

difference between time and space velocity gradients is negligible, and there may be, therefore, a non-negligible difference between time and space microscales of turbulence.

An extensive investigation is needed before complete experimental results can be given concerning the rela-

tion between time and space characteristics of turbulence. This work is now in process in cooperation with the National Bureau of Standards.⁶

⁶ New experimental measurements, now in process, are being made in cooperation with Dr. J. Laufer (National Bureau of Standards) and Mr. I. Katz (Applied Physics Laboratory).

Statistical Mechanics of Irreversibility*

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The fluctuation-dissipation theorem relating spontaneous equilibrium fluctuations to the conductance in a dissipative thermodynamic system is extended to the case of several variables, using a quantum statistical analysis. The conductance matrix is shown to be subject to certain symmetry relations, providing a generalization of the Onsager reciprocity theorem. The susceptance matrix is also shown to be subject to similar symmetries. The symmetries apply to all frequency components, and hence to arbitrary transient processes.

1. INTRODUCTION

THE theory of irreversible processes consists essentially of two types of theorems. The first of these theorems is the reciprocity relations of Onsager, treating of the symmetry of the mutual interference among several simultaneously occurring irreversible processes.^{1,2} The second is the fluctuation-dissipation theorem, relating the spontaneous fluctuations in an equilibrium system and the parameter (the conductance) which characterizes the dissipative aspects of an irreversible process.³⁻⁵ The purpose of this and the following paper is to extend the fluctuation-dissipation theorem to several variables and to exhibit its relation to a generalization of the Onsager reciprocity theorem.

Both the Onsager theorem and the fluctuation-dissipation theorem have been investigated by quantum statistical and thermodynamic methods. In the present paper we shall be concerned exclusively with the quantum statistical analysis.

We shall show that the fluctuation-dissipation theorem may be interpreted as a matrix equation when extended to several variables. The mean square fluctuation of a single variable $\langle Q^2 \rangle$ is replaced by a matrix, the elements of which are the spontaneous mutual correlation moments of two fluctuating variables $\langle Q_j Q_k \rangle$. The admittance (and hence the conductance) is replaced by an admittance matrix, the element Y_{jk} describing the response of the variable Q_j to the force V_k .

Furthermore, we shall show that both the conductance and susceptance matrices are subject to a symmetry relation. The symmetries so established apply to all frequency components and consequently are applicable to arbitrary types of transient processes. An indication will be given of the application of this reciprocity theorem to steady-state processes.

2. THE ADMITTANCE MATRIX

In this section we shall define the admittance matrix and develop a useful quantum statistical expression for it.

We consider a system whose Hamiltonian in isolation is H_0 . Let the system be acted on by a perturbation which induces the irreversible processes of interest. For a single variable this perturbation may be written in the form³ $V(t)Q(\cdots q_r \cdots p_r \cdots)$, in which $V(t)$ is a time-dependent scalar which measures the instantaneous strength of the applied perturbation, and which therefore plays the role of a driving force, and in which $Q(\cdots q_r \cdots p_r \cdots)$ is a function of the coordinates and momenta of the particles composing the system. For the general case in which several simultaneous perturbations act, we shall write the total perturbation as $\sum_k V_k(t)Q_k(\cdots q_r \cdots p_r \cdots)$.

We shall assume the perturbations to be sufficiently small so that first-order perturbation theory is valid. As we shall see, this assumption linearizes the system in the following sense. Under the influence of the perturbations, the expectation value of Q_j becomes a function of time, and if $\dot{Q}_j(\omega)$ denotes the Fourier component of the time derivative of this expectation value, then $\dot{Q}_j(\omega)$ is a linear function of the Fourier

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¹ L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).

² H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).

³ H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

⁴ J. L. Jackson, Phys. Rev. **87**, 471 (1952).

⁵ H. B. Callen and R. F. Greene, Phys. Rev. **86**, 702 (1952).

components $V_k(\omega)$ of the several driving forces. That is,

$$\dot{Q}_j(\omega) = -\sum_k Y_{jk}(\omega) V_k(\omega). \quad (2.1)$$

The minus sign⁶ is here included in order to indicate explicitly the tendency of \dot{Q}_j to be of such a sign as to decrease the perturbing energy $V_j Q_j$.⁴ The matrix $\{Y_{jk}\}$ may be called the admittance matrix. The elements of this matrix are, in general, complex, indicating by the usual convention the phase relations between the response and the several driving forces. That is,

$$Y_{jk}(\omega) = g_{jk}(\omega) - ib_{jk}(\omega). \quad (2.2)$$

The real and imaginary parts of the admittance matrix are respectively the conductance and susceptance matrices, $\{g_{jk}\}$ and $\{b_{jk}\}$.

The method we use in order to obtain explicit expressions for the elements of the admittance matrix is simply to compute the time dependent expectation value of \dot{Q}_j in the perturbed states of the system.⁴ The initial state of the system is represented by an ensemble in which the occupation numbers of the unperturbed energy states are in accordance with the equilibrium distribution associated with a temperature T .

In the presence of sinusoidal perturbations $V_k(t) = V_k^0 \sin \omega t$, the Hamiltonian for the system is

$$H = H_0(\cdots q_r \cdots, \cdots p_r \cdots) + \sum_k V_k^0 \sin \omega t Q_k(\cdots q_r \cdots, \cdots p_r \cdots), \quad (2.3)$$

where

$$H_0 \Psi_n = E_n \Psi_n. \quad (2.4)$$

Writing the perturbed wave functions as

$$\Phi_n = \sum_m b_{nm}(t) \Psi_m \exp(-iE_m t/\hbar), \quad (2.5)$$

we find, to first order, that for $n \neq m$

$$2ib_{nm}(t) = -\sum_k V_k^0 \langle \Psi_m | Q_k | \Psi_n \rangle \times \left\{ \frac{\exp[-it(E_n - E_m + \hbar\omega)/\hbar] - 1}{E_n - E_m + \hbar\omega} - \frac{\exp[-it(E_n - E_m - \hbar\omega)/\hbar] - 1}{E_n - E_m - \hbar\omega} \right\}, \quad (2.6)$$

and for $n = m$

$$b_{nn}(t) = 1 + (1/i\hbar) \sum_k V_k^0 \langle \Psi_n | Q_k | \Psi_n \rangle (1 - \cos \omega t) / \omega. \quad (2.7)$$

The expectation value $\langle \Phi_n | \dot{Q}_j | \Phi_n \rangle$ of \dot{Q}_j in the n th perturbed eigenstate may now be computed.

The operator associated with \dot{Q}_j is given by the commutator $[H, Q_j]/\hbar$ from which, keeping only first-order terms, we have

$$\langle \Phi_n | \dot{Q}_j | \Phi_n \rangle = \frac{1}{2\hbar} \sum_k \sum_{m \neq n} V_k^0 \langle E_n | Q_j | E_m \rangle \times \langle E_m | Q_k | E_n \rangle (E_m - E_n) \times \left\{ \frac{e^{-i\omega t} - e^{-it(E_m - E_n)/\hbar}}{E_n - E_m + \hbar\omega} - \frac{e^{i\omega t} - e^{-it(E_m - E_n)/\hbar}}{E_n - E_m - \hbar\omega} \right\} + \text{complex conjugate.} \quad (2.8)$$

⁶ The negative sign was unfortunately omitted in Eqs. (2.12) and (2.14) of reference 3.

Now to obtain the response for a macroscopic system we average (2.8) over the ensemble. The summations over both n and m may be replaced by integrations over energy.³ Introducing the density of levels $\rho(E)$ and the distribution function

$$f(E_n) = (\text{const.}) \exp(-E_n/kT), \quad (2.9)$$

we find

$$\langle \dot{Q}_j \rangle = \frac{1}{2\hbar} \int_0^\infty \int_0^\infty dE_m dE_n \rho(E_m) \rho(E_n) f(E_n) (E_m - E_n) \times \sum_k V_k^0 \langle E_m | Q_j | E_n \rangle \langle E_n | Q_k | E_m \rangle \times \left\{ \frac{e^{i\omega t} - e^{it(E_m - E_n)/\hbar}}{E_n - E_m + \hbar\omega} \right\} - \frac{1}{2\hbar} \int_0^\infty \int_0^\infty dE_m dE_n \rho(E_m) \rho(E_n) f(E_n) (E_m - E_n) \times \sum_k V_k^0 \langle E_m | Q_j | E_n \rangle \langle E_n | Q_k | E_m \rangle \times \left\{ \frac{e^{-i\omega t} - e^{it(E_m - E_n)/\hbar}}{E_n - E_m - \hbar\omega} \right\} + \text{complex conjugate.} \quad (2.10)$$

For large t the first integral becomes

$$\frac{i\pi\omega}{2} \exp(i\omega t) \int_0^\infty dE_m \rho(E_m) \rho(E_m - \hbar\omega) f(E_m - \hbar\omega) \times \sum_k V_k^0 \langle E_m | Q_j | E_m - \hbar\omega \rangle \langle E_m - \hbar\omega | Q_k | E_m \rangle + \frac{\exp(i\omega t)}{2\hbar} \int_0^\infty \int_0^\infty dE_m dE_n \rho(E_m) \rho(E_n) \times f(E_n) (E_m - E_n) \sum_k \frac{\langle E_m | Q_j | E_n \rangle \langle E_n | Q_k | E_m \rangle}{E_n - E_m + \hbar\omega},$$

and the other integrals may be evaluated similarly. As in reference 3, these integrals may be further reduced, yielding

$$\langle \dot{Q}_j \rangle = -\sin \omega t \sum_k g_{jk} V_k^0 + \cos \omega t \sum_k b_{jk} V_k^0, \quad (2.11)$$

with

$$g_{jk} = \frac{1}{2} \pi \omega (1 - \exp[-\hbar\omega/kT]) \times \int_0^\infty dE_m \rho(E_m) \rho(E_m + \hbar\omega) f(E_m) \times \{ \langle E_m + \hbar\omega | Q_k | E_m \rangle \langle E_m | Q_j | E_m + \hbar\omega \rangle + \text{c.c.} \} + 2\omega \int_0^\infty \int_0^\infty dE_m dE_n \frac{\rho(E_m) \rho(E_n) f(E_n) (E_n - E_m)}{(E_n - E_m)^2 - (\hbar\omega)^2} \times \text{Im} \{ \langle E_m | Q_k | E_n \rangle \langle E_n | Q_j | E_m \rangle \}, \quad (2.12)$$

and

$$\begin{aligned}
 b_{jk} &= \pi\omega(1 - \exp[-\hbar\omega/kT]) \\
 &\times \int_0^\infty dE_m \rho(E_m) \rho(E_m + \hbar\omega) f(E_m) \\
 &\times \text{Im}\{\langle E_m + \hbar\omega | Q_k | E_m \rangle \langle E_m | Q_j | E_m + \hbar\omega \rangle\} \\
 &+ \omega \int_0^\infty \int_0^\infty dE_m dE_n \frac{\rho(E_m) \rho(E_n) f(E_n) (E_n - E_m)}{(E_n - E_m)^2 - (\hbar\omega)^2} \\
 &\times \{\langle E_m | Q_k | E_n \rangle \langle E_n | Q_j | E_m \rangle + \text{c.c.}\}. \quad (2.13)
 \end{aligned}$$

3. THE SPONTANEOUS FLUCTUATIONS IN EQUILIBRIUM

Having in the previous section investigated the response of a system to a driving force, we now turn our attention to the spontaneous fluctuations in equilibrium. In particular, we shall compute the correlation moment $\langle Q_j Q_k \rangle$ of two arbitrary functions of the coordinates and momenta of the particles of the system.

We shall find it convenient to first compute $\langle \dot{Q}_j \dot{Q}_k \rangle$, from which the moment $\langle Q_j Q_k \rangle$ may easily be obtained. We proceed in this calculation by formulating the expectation value of $\dot{Q}_j \dot{Q}_k$ in a pure state of the system and then averaging over all pure states in accordance with the equilibrium distribution function. Since the quantum-mechanical operators \dot{Q}_j and \dot{Q}_k do not necessarily commute, the appropriate operator for which we seek the expectation value becomes $\frac{1}{2}(\dot{Q}_j \dot{Q}_k + \dot{Q}_k \dot{Q}_j)$. The expectation value of $\dot{Q}_j \dot{Q}_k$ in the unperturbed state Ψ_n is then

$$\begin{aligned}
 \frac{1}{2} \langle E_n | \dot{Q}_j \dot{Q}_k + \dot{Q}_k \dot{Q}_j | E_n \rangle &= 1/2\hbar^2 [\sum_m (E_n - E_m)^2 \\
 &\times \langle E_n | Q_k | E_m \rangle \langle E_m | Q_j | E_n \rangle + \text{c.c.}]. \quad (3.1)
 \end{aligned}$$

The summation over m may be replaced by an integration over E_m . With the substitution

$$\hbar\omega = |E_n - E_m|, \quad (3.2)$$

we then obtain

$$\begin{aligned}
 \frac{1}{2} \langle E_n | \dot{Q}_j \dot{Q}_k + \dot{Q}_k \dot{Q}_j | E_n \rangle &= \frac{1}{2\hbar^2} \int_0^\infty (\hbar\omega)^2 \\
 &\times \langle E_n + \hbar\omega | Q_k | E_n \rangle \langle E_n | Q_j | E_n + \hbar\omega \rangle \rho(E_n + \hbar\omega) \hbar d\omega \\
 &+ \frac{1}{2\hbar^2} \int_0^\infty (\hbar\omega)^2 \langle E_n - \hbar\omega | Q_k | E_n \rangle \\
 &\times \langle E_n | Q_j | E_n - \hbar\omega \rangle \rho(E_n - \hbar\omega) \hbar d\omega + \text{c.c.} \quad (3.3)
 \end{aligned}$$

We compute the macroscopic correlation moment by summing over unperturbed states Ψ_n , weighting them by $f(E_n)$ as previously. This summation may also be replaced by an integration over E_n . Using the transformation

$$E \rightarrow E' + \hbar\omega \quad (3.4)$$

as before, we have the result

$$\begin{aligned}
 \langle \dot{Q}_j \dot{Q}_k \rangle &= \frac{1}{2} \int_0^\infty d\omega \hbar\omega^2 (1 + \exp[-\hbar\omega/kT]) \\
 &\times \int_0^\infty dE_m \rho(E_m) \rho(E_m + \hbar\omega) f(E_m) \\
 &\times [\langle E_m + \hbar\omega | Q_k | E_m \rangle \langle E_m | Q_j | E_m + \hbar\omega \rangle + \text{c.c.}]. \quad (3.5)
 \end{aligned}$$

Since the Fourier component of Q_j is simply the Fourier component of \dot{Q}_j divided by $i\omega$, it follows that

$$\begin{aligned}
 \langle Q_j Q_k \rangle &= \frac{1}{2} \int_0^\infty d\omega \hbar (1 + \exp[-\hbar\omega/kT]) \\
 &\times \int_0^\infty dE_m \rho(E_m) \rho(E_m + \hbar\omega) f(E_m) \\
 &\times [\langle E_m + \hbar\omega | Q_k | E_m \rangle \langle E_m | Q_j | E_m + \hbar\omega \rangle + \text{c.c.}]. \quad (3.6)
 \end{aligned}$$

These two equations constitute our desired expressions for the correlation moments of the spontaneously fluctuating variables in an equilibrium system.

4. THE FLUCTUATION-DISSIPATION THEOREM

A theorem has previously been proved³ which is equivalent to a relation between the diagonal elements of the fluctuation-correlation matrix and of the conductance matrix. In this section we obtain an extension of this theorem to the off-diagonal elements of the respective matrices.

Comparison of Eqs. (3.6) and (2.12) yields directly the theorem

$$\langle Q_j Q_k \rangle = \frac{2}{\pi} \int_0^\infty d\omega E(\omega, T) \left[\frac{g_{jk}(\omega) + g_{kj}(\omega)}{2\omega^2} \right]. \quad (4.1)$$

Here

$$E(\omega, T) \equiv \frac{1}{2}\hbar\omega + \hbar\omega [\exp(\hbar\omega/kT) - 1]^{-1}, \quad (4.2)$$

which is formally the mean energy at temperature T of a harmonic oscillator of natural frequency ω . It may be noted that at high T ($kT \gg \hbar\omega$), $E(\omega, T)$ assumes the classical limiting value of kT .

It is sometimes useful to introduce fictitious fluctuating forces defined in such a way that they would induce the observed values of the fluctuating responses. It is clearly possible to use relations of the form $V = Z\dot{Q}$ to transform (4.1) into an expression for the correlation moments of these fictitious forces. Because of the artificiality of such forces and because the expressions for the off-diagonal elements become rather complicated in such a formulation, we prefer to restrict ourselves to the theorem as stated in Eq. (4.1). The diagonal form of Eq. (4.1), written in terms of the fluctuating forces, has been applied elsewhere to the problems of Brownian motion, the fluctuating electric field in the vacuum, and pressure fluctuations in gases.³

5. SYMMETRY PROPERTIES OF THE ADMITTANCE MATRIX

In this section we shall consider certain symmetry properties of the admittance matrix.

We have

$$Y_{jk}(\omega, A) = g_{jk}(\omega, A) - ib_{jk}(\omega, A), \quad (5.1)$$

where we have explicitly indicated that the admittance matrix may depend upon an applied magnetic field, described by the vector potential A . We consider the behavior of the admittance matrix under the simultaneous transformations $j \leftrightarrow k$ and $A \rightarrow -A$; that is, we shall investigate the relationship of $Y_{jk}(\omega, A)$ and $Y_{kj}(\omega, -A)$. It may be noted that the dependence of $Y_{jk}(\omega, A)$ on the indices j and k and on the field A is only through constructs of the form $\langle E_m | Q_j | E_n \rangle \times \langle E_n | Q_k | E_m \rangle$. The transformation $j \leftrightarrow k$ is equivalent to the replacement of each of these matrix elements by its complex conjugate. Thus, we are led to study the behavior of the unperturbed wave functions and the operators Q_k (these being the quantities entering into the matrix elements) under a particular operator T . This operator is so defined that applied to a given wave function which depends parametrically on A , it takes the complex conjugate of that function and also replaces A by $-A$:

$$\begin{aligned} T\Psi(\dots q \dots, \dots A \dots) \\ = \Psi^*(\dots q \dots, \dots -A \dots). \end{aligned} \quad (5.2)$$

The unperturbed wave functions may be chosen as real in the absence of a magnetic field. In the presence of a field, the momenta in the unperturbed Hamiltonian are replaced by $(P_r - e_r/cA_r)$ and thence by $-i\hbar[\nabla_r - (e_r/\hbar c)iA_r]$. Therefore, the convention which made the wave functions real in the absence of a field will cause them to involve both i and A only through the product iA . The unperturbed wave functions are therefore invariant under the T operation.

Similarly the classical function Q_j is a real function of the coordinates and of the quantities $(P_r - e_r/cA_r)$. The operator Q_j is consequently a function of the coordinates and of the quantities $-i\hbar[\nabla_r - (e_r/\hbar c)iA_r]$. Since the T operator leaves the square bracket invariant, it merely replaces $(P_r - e_r/cA_r)$ by $-(P_r - e_r/cA_r)$. That is, the symmetry of the operator Q_j under T is equivalent to the symmetry of the classical function Q_j under the reversal of all particle velocities.

In the above discussion we have, for convenience, implied a scalar wave function and thereby ignored spin. If spin is included the operator T must also be considered as causing the reversal of all spins. The T operator is essentially the Wigner time-reversal operator.⁷ The symmetry of the operator Q_j under T is then equivalent to the symmetry of the semiclassical function Q_j under the simultaneous reversal of all particle velocities and spins.

⁷ A simple discussion of the time-reversal operator is given by M. J. Klein, *Am. J. Phys.* **20**, 65 (1952).

Returning now to Eq. (5.1), we recall that $Y_{jk}(\omega, A)$ depends on j and k only through constructs of the form $\langle E_m | Q_j | E_n \rangle \langle E_n | Q_k | E_m \rangle$. The simultaneous transformation $j \leftrightarrow k$ and $A \rightarrow -A$ corresponds to the application of the T operation within these matrix elements. The T operation leaves the unperturbed wave functions invariant, and yields a symmetry, in its action on the Q_j , which derives from the dependence of the Q_j on the particle velocities and spins. If both Q_j and Q_k are even under the reversal of particle velocities and spins, then $Y_{jk}(\omega, A)$ is invariant under the transformation considered. If both Q_j and Q_k are odd under the reversal of particle velocities and spins, then $Y_{jk}(\omega, A)$ is again invariant, whereas if Q_j is even and Q_k odd (or vice versa), $Y_{jk}(\omega, A)$ changes sign under this transformation.

Thus, we have derived our basic symmetry relations. If Q_j and Q_k are both odd or both even under reversal of the particle velocities and spins,

$$Y_{jk}(\omega, A) = Y_{kj}(\omega, -A). \quad (5.3)$$

If Q_j is even and Q_k odd (or vice versa) under reversal of the particle velocities and spins,

$$Y_{jk}(\omega, A) = -Y_{kj}(\omega, -A). \quad (5.4)$$

It may now be noted that the general case, in which the Q_j and Q_k are neither even nor odd in the particle velocities and spins, may be easily subsumed under the above analysis by a simple artifice. It is always possible to write any given function Q_j as the sum of two functions, one even, $\equiv Q_j^{(e)}$ and one odd, $\equiv Q_j^{(o)}$, in the particle velocities and spins. The case in which there is a single driving force associated with the single function Q_j may, therefore, be considered to be a special case of the situation in which there are two independent driving forces for $Q_j^{(e)}$ and $Q_j^{(o)}$, these two driving forces being taken equal:

$$V_j Q_j = V_j^{(e)} Q_j^{(e)} + V_j^{(o)} Q_j^{(o)}, \quad (5.5)$$

with

$$V_j^{(e)} = V_j^{(o)} = V_j. \quad (5.6)$$

This device reduces any situation to one in which all functions Q_j or Q_k are either even or odd under reversal of the particle velocities and spins.

The symmetry theorem expressed in Eqs. (5.3) and (5.4) is a generalization of the reciprocity theorem of Onsager. Whereas the Onsager theorem applies only to relaxation processes, the above theorem applies to all frequency components and hence to arbitrary transient processes. Both the real and the imaginary components of the admittance are subject to the symmetry relations.

6. THE APPLICATION TO STEADY-STATE PROCESSES

The application of the symmetry theorem to steady-state processes requires an extension of the analysis and the introduction of a particular type of approxi-

mation. This situation exists also in the application of the Onsager theorem to steady-state processes.^{8,9} An appropriate extension of the analysis will appear in a subsequent paper, but it seems desirable to indicate briefly here the general aspects of the relationship of the symmetry theorem to steady-state processes.

It is immediately apparent that our formalism is not appropriate for a direct application to steady-state processes. The admittance as given in Eqs. (2.12) and (2.13) vanishes for zero frequency, whereas in a steady-state process a time-independent force leads to a non-zero time-independent response. A specific example brings out very clearly the essential difference in the situations described by our formalism and those appropriate to the study of steady-state phenomena. Consider, in particular, the application of an electric field to a conductor. As indicated in reference 3, this situation may be described by taking the driving force V as the applied potential difference and Q as $\sum_i e_i x_i/L$, wherein e_i is the charge on the i th particle, x_i its distance from one end of the conductor, and L the total length of the conductor. The system which is properly described by this Hamiltonian is an electrical resistor placed between two condenser plates which impress the voltage V across it, the resistor, however, *not* being in electrical contact with the external circuit. As indicated above, the time independent applied driving force V eventually leads to a vanishing current \dot{Q} . On the other hand, a steady-state process results if the electrical isolation between the conductor and the potential source is destroyed. Whereas the distribution of electrons along the length of the conductor is radically different from the equilibrium distribution in the situation discussed (the electrons accumulating toward one end of the conductor), the effect of making an actual physical contact between the conductor and the rest of the circuit is to provide an external reservoir of electrons which attempts to maintain the equilibrium distribution.

The above example suggests one approximate method of applying our analysis to steady-state processes: this method has been previously employed in a discussion of the Onsager relations by one of us.⁹ A steady-state process may be considered as involving the action of two distinct external agencies on the dissipative system. One of these applies a perturbation to the system; the second is an agency which attempts to restore the equi-

librium statistical distribution function. The analysis of such a steady-state process may then be conveniently carried out by an artifice which successfully avoids the requirement of explicit consideration of the restoring agency. We assume that the response \dot{Q} observed in the steady-state is equal to the instantaneous response $\dot{Q}(\tau)$ which would be exhibited at some particular time τ in a system which is not acted on by a restoring agency but to which is applied, at time $t=0$, the driving force V . We see that for such a system the distribution function is of precisely the equilibrium form immediately after the application of the perturbation. If the restoring agency is a very effective one, so that in its competition with the applied perturbation it is able to maintain very nearly the equilibrium distribution function in the steady-state process, the parameter τ which appears in our analysis will be very small; conversely, weak restoring agencies and/or strong perturbations are represented in our formalism by large values of τ . By this device the action of the restoring agency is represented approximately by a single parameter τ , and the analysis of steady-state processes is reduced to the calculation of the response, at a particular time, of an appropriately defined transient process; this latter type of process being completely within the scope of the formalism previously developed.

We consider, then, a system to which are applied the driving forces

$$V_j(t) = \begin{cases} V_j^0, & t > 0, \\ 0, & t < 0, \end{cases} \quad (6.1)$$

and we seek the response at time τ . It follows immediately from Eq. (2.1) and from the transform $1/i\omega$ of the unit step function that

$$\dot{Q}_j(\tau) = \sum_k L_{jk} V_k^0, \quad (6.2)$$

where

$$L_{jk} = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \exp(i\omega\tau) \frac{Y_{jk}(\omega)}{i\omega}. \quad (6.3)$$

$\dot{Q}_j(\tau)$ is to be interpreted as the *time-independent* response in the steady-state process. It is evident from Eq. (6.3) that the L_{jk} satisfy symmetry relations identical in form to those satisfied by the Y_{jk} , these symmetries being the basis of the modern theory of steady-state irreversible processes.^{8,10}

⁸ See H. B. Callen, Phys. Rev. **73**, 1349 (1948).

⁹ H. B. Callen, thesis, Massachusetts Institute of Technology, 1947, unpublished.

¹⁰ S. R. DeGroot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, Netherlands, 1951).