{d^2}{ds^2}\langle F\rangle(t+s)=\Phi(I,\dot{R};s),$$

$$\qquad (7.2)$$

$$=\sum_{\alpha}\int \Phi(I,J_{\alpha}^{0}(\mathbf{x});s)X_{\alpha}(\mathbf{x})d\mathbf{x},$$

since $Q=0$ in (2.26) as can be seen from (5.1) and (5.3). Thus we can say that the quantity $\dot{R}$ expresses the coupling of the ideal fluid process and the unperturbed relaxation in uniform small mass elements. This coupling gives rise to the approach of the fluid to complete equilibrium, and, at the same time, to the continual excitation of the unperturbed relaxation. This coupling ceases with the attainment of complete equilibrium.

To obtain a more detailed picture of these situations, we take a dilute gas of one component with spherically symmetric forces between molecules. As has been discussed in Sec. 2, the relaxation processes in momentum space couple with the hydrodynamical process due to the collisions between molecules from different mass elements, i.e., the dissipative mechanism. The relaxation processes in momentum space can be described by the spectrum of the master collision operator, whose eigenvalues are the decay constants of the different modes of relaxation.[25] As has been shown in (II), the

dynamical fluxes are approximate eigenfunctions of the master collision operator, and the time dependence of the autocorrelation functions of the dynamical fluxes represents the corresponding modes of relaxation. Therefore, from the discussion of the dissipative terms in the preceding paragraph, the quantity $\dot{R}$ expresses the coupling between the unperturbed relaxation processes in momentum space and the ideal-fluid process. Take a uniform small mass element and cut off the influence of the neighboring mass elements, and make the spectral analysis of the relaxation thus obtained. Then we have only those modes of relaxation which are excited due to the coupling with the hydrodynamical process. The excited modes turn out to be, according to (7.1), those whose eigenfunctions are the fluxes of viscosity and thermal conduction. We thus arrive at the fact that those modes of relaxation which are represented by the autocorrelation of the equilibrium fluctuations of the dynamical fluxes are excited in the hydrodynamical stage due to the coupling $\dot{R}$.

The present theory should be compared with Green's theory[6] on the same problem, and with Kubo's theory[11] on the linear response of thermodynamic systems to mechanical disturbances.[26]

Green's theory is concerned with the classical derivation of the hydrodynamical equations. His expressions for the transport coefficients are given in terms of the correlation functions in a similar way as the classical limits of the present equations. However, the averages involved are formed with the microcanonical ensemble, whereas, in our theory, they are computed with the (grand) canonical ensemble. This not only reflects the difference of approach, but also results in a serious difference in the calculation of the transport coefficients. For instance, the second term of the thermal conduction flux (6.21) is missing in Green's corresponding expression. In essence the difference is as follows. Green assumes that the time behavior of the state variables of a fluid is described by a Markoffian random process. He shows that such processes in aged isolated systems obey a Fokker-Planck type equation, and he can derive the macroscopic equation of motion. We, however, begin with the investigation of the change in time of the average values of dynamical quantities in nonequilibrium fluids in contact with reservoirs, and we derive the macroscopic equation governing the motion of the state variables. Furthermore, our method has been formulated to apply to the quantum-mechanical case.

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[24] Note that use of the relation (3.42), $\langle J_{\alpha}(\mathbf{x})\rangle_{t}=0$, and the definition of the square bracket, (2.25), lead to $[J_{\alpha}(\mathbf{x})]$ $=\mathrm{Tr}J_{\alpha}(\mathbf{x})\bar{\rho}(t)$.

[25] M. Kac, *Proceedings of the Third Berkeley Symposium on Mathematical Statistics and Probability* (University of California Press, Berkeley, 1956), Vol. 3, p. 171; G. E. Uhlenbeck, Higgins lecture given at Princeton University, 1954 (unpublished).

[26] It is worthwhile to note here an essential difference between our system and the nonequilibrium system whose deviation from equilibrium is produced by mechanical disturbances. The driving forces of the latter system are the external forces, which can be controlled directly by outer bodies and be changed appreciably in small time intervals comparable to the average relaxation time of the microscopic processes associated with the external forces. In our system, however, the driving forces are state functions and decay to zero due to the coupling with the microscopic processes, the average decay time τ_{r} being subject to (2.6).

Kubo's theory is exact in the sense that it does not need the notion of local equilibrium and therefore avoids any approximation like (2.29). Therefore, it is worth while to compare both results in the case of electrical conductivity to which Kubo's method is applicable. Let us suppose that the fluid consists of an electron gas $(k=e)$ and ions $(k=i)$ with the average velocity $\mathbf{v}=0$. Then we have, from (5.11), (5.16), and (5.25),

$$\delta\langle\rho^e\rangle/\partial t=-\nabla\cdot[\mathbf{j}^e], \quad \delta\langle H\rangle/\partial t=-\nabla\cdot[\mathbf{J}_H],$$

$$g=\frac{1}{T_0}\left\{[\mathbf{J}_H]\cdot\mathbf{X}_T-\sum_{k=e,i}[\mathbf{j}^k]\cdot\frac{T_0}{m^k}\nabla\left(\frac{\mu^k}{T}\right)\right\}, \quad (7.3)$$

where the energy flow $\mathbf{J}_H$ has been used instead of the thermal conduction flow $\mathbf{J}_T$. The linear relations are obtained from (4.16). In the case in which the ions pursue lattice vibrations about fixed points, $\mu^i=0$ in (7.3) and the linear relations become

$$[\mathbf{j}^e]=V^{-1}\left\{L(\mathfrak{J}^e,\mathfrak{J}^e)\cdot\left(-\frac{T_0}{m^e}\nabla\frac{\mu^e}{T}\right)\right.$$

$$\left.+L(\mathfrak{J}^e,\mathfrak{J}_H)\cdot\mathbf{X}_T\right\},$$

$$(7.4)$$

$$[\mathbf{J}_H]=V^{-1}\left\{L(\mathfrak{J}_H,\mathfrak{J}^e)\cdot\left(-\frac{T_0}{m^e}\nabla\frac{\mu^e}{T}\right)\right.$$

$$\left.+L(\mathfrak{J}_H,\mathfrak{J}_H)\cdot\mathbf{X}_T\right\},$$

which agree with the equations obtained in (I) and with the phenomenological treatment of thermoelectricity.[27] The electrical conductivity can thus be expressed in terms of the diffusion coefficient; for a metal, the x, y component of the conductivity tensor is

$$\sigma_{xy}=\frac{1}{V}\left(\frac{e}{m}\right)^2\int_0^\infty ds\int_0^\beta \langle\mathfrak{J}_y^e\mathfrak{J}_x^e(s+i\hbar\lambda)\rangle^0 d\lambda, \quad (7.5)$$

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[27] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1953), Chap. VIII.

e and m being the charge and the mass of electron. Equation (7.5) is the same as obtained by Kubo's method.[28] This agrees with the previously-obtained fact that the coarse-graining approximation (2.29) yields only negligible errors.

APPENDIX. DERIVATION OF EQ. (4.6)

Equation (4.4) can be written, by inserting (2.4), as

$$\delta_2 S(t)=k\ln(Z_{t+\tau}/Z_t)+\int d\mathbf{x}\{\delta(1/T)\langle H(\mathbf{x})\rangle(t+\tau)$$

$$-\delta(\mathbf{v}/T)\cdot\langle\mathbf{j}(\mathbf{x})\rangle(t+\tau)+\delta(\tfrac{1}{2}v^2/T)\langle\rho(\mathbf{x})\rangle(t+\tau)$$

$$-\sum_k\delta(\mu^k/T)\langle n^k(\mathbf{x})\rangle(t+\tau)\}, \quad (A.1)$$

where $\delta(f)$ means the increment of f in τ. The first term can be written as

$$k\ln\left(1-\frac{1}{k}\int d\mathbf{x}\{\delta(1/T)\langle H\rangle_t-\delta(\mathbf{v}/T)\cdot\langle\mathbf{j}\rangle_t\right.$$

$$\left.+\delta(\tfrac{1}{2}v^2/T)\langle\rho\rangle_t-\sum_k\delta(\mu^k/T)\langle n^k\rangle_t\}+O(\delta^2)\right).$$

Therefore, by expanding this equation and inserting into (A.1), we arrive at Eq. (4.6) with the aid of the relations (2.9).

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[28] In applying this method, suppose the system to be in contact with a heat reservoir before the contact has been cut off and an electric field has been turned on, to obtain the average with the canonical ensemble.