

Collective Motion of Particles at Finite Temperatures^{*)}

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A quantum-statistical theory of frequency spectra and damping constants of the collective motion of interacting particles at finite temperatures is presented, and used to clarify several problems. The formulation is based on the explicit recognition of the fact that a set of collective variables, properly chosen describe the collective motion in such a way that the average values of the collective variables at a time determine their average values thereafter.

The frequency distribution of the density fluctuations in fluids is thus analyzed, and molecular expressions for the intensities and widths of the spectral lines are obtained. The widths are written in terms of generalized transport coefficients which depend upon the wavelength of the collective oscillation or the frequency spectrum. The expressions are valid even in the case in which the hydrodynamical description is inapplicable, and turn out to be useful for describing the sound attenuation in liquid helium II at low temperatures and the inelastic scattering of neutrons by liquids.

The transport coefficients of fluids are formulated in terms of equilibrium fluctuations from a new point of view without the use of the local equilibrium ensemble. The results for the shear viscosity and thermal conductivity agree with those obtained by the author previously. A new term, however, is found to be added to the dynamical flux determining the bulk viscosity. This term arises as a result of subtracting a pressure fluctuation associated with the fluctuation of the mass and energy densities to define a random force.

§ 1. Introduction

In spite of atomic random motion, a macroscopic body exhibits a variety of types of collective organized motion, such as sound waves and thermal conduction. The hydrodynamical equations are known to describe the collective motion of fluids. A number of investigations¹⁻⁵⁾ have been devoted to the statistical-mechanical foundation of these equations with the purpose, in particular, of deriving molecular expressions for the transport coefficients involved, and with the hope of finding a general prescription for dealing with the collective motion of interacting particles. If the macroscopic state of fluids can be described by one local velocity, one local temperature, and one local mass density, then the usual hydrodynamical equations were shown to hold in the limitation of linear dissipative process, and molecular expressions for the transport coefficients were derived in terms of the time fluctuation of dynamical fluxes in equilibrium.⁶⁾

In the derivation it was assumed that the collective motion takes place slowly

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so that the transport coefficients are independent of the frequency of the collective oscillation. However, there are a number of important phenomena not satisfying this assumption; for instance, sound attenuation in liquids and solids at very low temperatures, and transport in plasmas. The treatment of the second sound waves in liquid He II also requires a more general theory of collective motion.

Recently the method of two-time Green's function has been developed to study many-body systems.^{6),7)} However, the existing approximations suffer from several defects,^{7),8)} and there is no powerful approximation found for truncating the hierarchy equations for the Green's functions of different orders which is generally valid for treating the damping of collective motion. For instance, the treatment of the sound waves with this method has not been successful.⁹⁾

The collective motion of ferro- and antiferromagnetic spins has been studied on the basis of the statistical mechanics of irreversible processes to clarify the dynamical cooperative phenomena of spins below and above the Curie points.¹⁰⁾ In this paper, the collective motion of fluids will be studied from a similar, but more refined, point of view.

Since Kubo's complete formulation of the linear response of macroscopic systems to mechanical disturbances,¹¹⁾ the importance of obtaining the time-fluctuation expression for a transport coefficient has been fully recognized. However, there still remains an ambiguity in the formulation of transport coefficients for thermodynamical disturbances. For instance, thermodynamical parameters, such as pressure and chemical potential, have been introduced in the theory without deriving them explicitly from the nonequilibrium density matrix of the system. One of the aims of the present paper is to remove such an ambiguity by avoiding the use of the local equilibrium ensemble.

In § 2, a set of relaxation functions are discussed to describe a disturbed state of a fluid. It is pointed out that the use of the relaxation function is particularly convenient for determining the collective motion at finite temperatures. In § 3, we present a method for calculating the relaxation functions of the collective variables. For illustration, the damping constant of the plasma oscillation is calculated. An expression for the isothermal sound attenuation is derived, and its application to the problem of the first sound attenuation in liquid He II at low temperatures is suggested. In § 4, the density fluctuation in liquids is studied, and three normal modes and their frequencies and damping constants are determined. In § 5, the damping constants are calculated for small wave numbers, and a new theory of transport coefficients is obtained. The last section is devoted to a summary and discussions.

§ 2. A set of relaxation functions

A collective motion is produced by the excitation of the system by an external disturbance, being able to be determined by studying the corresponding

response of the system.

Let us take the inelastic scattering of neutrons by a monatomic liquid without spin. According to van Hove,¹²⁾ the scattering cross section is simply related to the time correlation function of the number density of the liquid, $\langle n_{\mathbf{k}}(t) n_{\mathbf{k}}^* \rangle$, where

$$\langle A \rangle = \text{Tr } \rho A, \quad \rho = e^{-\beta H} / \text{Tr } e^{-\beta H}, \quad (2.1)$$

H being the Hamiltonian of the liquid, and

$$n_{\mathbf{k}} = \int_V d\mathbf{r} \exp(i\mathbf{k} \cdot \mathbf{r}) n(\mathbf{r}) = \sum_{j=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_j), \quad (2.2)$$

where the liquid has been assumed to consist of N particles in a volume V , and \mathbf{r}_j denotes the coordinate of the j -th particle. The wave vector \mathbf{k} corresponds to the momentum transfer of the scattered neutron, $n_{\mathbf{k}}(t)$ is the Heisenberg operator after time t , and the asterisk $*$ means the Hermitean conjugate. The time dependence of the correlation function determines the collective excitation produced by the neutron scattering, and has been studied by many authors.^{12),13)} However, it is more convenient to consider the relaxation matrix

$$\chi_{\mathbf{k}}(t) = \begin{bmatrix} (n_{\mathbf{k}}(t), n_{\mathbf{k}}^*) & (n_{\mathbf{k}}(t), H_{\mathbf{k}}^*) & (n_{\mathbf{k}}(t), \dot{n}_{\mathbf{k}}^*) \\ (H_{\mathbf{k}}(t), n_{\mathbf{k}}^*) & (H_{\mathbf{k}}(t), H_{\mathbf{k}}^*) & (H_{\mathbf{k}}(t), \dot{n}_{\mathbf{k}}^*) \\ (\dot{n}_{\mathbf{k}}(t), n_{\mathbf{k}}^*) & (\dot{n}_{\mathbf{k}}(t), H_{\mathbf{k}}^*) & (\dot{n}_{\mathbf{k}}(t), \dot{n}_{\mathbf{k}}^*) \end{bmatrix}, \quad (2.3)$$

where

$$(A, B) = \int_0^\beta d\lambda \langle e^{\lambda H} A e^{-\lambda H} B \rangle - \beta \langle A \rangle \langle B \rangle \quad (2.4)$$

$$= (B, A) = (A^*, B^*)^*, \quad (2.5)$$

and $H_{\mathbf{k}}$ is the Fourier component of the Hamiltonian density, and $\dot{n}_{\mathbf{k}}$ denotes the time derivative of $n_{\mathbf{k}}$, $(i/\hbar) [H, n_{\mathbf{k}}]$. The relation between the correlation function $\langle n_{\mathbf{k}}(t) n_{\mathbf{k}}^* \rangle$ and the relaxation function $(n_{\mathbf{k}}(t), n_{\mathbf{k}}^*)$ can be obtained from the fluctuation-dissipation theorem.¹¹⁾ In the classical limit, we have $(A, B) = \beta \langle AB \rangle$.

The reason for taking the relaxation matrix $\chi_{\mathbf{k}}(t)$ is the following. When a density fluctuation $n_{\mathbf{k}}$ occurs, a flow $\dot{n}_{\mathbf{k}}$ is produced according to the equation of continuity. A work due to the expansion and compression of mass elements is described by $H_{\mathbf{k}}$. Thus $n_{\mathbf{k}}$, $\dot{n}_{\mathbf{k}}$, and $H_{\mathbf{k}}$ are strongly coupled, and form a set of collective variables for describing the density fluctuation. Then we can assume the following relation for small wave numbers :

$$\Xi_{\mathbf{k}}(t+s) = \Xi_{\mathbf{k}}(t) \cdot \Xi_{\mathbf{k}}(s), \quad (2.6)$$

where

$$\Xi_{\mathbf{k}}(t) = \chi_{\mathbf{k}}(t) \cdot [\chi_{\mathbf{k}}(0)]^{-1}. \quad (2.7)$$

The only nonsingular solution for (2.6) is $\Xi_k(t) = \exp(t\Theta_k)$ for $t > 0$. Θ_k is a constant matrix, and the imaginary and real parts of its eigenvalues give the eigenfrequencies and damping constants of the collective modes involved in the density fluctuation. Explicit expressions for Θ_k and its eigenvalues will be derived later.

The translation-operator property (2.6) is the fundamental relation in the present theory. To clarify its meaning, let us consider a nonequilibrium monatomic liquid with local temperature $T(\mathbf{r})$, velocity potential $\phi(\mathbf{r})$, and local chemical potential $\mu(\mathbf{r})$. In the linear approximation, the local equilibrium ensemble then becomes

$$\rho_t = \rho \left\{ 1 + \sum_q \int_0^\beta d\lambda e^{\lambda H} [T_q' H_q^* + \phi_q \dot{n}_q^* + (\mu_q - \mu T_q') n_q^*] e^{-\lambda H} \right\}, \quad (2.8)$$

where $T_q' = T_q/T$, and T_q , ϕ_q , and μ_q are the Fourier components of the deviations of the corresponding parameters from the equilibrium values. The precise density matrix $\rho(t)$ of the liquid deviates from the local equilibrium ensemble (2.8). However, since the temporal development of a macroscopic system is, except an initial transient period of a microscopic time scale τ_m , independent of the way of the initial preparation of the system as far as the initial values of the macroscopic state variables are fixed to be the same, we take $\rho(0) = \rho_{t=0}$ as the initial condition to know the nonequilibrium state of the liquid after time $t > \tau_m$.³⁾ Since the average value at time t is given by $\langle A \rangle(t) = \text{Tr } \rho(0) A(t)$, we thus obtain

$$\begin{bmatrix} \langle n_k \rangle(t) \\ \langle H_k \rangle(t) \\ \langle \dot{n}_k \rangle(t) \end{bmatrix} = \Xi_k(t) \cdot \begin{bmatrix} \langle n_k \rangle(0) \\ \langle H_k \rangle(0) \\ \langle \dot{n}_k \rangle(0) \end{bmatrix}. \quad (2.9)$$

Since the collective variables n_k , H_k , and \dot{n}_k become the constants of motion as k goes to zero, the relaxation time of (2.9) is, for small values of k , much larger than the initial transient time τ_m so that (2.9) can be used to study the time dependence of the normalized relaxation matrix $\Xi_k(t)$. The average values of the collective variables at a time determine their average values thereafter. This prediction property of the average behavior is formulated in the form of (2.6). Thus the translation-operator property (2.6) represents the deterministic property of the macroscopic laws.

It is instructive to consider a Gaussian random process and see a parallelism between our theory and the Gaussian Markoff process. For a system performing small fluctuations around an equilibrium state, it is assumed that the macroscopic variables defining a state are Gaussian random variables.^{14),15)} As is well known, a classical Gaussian random process is determined by a set of the time-correlation functions of the random variables. The average behavior of the process, defined by the conditional average values of the state variables with their initial values

given, is described by the time-correlation functions.¹⁴⁾ On the other hand, since the average regression of spontaneous fluctuations in equilibrium is equivalent to the macroscopic motion of disturbed states, the conditional average values should obey the same laws as the corresponding nonequilibrium average values described by the relaxation functions, (2.9). This situation implies taking the relaxation functions rather than the time-correlation functions in defining a quantum Gaussian random process. In the quantum-mechanical case, a Gaussian random process in aged systems is thus given by the Gaussian probability distributions whose covariance matrices are defined by the relaxation functions (divided by β) of the random variables, and the average behavior of the state variables is described by the corresponding relaxation matrix. Therefore, if one assumes a Gaussian random process for describing the spontaneous fluctuations of the collective variables n_k , H_k , and \dot{n}_k , then the translation-operator property (2.6) corresponds to Doob's condition for the process to be Markoffian.¹⁵⁾

We note some properties of the relaxation function. Let F_k and G_k be the Fourier components of Hermitean density operators; $F_k^* = F_{-k}$. Since the liquid is isotropic, $(F_k(t), G_k^*)$ is invariant with respect to the inversion $\mathbf{k} \rightarrow -\mathbf{k}$ and turns out to be real. In the absence of an external parameter odd with respect to the time reversal, the Hamiltonian and the dynamical motion of the system are invariant with respect to the time reversal so that we have

$$(F_k(t), G_k^*) = \varepsilon_F \varepsilon_G (F_k(-t), G_k^*) = \varepsilon_F \varepsilon_G (G_k(t), F_k^*), \quad (2.10)$$

$$(F_k, G_k^*) = 0, \quad \text{if } \varepsilon_F \varepsilon_G = -1, \quad (2.11)$$

where ε_F is +1 for an even variable and -1 for an odd variable with respect to the time reversal.

§ 3. Normal modes at finite temperatures

The dynamical behavior of the collective variables was shown to be described most conveniently by the relaxation functions. In this section, we shall first formulate mathematical techniques required for the study of the relaxation functions, taking a simple example, and secondly discuss a few applications.

Let us consider a collective motion which is described by two variables Q and P . The variables are assumed to have the following properties: denoting the time-reversal operator by K ,¹⁶⁾

$$KQK^{-1} = Q^*, \quad KPK^{-1} = -P^*. \quad (3.1)$$

The relaxation matrix is then

$$\mathbf{z}(t) = \begin{bmatrix} (Q(t), Q^*) & (Q(t), P^*) \\ (P(t), Q^*) & (P(t), P^*) \end{bmatrix}. \quad (3.2)$$

The matrix elements are assumed to be real in accordance with the relaxation

function $(F_k(t), G_k^*)$ defined just before (2.10). It is also assumed that any external parameter odd with respect to the time reversal is not present. Then, from (2.11) we have

$$(Q, P^*) = (\dot{Q}, Q^*) = (\dot{P}, P^*) = 0. \quad (3.3)$$

The normalized relaxation matrix thus takes the form

$$\mathbf{E}(t) = \chi(t) \cdot \chi^{-1}(0) = \begin{bmatrix} \frac{(Q(t), Q^*)}{(Q, Q^*)} & \frac{(Q(t), P^*)}{(P, P^*)} \\ \frac{(P(t), Q^*)}{(Q, Q^*)} & \frac{(P(t), P^*)}{(P, P^*)} \end{bmatrix}. \quad (3.4)$$

Now the problem is to determine the time dependence of (3.4) or the following moments of the normalized relaxation matrix:

$$\langle \omega^n \rangle = \int_{-\infty}^{\infty} d\omega \omega^n \mathbf{E}(\omega) = (-i)^n [d^n \mathbf{E}(t) / dt^n]_{t=0}. \quad (3.5)$$

The first moment matrix has the form

$$i\hat{\omega} = i\langle \omega \rangle = \begin{bmatrix} 0 & 1 \\ -\Omega^2 & 0 \end{bmatrix}, \quad (3.6)$$

where

$$\Omega^2 = (P, \dot{Q}^*) / (Q, Q^*) = (P, P^*) / (Q, Q^*), \quad (3.7)$$

and P has been assumed to be normalized so that

$$(\dot{Q}, P^*) / (P, P^*) = 1. \quad (3.8)$$

The first moment matrix can easily be diagonalized. Namely,

$$U \cdot i\hat{\omega} \cdot U^{-1} = \begin{bmatrix} i\Omega & 0 \\ 0 & -i\Omega \end{bmatrix}. \quad (3.9)$$

The diagonal transformation U is found to be

$$U = \begin{bmatrix} i\Omega & 1 \\ -i\Omega & 1 \end{bmatrix}, \quad U^{-1} = \frac{1}{2i\Omega} \begin{bmatrix} 1 & -1 \\ i\Omega & i\Omega \end{bmatrix}. \quad (3.10)$$

Equation (3.7) for Ω provides us with the eigenfrequencies of the collective motion. The higher moments $\langle \omega^n \rangle$, $n \geq 2$, yield a damping and a shift of frequency. To proceed further, it is convenient to define the normal coordinates by

$$\begin{bmatrix} I \\ \bar{I} \end{bmatrix} = U \cdot \begin{bmatrix} Q \\ P \end{bmatrix} = \begin{bmatrix} P + i\Omega Q \\ P - i\Omega Q \end{bmatrix}, \quad (3.11)$$

which fulfill

$$\begin{aligned}(I, I^*) &= (\bar{I}, \bar{I}^*) = 2(P, P^*), \\ (I, \bar{I}^*) &= (\bar{I}, I^*) = 0.\end{aligned}\quad (3.12)$$

The transformation of $\mathcal{E}(t)$ by U thus leads to

$$\tilde{\mathcal{E}}(t) = U \cdot \mathcal{E}(t) \cdot U^{-1} = \begin{bmatrix} \xi(t) & \eta(t) \\ \eta(t) & \xi^*(t) \end{bmatrix}, \quad (3.13)$$

where

$$\xi(t) = (I(t), I^*) / (I, I^*), \quad (3.14)$$

$$= [(P(t), P^*) + \Omega^2(Q(t), Q^*) - 2i\Omega(P(t), Q^*)] / 2(P, P^*), \quad (3.15)$$

$$\eta(t) = (I(t), \bar{I}^*) / (\bar{I}, \bar{I}^*), \quad (3.16)$$

$$= [(P(t), P^*) - \Omega^2(Q(t), Q^*)] / 2(P, P^*), \quad (3.17)$$

where, in deriving (3.15) and (3.17), use has been made of the relation $(P(t), Q^*) = -(Q(t), P^*)$ which is obtained from (2.10). The function $\xi(t)$ represents the time-dependent autocorrelation of the normal modes, and $\eta(t)$ provides us with a measure of coupling between the two normal coordinates. The inverse transformation of (3.13) leads to

$$\mathcal{E}(t) = \begin{bmatrix} \text{Re } \xi(t) - \eta(t) & \text{Im } \xi(t) / \Omega \\ -\Omega \text{Im } \xi(t) & \text{Re } \xi(t) + \eta(t) \end{bmatrix}. \quad (3.18)$$

$\tilde{\mathcal{E}}(t)$ represents the transformation between the normal coordinates at different times. If one could guess the normal coordinates from the beginning, one would at once obtain (3.13) instead of (3.4), the frequency being given by

$$\Omega = (\dot{I}, I^*) / i(I, I^*) = -\langle [I, I^*] \rangle / \hbar (I, I^*). \quad (3.19)$$

If one neglects the dynamical coupling between the normal modes, $\eta(t)$, the damping and shift of frequency of the normal modes can be calculated in the same way as in the case of the ferromagnetic spin waves.¹⁰ The result is

$$\xi(t) = \exp[t(i\Omega - \Gamma)], \quad (3.20)$$

where

$$\Gamma = \int_0^\infty dt e^{-it\Omega} (K(t), K^*) / (I, I^*), \quad (3.21)$$

$$K = \dot{I} - i\Omega I. \quad (3.22)$$

Here it has been assumed that $1 \gg \gamma\tau_c$, where γ is the real part of Γ and τ_c

denotes the correlation time of the force $K(t)$ in which the integrand of (3·21) vanishes. The time $\tau_r = \gamma^{-1}$ represents the relaxation time of the normal mode, and τ_c is a microscopic time in which a dynamical coherence disappears. This assumption is a formulation of the fact that a collective coordinate is an approximate constant of motion. From (3·19) and (3·22) we have $(K, I^*) = 0$. This means that the force K acting on the collective mode is nearly statistically-independent of the normal coordinate. The fluctuation of this force thus determines the damping and shift of frequency. It should be noted here that, when $\Omega\tau_c \ll 1$, the imaginary part of (3·21) vanishes, thus leading to no shift of frequency.

A general formulation including the coupling between the normal modes is obtained in the following manner. The transformed normalized relaxation matrix (3·13) is written as

$$\tilde{\mathcal{E}}(t) = (\mathcal{J}(t), \mathcal{J}^*) \cdot (\mathcal{J}, \mathcal{J}^*)^{-1}, \quad (3\cdot23)$$

where \mathcal{J} denotes a column vector consisting of the normal coordinates and the asterisk * means the Hermitean conjugate, \mathcal{J}^* being thus a row vector. Let us denote the diagonal matrix of eigenfrequencies by $\hat{\Omega}$. With the aid of the identity

$$\mathcal{J}(t) = \exp(it\hat{\Omega}) \cdot [\mathcal{J} + \int_0^t ds \exp(-is\hat{\Omega}) \cdot \mathcal{K}(s)], \quad (3\cdot24)$$

where \mathcal{K} denotes the corresponding column vector of the forces, we obtain

$$\tilde{\mathcal{E}}(t) = \exp(it\hat{\Omega}) [\mathbf{1} - \int_0^t ds \exp(-is\hat{\Omega}) \cdot \hat{\Gamma}_s \cdot \exp(is\hat{\Omega})], \quad (3\cdot25)$$

where

$$\hat{\Gamma}_s = \int_0^s d\tau (\mathcal{K}(\tau), \mathcal{K}^*) \cdot (\mathcal{J}, \mathcal{J}^*)^{-1} \cdot \exp(-i\tau\hat{\Omega}), \quad (3\cdot26)$$

and it has been used that $(\mathcal{J}, \mathcal{J}^*)$ is a diagonal matrix. Let us assume that the matrix elements of the integrand matrix of (3·26) vanish in a short time interval τ_c . When time intervals t of interest are much longer than the correlation time τ_c , we replace $\hat{\Gamma}_s$ in (3·25) by $\hat{\Gamma}_\infty$, neglecting terms newly produced. The neglect is valid for time intervals much smaller than the relaxation time $\tau_r = \gamma^{-1}$. Then (3·25) is equal to the first two terms in the ordered exponential expansion of the following expression in terms of $\hat{\Gamma}$:

$$\tilde{\mathcal{E}}(t) = \exp[t(i\hat{\Omega} - \hat{\Gamma})], \quad (3\cdot27)$$

where

$$\hat{\Gamma} = \int_0^\infty dt (\mathcal{K}(t), \mathcal{K}^*) \cdot (\mathcal{J}, \mathcal{J}^*)^{-1} \cdot \exp(-it\hat{\Omega}), \quad (3\cdot28)$$

$$\mathcal{K} = \dot{\mathcal{G}} - i\hat{\Omega} \cdot \mathcal{G}. \quad (3.29)$$

Equation (3.27) fulfills the translation-operator property

$$\tilde{\mathcal{E}}(t+s) = \tilde{\mathcal{E}}(t) \cdot \tilde{\mathcal{E}}(s). \quad (3.30)$$

From this property, it turns out that (3.27) is valid for any time interval much longer than the correlation time τ_c . Equation (3.27) is thus an asymptotic equation derived on the basis of the macroscopic prediction property and the fact that the relaxation time of the collective motion τ_r is much larger than the correlation time of the forces τ_c . If one neglects the off-diagonal elements of (3.28) arising from the coupling between the different forces, then (3.27) leads to the previous results (3.20) and (3.21).

Equations (3.20) and (3.27) correspond to the Lorentzian limit well known in the theory of line shape.¹⁷⁾ Thus the Lorentzian limit is valid for a good collective mode. However, we often meet with the situation that a collective coordinate ceases to be a good constant of motion, as in the case of large momentum transfers in the neutron scattering. Such a case would be described very well by the assumption of Gaussian random process. Corresponding to this phenomenological treatment, (3.25) may be written as

$$\tilde{\mathcal{E}}(t) = \exp_{(+)} \left[\int_0^t ds (i\hat{\Omega} - \hat{\Gamma}_s) \right], \quad (3.31)$$

where $\exp_{(+)}$ denotes the ordered exponential (time ordering from the right). In the Lorentzian limit in which $\tau_r \gg \tau_c$, (3.31) agrees with (3.27). In the Gaussian limit in which $\tau_r \ll \tau_c$ and $\Omega\tau_r \ll 1$, (3.31) leads to

$$\tilde{\mathcal{E}}(t) = \exp(it\hat{\Omega}) \cdot \exp[-(t^2/2) (\mathcal{K}, \mathcal{K}^*) \cdot (\mathcal{G}, \mathcal{G}^*)^{-1}], \quad (3.32)$$

which does not fulfill the translation-operator property (3.30).

As an application, we consider an isothermal density fluctuation. Taking $Q = n_k$ and $P = \dot{n}_k$, we obtain

$$I_k = \dot{n}_k + i\Omega_k n_k, \quad (3.33)$$

where Ω_k is the eigenfrequency; from (3.7),

$$\Omega_k^2 = (\dot{n}_k, \dot{n}_k^*) / (n_k, n_k^*), \quad (3.34)$$

$$\cong [k^2/mS(k)] (\hbar\Omega_k/2) \coth(\beta\hbar\Omega_k/2), \quad (3.35)$$

where $S(k) \equiv \langle n_k n_k^* \rangle / N$, $k \neq 0$, is the pair correlation function of particles. Equation (3.35) is obtained by neglecting the coupling between the normal modes $\eta(t)$ and the quantity Γ_{k^*} . This neglect would be justified for small

*) From (3.18) and (3.20), we obtain

$$(n_k(t), n_k^*) \cong (n_k, n_k^*) \cos(\Omega_k t).$$

The fluctuation-dissipation theorem¹¹⁾ thus leads to

$$(n_k, n_k^*) \cong \langle n_k n_k^* \rangle / \frac{1}{2} \hbar \Omega_k \coth(\frac{1}{2} \beta \hbar \Omega_k).$$

Therefore, we obtain (3.35) by using the relation

$$(\dot{n}_k, \dot{n}_k^*) = -(i/\hbar) \langle [n_k, \dot{n}_k^*] \rangle = Nk^2/m.$$

wave numbers. Since $(I_k, I_k^*) = 2(\dot{n}_k, \dot{n}_k^*) = 2Nk^2/m$, (3.21) leads to

$$\Gamma_k = \frac{m}{2Nk^2} \int_0^\infty dt \exp(-it\Omega_k) (K_k(t), K_k^*), \quad (3.36)$$

where

$$K_k = \dot{I}_k - i\Omega_k I_k = \dot{n}_k + \Omega_k^2 n_k. \quad (3.37)$$

The real part γ_k of (3.36) provides us with the damping of the isothermal density oscillation.

A calculation of (3.34) and (3.36) leads to approximate expressions for the plasma frequency and damping for an electron gas with a uniform background of positive charge ensuring the overall neutrality of the system. It would be interesting to see how the Landau damping comes out from these expressions. The use of the equation of motion for \ddot{n}_k yields

$$\Omega_k^2 = (4\pi e^2 N/m) + (\hbar k^2/2m)^2, \quad (3.38)$$

$$K_k = \sum_q W(\mathbf{k}, \mathbf{q}) a_{k+q}^* a_q, \quad (3.39)$$

where

$$W(\mathbf{k}, \mathbf{p}/\hbar) = - [(\mathbf{k} \cdot \mathbf{p})^2 + \hbar k^2 (\mathbf{k} \cdot \mathbf{p})] / m^2, \quad (3.40)$$

$$a_q a_{q'}^* + a_{q'}^* a_q = \delta_{q, q'}. \quad (3.41)$$

Here we have neglected the Coulomb interaction terms other than that of yielding the first term of (3.38). Equation (3.39) comes out from the kinetic energy of electrons, and represents an effective force acting on the plasma oscillation as a result of thermal motion of electrons. This thermal motion produces the plasma damping. Inserting (3.39) into (3.36) and calculating the time dependence and the ensemble average with the free electron Hamiltonian, we obtain

$$\gamma_k = \frac{\pi m}{2Nk^2} \frac{1}{\hbar \Omega_k} \sum_q [f_q - f_{k+q}] W^2(\mathbf{k}, \mathbf{q}) \delta(\Omega_k + \varepsilon_q/\hbar - \varepsilon_{k+q}/\hbar), \quad (3.42)$$

where $f_q = \langle a_q^* a_q \rangle$ is the Fermi distribution, and $\varepsilon_q = (\hbar q)^2/2m$. In the classical limit $\hbar=0$, the integration region of (3.42) is limited to $\infty > p > (m\Omega_k/k)$ in the momentum space due to the energy conservation $\mathbf{k} \cdot \mathbf{p}/m = \Omega_k$. Taking the Boltzmann distribution, we thus obtain

$$\gamma_k = (\pi/8)^{1/2} \Omega_k (kr_d)^{-3} \exp[-(kr_d)^{-2}/2], \quad (3.43)$$

where $r_d = (k_B T/m\Omega_k^2)^{1/2}$ is the Debye shielding radius. Equation (3.43) is just equal to that obtained first by Landau.¹⁸⁾ In order to clarify the problem of the k^2 term in the plasma frequency, however, we would have to consider the possibility of existence of a better normal coordinate than (3.33), and the coupling with the heat flow.

The isothermal sound frequency and attenuation are also obtained from

(3.35) and (3.36). The attenuation constant is given by $\alpha_k = \gamma_k/c$, c being the speed of sound. Equation (3.35) gives us the energy spectrum of excitations with small wave numbers in liquid He II. The result is in agreement with the quantum theory of weakly excited states.^{7,19)} Therefore, the present theory is expected to be useful for the investigation of transport phenomena in liquid He II. The first sound attenuation at temperatures below 1°K has been measured at a frequency of 12 Mc/sec by Chase and Herlin and by others, and Khalatnikov's theory turned out to yield values too much smaller than those observed.²⁰⁾ According to Landau's theory, liquid He II at low temperatures is described as being a gas of elementary excitations, phonons and rotons. The interactions between them result in various transport phenomena. Since an explicit expression for the interaction, however, is not completely fixed, the study of the sound attenuation is of particular interest. Let us write the Hamiltonian in the form

$$H = H_0 + H_1, \quad H_0 = \sum_q \hbar \Omega_q a_q^* a_q, \tag{3.44}$$

$$[a_q, a_{q'}^*] = \delta_{q,q'}, \quad a_q \doteq i\nu_q I_q^*, \tag{3.45}$$

where $\nu_q = (m/2q^2 \hbar \Omega_q N)^{1/2}$, and H_1 is the interaction Hamiltonian between phonons. Equation (3.45) can be derived by applying the random phase approximation [to the commutation relations for n_q and \dot{n}_q . The random force K_k is then written as

$$K_k \doteq -(\hbar\nu_k)^{-1} [H_1, a_k^*]. \tag{3.46}$$

A method for determining the dynamical interaction between phonons is obtained by incorporating the hydrodynamical investigation of the force K_k . The use of the conservation laws of mass and momentum densities leads, for small values of k , to

$$K_k = -(\hbar k/m) : \Pi_k - (ck) \mathbf{k} \cdot \mathbf{j}_k - i\Omega_k I_k, \tag{3.47}$$

where Π_k is the momentum flux and \mathbf{j}_k the mass flux. The third term cancels the contribution from the collective isothermal fluctuation of the mass density, K_k thus representing the effective force responsible for the random fluctuations of density. Namely, linear terms of Π_k and \mathbf{j}_k in a_q^* and a_q cancel out the third term so that the parts of the fluxes Π_k and \mathbf{j}_k , which enter into the force, can be assumed to consist of terms of higher order than the bilinear in the normal coordinates. The main part of (3.47) thus have the form

$$K_k = -\sum_q U_{k+q}^{k,q} a_{k+q}^* a_q, \tag{3.48}$$

and U may be determined from the quantum-hydrodynamical study of the fluxes in phonon gases. From (3.46), this approximation is equivalent to the following effective Hamiltonian :

$$H_1 \doteq (1/2) \sum_{k,q} \hbar\nu_k U_{k+q}^{k,q} a_{k+q}^* a_k a_q. \tag{3.49}$$

Thus we can determine the dynamical interaction responsible for the sound attenuation. This program has been carried out by Kawasaki and the author.²¹⁾ It will be shown that the matrix elements of three phonon process of the confluence form have the form

$$U_{q+\frac{q-k}{2}}^{k, \frac{q-k}{2}} = \frac{k^2 q}{m} \left[\rho \left(\frac{\partial c}{\partial \rho} \right)_T + c \left(\frac{\mathbf{k} \cdot \mathbf{q}}{kq} \right) + c \left(\frac{\mathbf{k} \cdot \mathbf{q}}{kq} \right)^2 \right], \quad q \gg k, \quad (3.50)$$

ρ being the mass density, and the attenuation constant obtained by the perturbational calculation of (3.36) is in quantitative agreement with the observed values below 0.4°K, being proportional to $\Omega_k T^4$.

As will be seen in § 5, (3.36) can be written in terms of generalized coefficients of viscosity, and becomes proportional to Ω_k^2 in the high temperature region where $\Omega_k \tau_c \ll 1$. Thus (3.36) can be used to calculate the attenuation constant beyond 0.4°K. This problem will also be studied, and excellent agreement with the observed values will be obtained up to about 0.8°K by the use of a simple approximation.²¹⁾

§ 4. Density fluctuation in fluids

Sound wave propagation, inelastic scattering of neutrons, and the Rayleigh scattering of light are directly related to the density fluctuation. In this and the following sections, we shall study the density fluctuation in fluids by calculating the relaxation matrix (2.3).

From (2.11) we have

$$(n_k, \dot{n}_k^*) = (H_k, \dot{n}_k^*) = (\dot{H}_k, H_k^*) = (\ddot{n}_k, \dot{n}_k^*) = 0. \quad (4.1)$$

The normalized relaxation matrix thus takes the form

$$\Xi_k(t) = \begin{bmatrix} (n_k(t), [n_k^*]) & (n_k(t), [H_k^*]) & (n_k(t), [\dot{n}_k^*]) \\ (H_k(t), [n_k^*]) & (H_k(t), [H_k^*]) & (H_k(t), [\dot{n}_k^*]) \\ (\dot{n}_k(t), [n_k^*]) & (\dot{n}_k(t), [H_k^*]) & (\dot{n}_k(t), [\dot{n}_k^*]) \end{bmatrix}, \quad (4.2)$$

where

$$[n_k^*] = \{n_k^*(H_k, H_k^*) - H_k^*(n_k, n_k^*)\} / D_k, \quad (4.3)$$

$$[H_k^*] = \{H_k^*(n_k, n_k^*) - n_k^*(n_k, H_k^*)\} / D_k, \quad (4.4)$$

$$[\dot{n}_k^*] = \dot{n}_k^* / (\dot{n}_k, \dot{n}_k^*), \quad (4.5)$$

$$D_k = (n_k, n_k^*) (H_k, H_k^*) - |(n_k, H_k^*)|^2. \quad (4.6)$$

Calculation of the normalized relaxation matrix can be carried out in the same way as in § 3. Namely, diagonalizing the first-moment matrix of the normalized relaxation matrix, we obtain

$$U \cdot \dot{\mathbf{E}}_k(0) \cdot U^{-1} = \begin{bmatrix} i\Omega_k & 0 & 0 \\ 0 & -i\Omega_k & 0 \\ 0 & 0 & 0 \end{bmatrix}, \tag{4.7}$$

where

$$\Omega_k^2 = -(\dot{n}_k, [n_k^*]) - h_k(\ddot{n}_k, [H_k^*]), \tag{4.8}$$

$$h_k = (\dot{H}_k, \dot{n}_k^*) / (\dot{n}_k, \dot{n}_k^*). \tag{4.9}$$

It is convenient to introduce the following quantities :

$$\omega_{1k} = \{(\dot{n}_k, \dot{n}_k^*)(H_k, H_k^*) - (\dot{n}_k, \dot{H}_k^*)(H_k, n_k^*)\} / D_k \Omega_k, \tag{4.10}$$

$$\omega_{2k} = h_k \{(\dot{n}_k, \dot{H}_k^*)(n_k, n_k^*) - (\dot{n}_k, \dot{n}_k^*)(n_k, H_k^*)\} / D_k \Omega_k, \tag{4.11}$$

in terms of which

$$\Omega_k = \omega_{1k} + \omega_{2k}. \tag{4.12}$$

The normal coordinates are then obtained as

$$\begin{bmatrix} I_1 \\ \bar{I}_1 \\ I_2 \end{bmatrix} = U \cdot \begin{bmatrix} n_k \\ H_k \\ \dot{n}_k \end{bmatrix} = \begin{bmatrix} \dot{n}_k + i\omega_{1k} n_k + i(\omega_{2k}/h_k) H_k \\ \dot{n}_k - i\omega_{1k} n_k - i(\omega_{2k}/h_k) H_k \\ H_k - h_k n_k \end{bmatrix}, \tag{4.13}$$

which satisfy the following relations :

$$(I_1, I_1^*) = (\bar{I}_1, \bar{I}_1^*) = 2(\dot{n}_k, \dot{n}_k^*) = 2Nk^2/m, \tag{4.14}$$

$$(I_2, I_2^*) = D_k \Omega_k^2 / (\dot{n}_k, \dot{n}_k^*), \tag{4.15}$$

$$(I_1, \bar{I}_1^*) = (I_1, I_2^*) = (\bar{I}_1, I_2^*) = 0. \tag{4.16}$$

Neglecting the dynamical correlation between the normal modes, we obtain from (3.27)

$$(I_1(t), I_1^*) = (I_1, I_1^*) \exp[t(i\Omega_k - \Gamma_{1k})], \tag{4.17}$$

$$(\bar{I}_1(t), \bar{I}_1^*) = (I_1(t), I_1^*)^*, \tag{4.18}$$

$$(I_2(t), I_2^*) = (I_2, I_2^*) \exp(-t\Gamma_{2k}), \tag{4.19}$$

where

$$\Gamma_{1k} = \frac{m}{2Nk^2} \int_0^\infty dt \exp(-it\Omega_k) (K_1(t), K_1^*), \tag{4.20}$$

$$\Gamma_{2k} = \frac{Nk^2}{m D_k \Omega_k^2} \int_0^\infty dt (K_2(t), K_2^*), \tag{4.21}$$

where use has been made of (4.14) and (4.15). The forces acting on the

normal modes are given by

$$\begin{aligned} K_1 &= \dot{I}_1 - i\Omega_k I_1, \\ &= \ddot{n}_k + \Omega_k [\omega_{1k} n_k + (\omega_{2k}/h_k) H_k] + i(\omega_{2k}/h_k) K_2, \end{aligned} \quad (4.22)$$

$$K_2 = \dot{I}_2 = \dot{H}_k - h_k \dot{n}_k. \quad (4.23)$$

It should be noted that (4.17) and (4.19) are the asymptotic equations valid for time intervals larger than the correlation time τ_c in which the integrands of (4.20) and (4.21) vanish. In the Gaussian limit, we should employ (3.32).

The relaxation function of the mass density is obtained as

$$\begin{aligned} (n_k(t), n_k^*) &= (n_k, n_k^*) \{ \phi_k \exp(-t\gamma_{1k}) \cos[t(\Omega_k + \Delta\Omega_k)] \\ &\quad + (1 - \phi_k) \exp(-t\gamma_{2k}) \}, \end{aligned} \quad (4.24)$$

where

$$\phi_k = \frac{1}{\Omega_k} \left[\omega_{1k} + \frac{(H_k, n_k^*)}{(n_k, n_k^*) h_k} \omega_{2k} \right], \quad (4.25)$$

and γ and $\Delta\Omega$ denote the real and imaginary parts of Γ , respectively.

The three eigenfrequencies of (4.7) correspond to the three resonance lines observed in the Rayleigh scattering of light by liquids, the first two leading to the Brillouin doublet. The widths of the lines are given by γ_{1k} and γ_{2k} , and the intensities by ϕ_k and $(1 - \phi_k)$. In the limit of small wave numbers, these results will be shown later to agree with the hydrodynamical treatment. Recently de Gennes studied the moments of the time correlation function of the mass density, and clarified the inelastic scattering for large momentum transfer.¹³⁾ However, his method was not successful in covering the case of small momentum transfer. Our expressions, however, are valid for the intermediate as well as small values of k . Schofield has recently criticized the diffusion model of the neutron scattering in the quantum-mechanical case, and introduced a modified time correlation function for describing the diffusive motion.¹³⁾ However, our theory leads to taking the relaxation function for this purpose. The analysis of the widths and intensities will be discussed on a future occasion.

§ 5. Dynamical fluxes determining the transport coefficients

With the main purpose of removing the ambiguity in the previous formulations of the time-fluctuation expressions for transport coefficients discussed in § 1, we shall derive explicit expressions for the coefficients of viscosity and thermal conductivity by calculating (4.20) and (4.21) for small values of k .

Let us assume the conservation law of momentum density in the following form:

$$\ddot{n}_k = -(\mathbf{k}\mathbf{k}/m) : \Pi_k. \quad (5.1)$$

For instance, the plasma gases are thus excluded. For the values of k satisfying the relation $ak \ll 1$, a being the mean linear range of the intermolecular force, the momentum flux tensor takes the form

$$\begin{aligned} \Pi_k = & (1/4m) \sum_j \{ \mathbf{p}_j \mathbf{p}_j \exp (i\mathbf{k} \cdot \mathbf{r}_j) + \mathbf{p}_j \exp (i\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j \\ & + [\mathbf{p}_j \exp (i\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j]^\dagger + \exp (i\mathbf{k} \cdot \mathbf{r}_j) \mathbf{p}_j \mathbf{p}_j \} \\ & + (1/2) \sum_{j,l} \mathbf{F}_{jl} (\mathbf{r}_j - \mathbf{r}_l) \exp (i\mathbf{k} \cdot \mathbf{r}_j), \end{aligned} \quad (5.2)$$

where \mathbf{F}_{jl} denotes the intermolecular force between j and l , and \dagger means the transpose of the tensor. Since the intermolecular force is spherically symmetric, the momentum flux becomes a symmetric tensor. According to the virial theorem, the pressure p is given by

$$pV = (1/3) \langle \text{Trace} [\Pi_k]_{k=0} \rangle. \quad (5.3)$$

Therefore we obtain

$$\langle \ddot{n}_k \rangle' = - (k^2/m) pV, \quad (5.4)$$

where $\langle F_k \rangle'$ denotes the procedure of taking the ensemble average after expanding F_k in powers of the wave vector k and retaining the lowest order term.

Now we calculate various quantities involved for small values of k . First consider (n_k, n_k^*) and let k tend to zero. The thermal fluctuation of the number and Hamiltonian densities n_k and H_k arises due to the interaction between macroscopic portions in the liquid whose linear dimension is of the order of magnitude of k^{-1} . This thermal fluctuation can be calculated with the aid of the grand canonical ensemble in the following way. Let k tend to zero after letting the volume of the liquid to be infinity, and consider a large portion V of macroscopic dimension in the liquid. We denote the Hamiltonian and the number operator of particles of this portion by \mathcal{H} and \mathcal{N} , respectively, and redefine the density and flux operators in this portion. Then (n_k, n_k^*) for small values of k can be replaced by $\beta \langle (\mathcal{N} - N)^2 \rangle$, $N = \langle \mathcal{N} \rangle$, where the angular brackets mean the grand canonical average defined in this portion. \mathcal{N} and \mathcal{H} change in time due to the interaction with the surroundings, performing thermal fluctuations. This interaction corresponds to the above-mentioned interaction between macroscopic portions in the liquid. Thus, taking the limiting procedure of $k \rightarrow 0$, we obtain

$$(n_k, n_k^*) = Nn \chi_T, \quad (5.5)$$

$$(n_k, H_k^*) = N[h n \chi_T - \alpha T], \quad (5.6)$$

$$(H_k, H_k^*) = N[c_v T + (h n \chi_T - \alpha T)^2 / n \chi_T], \quad (5.7)$$

where $n = N/V$, and χ_T is the isothermal compressibility, h the enthalpy per molecule, α the coefficient of thermal expansion at constant pressure, and c_v the heat capacity per molecule. With the aid of (5.4) we also obtain

$$(\dot{n}_k, \dot{n}_k^*) = N(k^2/m), \quad (5.8)$$

$$(\dot{n}_k, \dot{H}_k^*) = N(k^2/m)h. \quad (5.9)$$

The use of the above equations thus leads to

$$D_k = N^2 n \chi_T c_v T, \quad h_k = h, \quad (5.10)$$

$$\Omega_k = ck, \quad c^2 = 1/mn\chi_S = (\partial p/\partial \rho)_s, \quad (5.11)$$

$$\left\{ \begin{array}{l} \omega_{1k} = \Omega_k [1 - (h\alpha/c_p)] = (\Omega_k/mc^2) (\partial p/\partial n)_E, \\ \omega_{2k} = \Omega_k (h\alpha/c_p) = (\Omega_k h/mc^2) (\partial p/\partial E)_n, \end{array} \right. \quad (5.12)$$

$$\left\{ \begin{array}{l} \omega_{1k} = \Omega_k [1 - (h\alpha/c_p)] = (\Omega_k/mc^2) (\partial p/\partial n)_E, \\ \omega_{2k} = \Omega_k (h\alpha/c_p) = (\Omega_k h/mc^2) (\partial p/\partial E)_n, \end{array} \right. \quad (5.13)$$

where $c_p/c_v = \chi_T/\chi_S = 1 + (\alpha^2 T/nc_v\chi_T)$, and χ_S is the adiabatic compressibility, c the adiabatic sound speed, and E the internal energy per unit volume. The intensity of the Brillouin doublet (4.25) is calculated to yield $\phi_k = c_v/c_p$.

In the derivation of (5.5-9) we replaced the (A, B) by the static correlation function $\beta\langle AB \rangle$, and calculated them by the use of the grand canonical ensemble. This is justified when the wavelength k^{-1} is of the order of magnitude of a macroscopic linear dimension and the frequency is small so that

$$\hbar\Omega_k \ll k_B T. \quad (5.14)$$

Insertion of (5.12) and (5.13) into (4.13) leads to the following expressions for the normal coordinates:

$$I_1 = \dot{n}_k + i(\Omega_k/mc^2) [(\partial p/\partial n)_E n_k + (\partial p/\partial E)_n H_k], \quad (5.15)$$

$$= \dot{n}_k + i\Omega_k [n_k + (\alpha/c_p) I_2], \quad (5.16)$$

$$I_2 = H_k - h n_k. \quad (5.17)$$

With the aid of (5.1) and the conservation laws of energy and number densities,

$$\dot{H}_k = ik \cdot \mathbf{J}_{Hk}, \quad (5.18)$$

$$\dot{n}_k = ik \cdot \mathbf{j}_k, \quad (5.19)$$

the normal forces (4.22) and (4.23) are written as

$$K_1 = -(\mathbf{k}k/m): J_{vk} - (1/mc) (\partial p/\partial E)_n k \cdot \mathbf{J}_{Tk}, \quad (5.20)$$

$$K_2 = \dot{I}_2 = ik \cdot \mathbf{J}_{Tk}, \quad (5.21)$$

where

$$J_{vk} = \Pi_k - \mathbf{1} [(\partial p/\partial n)_E n_k + (\partial p/\partial E)_n H_k], \quad (5.22)$$

$$\mathbf{J}_{Tk} = \mathbf{J}_{Hk} - h \mathbf{j}_k. \quad (5.23)$$

A physical picture of the normal mode I_2 is obtained as follows. Consider (5.21) and (5.23). Since $h = (E+p)/n$, the second term of (5.23) expresses the sum of a flow of thermal energy carried by the mass flow and a reversible flow of energy produced by the expansion and compression of mass elements.

Thus $K_2 = \dot{I}_2$ denotes the rate of increase in time of energy due to the flow of energy other than those associated with the mass flow, namely due to the thermal conduction of energy associated with a temperature gradient.

The J_{vk} and \mathbf{J}_{Tk} are the Fourier components of Hermitean density operators, satisfying (2.17), (2.19) and (2.20). The flux J_{vk} is even with respect to the time reversal, whereas the flux \mathbf{J}_{Tk} is odd. Therefore, we have

$$(J_{vk}^{\mu\nu}(t), J_{vk}^{\mu'\nu'*}) = (J_{vk}^{\mu'\nu'}(t), J_{vk}^{\mu\nu*}), \tag{5.24}$$

$$(J_{vk}^{\mu\nu}(t), J_{Tk}^{\xi*}) = - (J_{Tk}^{\xi}(t), J_{vk}^{\mu\nu*}), \tag{5.25}$$

where the superscripts μ and ν mean the μ, ν component of the tensor in the coordinate space, and ξ the ξ component of the vector. Using (5.20) and (5.21) we thus obtain

$$(K_1(t), K_1^*) = (1/m^2) \sum_{\mu\nu, \mu'\nu'} k_\mu k_\nu k_{\mu'} k_{\nu'} (J_{vk}^{\mu\nu}(t), J_{vk}^{\mu'\nu'*}) + [(1/mc) (\partial p / \partial E)_n]^2 k^2 \sum_{\nu, \nu'} k_\nu k_{\nu'} (J_{Tk}^\nu(t), J_{Tk}^{\nu'*}). \tag{5.26}$$

Namely, the dynamical fluxes J_{vk} and \mathbf{J}_{Tk} do not couple with each other due to the time-reversal property (5.25). This situation may be regarded as an example of the Curie law that a coupling of thermodynamic fluxes whose tensorial orders differ by an odd number does not occur in the entropy production.²²⁾ In fact, the Curie law may be looked as being a result of the time-reversal property. A flux results from a Hermitean scalar quantity by taking the time derivative. Thus the flux tensor of odd order is odd with respect to the time reversal, whereas the flux of even order is even. Therefore, fluxes whose orders differ by an odd number fulfill a relation similar to (5.25), which leads to the Curie law.

Since the system is isotropic, the relaxation functions of the fluxes can be written in the form

$$(J_{vk}^{\mu\nu}(t), J_{vk}^{\mu'\nu'*}) = \eta_k'(t) [\delta_{\mu, \mu'} \delta_{\nu, \nu'} + \delta_{\mu, \nu'} \delta_{\nu, \mu'}] + [\varphi_k'(t) - (2/3) \eta_k'(t)] \delta_{\mu, \nu} \delta_{\mu', \nu'}, \tag{5.27}$$

$$(J_{Tk}^\nu(t), J_{Tk}^{\nu'*}) = (1/T) \kappa_k'(t) \delta_{\nu, \nu'}, \tag{5.28}$$

where terms depending on the direction of the wave vector \mathbf{k} should vanish. The insertion of (5.26–28) into (4.20) leads to

$$\Gamma_{1k} = \frac{V}{2mN} k^2 \left[\left(\varphi_k + \frac{4}{3} \eta_k \right) + m \left(\frac{1}{c_v} - \frac{1}{c_p} \right) \bar{\kappa}_k \right], \tag{5.29}$$

where φ_k, η_k and $\bar{\kappa}_k$ are determined from the parameters $\varphi_k'(t), \eta_k'(t)$ and $\kappa_k'(t)$, respectively, and turn out to be

$$\varphi_k + \frac{4}{3} \eta_k = \frac{1}{V} \int_0^\infty dt \exp(-it\Omega_k) (J_{vk}^{zz}(t), J_{vk}^{zz*}), \tag{5.30}$$

$$\bar{\kappa}_k = \frac{1}{TV} \int_0^{\infty} dt \exp(-it\Omega_k) (J_{Tk}^x(t), J_{Tk}^{x*}), \quad (5.31)$$

$$\eta_k = \frac{1}{V} \int_0^{\infty} dt \exp(-it\Omega_k) (J_{vk}^{xy}(t), J_{vk}^{xy*}). \quad (5.32)$$

If one replaces the k dependent transport coefficients φ_k , η_k and $\bar{\kappa}_k$ by the coefficients of bulk viscosity, shear viscosity and thermal conductivity, respectively, then (5.29) agrees with the hydrodynamical expression for the sound attenuation constant multiplied by the sound speed, being proportional to Ω_k^2 . Therefore, (5.30), (5.31) and (5.32) define generalized coefficients of viscosity and thermal conductivity. Another type of expression for the shear viscosity is obtained from (5.27):

$$\eta_k = \frac{1}{4V} \int_0^{\infty} dt \exp(-it\Omega_k) (J_{vk}^{xx}(t) - J_{vk}^{yy}(t), J_{vk}^{xx*} - J_{vk}^{yy*}). \quad (5.33)$$

The φ_k can thus be expressed in terms of the flux $[J_{vk}^{xx} + J_{vk}^{yy} + J_{vk}^{zz}]/3$.

The insertion of (5.21) and (5.28) into (4.21) leads to

$$\Gamma_{2k} = (V/c_p N) k^3 \kappa_k, \quad (5.34)$$

where

$$\kappa_k = \frac{1}{TV} \int_0^{\infty} dt (J_{Tk}^x(t), J_{Tk}^{x*}). \quad (5.35)$$

Equation (5.35) does not have the factor $\exp[-it\Omega_k]$, being thus different from (5.31), although both are determined by the thermal conduction flux \mathbf{J}_{Tk} . The difference is due to that of the collective nature of the two normal modes (5.15) and (5.17), being related to the fact that the fluctuation of the mass density has a restoring force due to the pressure, represented by (5.4), whereas the fluctuation of the I_2 does not have a restoring force, $\langle \dot{I}_2 \rangle' = 0$. If one replaces the κ_k by the thermal conductivity, then (5.34) agrees with the hydrodynamical expression for the damping constant of isobaric fluctuation of temperature.

The correlation time τ_c of the normal forces represents a molecular time characteristic of the dissipative mechanism involved. For dilute gases, the correlation time is of the order of magnitude of the mean free time of particles.²⁸⁾ If the wavelength k^{-1} is large so that

$$\Omega_k \tau_c \ll 1, \quad (5.36)$$

we can neglect the k dependence of (5.30), (5.31), (5.32) and (5.35), and these equations provide us with molecular expressions for the usual coefficients of transport in fluids. The results for the shear viscosity and the thermal conductivity agree with those previously obtained.^{3),4)} However, (5.30) does not agree with the previous result for the bulk viscosity, since the second term of

the flux (5.22) is missing in the previous result. The difference can be seen more clearly by noting that (5.22) leads, in the limit of $k \rightarrow 0$, to

$$J_{vk}^{xx} = (\Pi_0^{xx} - pV) - \left[\left(\frac{\partial p}{\partial n} \right)_E (\mathcal{N} - \langle \mathcal{N} \rangle) + \left(\frac{\partial p}{\partial E} \right)_n (\mathcal{H} - \langle \mathcal{H} \rangle) \right]. \tag{5.37}$$

This new term represents a pressure fluctuation associated with the fluctuation of the mass and energy densities, and arises as a result of subtracting the pressure fluctuation to define the “random” part K_1 of the force acting on the collective motion. To obtain a physical picture, we denote the pressure fluctuation by p_k and write (5.15) as $I_1 = (1/mc^2) [\dot{p}_k + i\Omega_k p_k]$ by using the adiabatic approximation. The random force then takes the form $K_1 = (1/mc^2) [\dot{p}_k + \Omega_k^2 p_k]$. Setting the random force to be zero, we obtain the collective oscillation without damping. The fluctuation of the random force leads to the damping and, therefore, to the transport coefficients.

§ 6. Summary and some remarks

The framework of the present theory may be summarized as follows. Suppose that a physical phenomenon of interest is described by a relaxation function $(A(t), B^*)$, where A and B are approximate constants of motion. The treatment of the relaxation function requires an investigation of the collective motion associated. (1) First find the dynamical variables which strongly couple with the A , and denote them by A_1, \dots, A_n , including A and B . What to be obtained in this way depends upon the Hamiltonian and the temperature of the system. (2) The dynamical variables are approximate constants of motion, and their dynamical behavior represents a secular motion of the system, being described by the normalized relaxation matrix

$$\mathcal{E}(t) = (\mathcal{A}(t), \mathcal{A}^*) \cdot (\mathcal{A}, \mathcal{A}^*)^{-1}, \tag{6.1}$$

where \mathcal{A} denotes a column vector of the collective variables A_i . (3) The set of collective variables are closed in the sense that the temporal development of the secular motion are approximately deterministic. Namely, the normalized relaxation matrix fulfills the translation-operator property

$$\mathcal{E}(t+s) = \mathcal{E}(t) \cdot \mathcal{E}(s). \tag{6.2}$$

(4) Other degrees of freedom, which weakly couple with the collective variables, represent random motion and lead to the damping and shift of frequency of the secular organized motion. (5) The normal modes \mathcal{I} are obtained by diagonalizing the frequency matrix

$$i\hat{\omega} = (\hat{\mathcal{A}}, \hat{\mathcal{A}}^*) \cdot (\hat{\mathcal{A}}, \hat{\mathcal{A}}^*)^{-1}. \tag{6.3}$$

The eigenfrequency matrix $\hat{\omega}$ is assumed to be a nondegenerate and real matrix. Then $(\mathcal{I}, \mathcal{I}^*)$ is a diagonal matrix. (6) The damping constants of the normal

modes are given by (3·28) and (3·29) in terms of the normal modes $\mathcal{J}(t)$ and the corresponding random forces $\mathcal{K}(t)$. Thus the relaxation function $(A(t), B^*)$ is expressed as a superposition of the relaxation functions of the normal modes. A similar line of approach has been conceived by Kubo.¹⁷⁾ One may notice that the above procedure has some resemblance to the method of two-time Green's function. In fact, the above scheme would be helpful for finding a way of truncating the hierarchy equations. It should be noted, however, that the present theory is entirely based on the property of the relaxation function (6·2), and uses general properties of the many-body systems, such as the laws of conservation.

Following this line of approach, the density fluctuations in liquids were studied, and the line widths and intensities of the normal modes were determined. The results are valid even in the high frequency region where the hydrodynamical treatment is inapplicable. Application to the problems of the first sound attenuation in liquid He II and the inelastic scattering of neutrons by liquids was discussed.

By calculating the sound attenuation constant, we formulated the time-fluctuation expressions for the transport coefficients of liquids without the use of the local equilibrium ensemble. This formulation removes an ambiguity in the previous theories. The time-fluctuation expressions provide us with a starting point for the study of transport in condensed systems. Recently these expressions were used to clarify the transport properties of Fermi particle systems around the degeneracy temperature T_c where the transport coefficient is expected to have a minimum.²⁴⁾ It was found that the shear viscosity has a minimum at $T=0.6T_c$ and the thermal conductivity at $T=0.16T_c$, which are in agreement with recent experiments on liquid He³ below 0.6°K if we take $T_c=2.1^\circ\text{K}$ according to recent experiments on the specific heat.

What dynamical variables form a good set of collective variables depends on the system concerned. To describe a general type of motion of fluids, we take $(n_k, H_k, j_{zk}, j_{yk}, j_{zk})$ instead of (n_k, H_k, \dot{n}_k) . Then we can derive the hydrodynamical equations by using a relation corresponding to (2·9). To describe the zero sound wave in liquid He³ we take $Q_k = \sum_q \alpha_q a_q^* a_{q-k/2}$ and $P_k = \dot{Q}_k$, where α_q may be determined by the condition of minimizing the damping constant. Application to the problem of the second sound wave in liquid He II is of particular interest. The crucial point is to show the existence of a restoring force causing an isobaric temperature wave, which is, according to the two-fluid model, given by

$$\langle \ddot{Q}_k \rangle' = - (k^2/m) (sT\rho_s/\rho_n) [p - n\mu]V, \quad (6\cdot4)$$

where $Q_k = I_2 = H_k - hn_k$, and ρ_s and ρ_n are the mass densities of the super and normal parts, respectively. Thus the second sound wave would be described by $(n_k, Q_k, \dot{n}_k, \dot{Q}_k)$.

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