experimental evidence indicates in all respects satisfactory agreement with the classical theory of Schwinger.

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# Relationship between the Reciprocity Theorems of Onsager and of Callen-Greene*

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Onsager's reciprocity theorem is extended to linear non-Markoffian processes; the recipricity relation due to Callen-Greene is also extended to include the imaginary (as well as the real) part of the admittance matrix. In terms of these extensions, the two theorems are shown to be completely equivalent.

## I. INTRODUCTION

THE Onsager reciprocity theorem[1] forms the basis of virtually the entire existing theory of irreversible processes.[2] More recently a "fluctuation-dissipation" theorem has been proved,[3] relating the equilibrium fluctuations to the dissipation parameter of an irreversible process. Extension[4] of the theorem to simultaneous processes again yields a form of reciprocity relation. This latter reciprocity theorem forms an apparent generalization of the Onsager theorem, as the symmetry is obtained for each Fourier component for general linear transient processes. The purpose of this paper is a critical examination of each of the reciprocity theorems so as to clarify their ranges of validity and their relationships to each other. It is shown that a reinterpretation of the Onsager theorem permits of its extension to linear non-Markoffian processes; that is, such an interpretation allows the kinetic coefficients to be considered as general functions of the time rather than as constants. Our examination of the fluctuation-dissipation theorem similarly leads to an extension of the reciprocity theorem derived therefrom: the imaginary part of the admittance matrix, as well as the real part, is shown to be symmetric. Finally, with the above described extensions of each of the reciprocity theorems, it is shown that both theorems have the same range of validity and are, in fact, completely equivalent.

## II. SUMMARY AND DISCUSSION OF THE TWO THEOREMS

### A. Onsager's Theorem

Let us consider a closed system which may be described thermodynamically by a set of extensive variables $x_i$. For example we might have a closed system made up of two subsystems separated by a wall which permits the flow of heat and matter. Then the energy $u$ and mole number $n$ of one of the subsystems would constitute the set $x_i$. Equilibrium thermodynamics describes such a system in terms of the constrained equilibrium states accessible to the system. In the above example, a constrained equilibrium state would be one in which the differences in temperature and electrochemical potential between the two subsystems are nonzero, equilibrium being attained by replacing the diathermal, permeable wall by an adiabatic, impermeable wall. The unconstrained equilibrium state is the one for which the temperature and electrochemical potential differences are zero, this being reached physically if the diathermal, permeable wall is kept intact. Letting $X_i$ be the values of the extensive variables in the unconstrained equilibrium state and $a_i$ be the deviations $x_i-X_i$, we may define a set of "forces" $\gamma_i$ in terms of the entropy function $S(\cdots x_i\cdots)$ (the total entropy of the closed system), by

$$\gamma_i\equiv\sum_k S_{ik}a_k, \tag{1}$$

where

$$S_{ik}=\partial^2S(\cdots X_j\cdots)/\partial X_i\partial X_k. \tag{2}$$

Note that the $\gamma_i$ as defined by Eq. (1) are approxi-

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[1] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).
[2] S. R. DeGroot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951).
[3] H. B. Callen and R. F. Greene, Phys. Rev. **86**, 702 (1952).
[4] H. B. Callen and R. F. Greene, Phys. Rev. **88**, 1387 (1952).

mately equal, for small $a_i$, to the usual "entropy language" intensive parameters $\partial S(\cdots x_j \cdots)/\partial x_i$.

Onsager's reciprocity theorem may now be stated as the following. Let us imagine that the behavior of the system following the removal at time $\tau=0$ of constraints, (which had previously held the system in the constrained equilibrium state $[\cdots a_i(t)\cdots]$), may be represented phenomenologically by a set of equations of the form

$$a_i(t+\tau)-a_i(t)=\tau \textstyle\sum_k L_{ik}\gamma_k(t), \quad T\gg\tau>0. \tag{3}$$

(Here $T$, as discussed by Casimir,[5] is the time in which a disturbance from the unconstrained equilibrium state is appreciably reduced.) Then the reciprocal relations in the absence of magnetic and Coriolis fields are

$$L_{ik}=L_{ki}. \tag{4}$$

We shall now generalize this theorem in a simple way, incidentally removing the restriction[1,5] that $\tau$ not be allowed to go to zero in Eq. (3). The argument which has been adduced in *favor* of this restriction is as follows. One can show[6] from statistical mechanics that

$$\lim_{\tau\to 0}\frac{\langle a_i(t+\tau)\rangle\cdots_{a_j(t)}\cdots - a_i(t)}{\tau}=0,$$

where $\langle a_i(t+\tau)\rangle\cdots_{a_j(t)}\cdots$ is the average value of $a_i$ a time $\tau$ after one had only the knowledge that the values of the $a$'s were $\cdots a_j(t)\cdots$. As a result of this relation, it has been felt[1,5] that Eq. (3) cannot be valid in the limit $\tau\to 0$, and that there must exist some very small time $\tau_1>0$ such that Eq. (3) is valid only for $\tau>\tau_1$. We point out that such a statement is called for if and only if the $L_{ij}$ are presumed to be independent of $\tau$. As a matter of fact, however, our generalization is simply the observation that Onsager's proof of Eq. (4) starting from Eq. (3) in no way requires the $L_{ij}$ to be constant; also we may remove the restriction as to the smallness of $\tau$. This may readily be seen by briefly reconstructing Onsager's derivation, as we shall now do.

Since the prediction of statistical mechanics for the phenomenologically observed quantity $a_i(t+\tau)$ may properly be taken as the expectation value $\langle a_i(t+\tau)\rangle\cdots_{a_j(t)}\cdots$, it follows from Eq. (3) that

$$\langle a_i(t+\tau)\rangle\cdots_{a_j(t)}\cdots - a_i(t)=\tau \textstyle\sum_k L_{ik}\gamma_k(t).$$

Multiplying by $a_l(t)$ and averaging over all sets $\cdots a_j(t)\cdots$ according to the Boltzmann weighting factor, we obtain

$$\langle a_l(t)a_i(t+\tau)\rangle-\langle a_l(t)a_i(t)\rangle=\tau \textstyle\sum L_{ik}\langle a_l(t)\gamma_k(t)\rangle. \tag{5}$$

Using the result of fluctuation theory that $\langle a_l(t)\gamma_k(t)\rangle = -k\delta_{lk}$ ($k$ is Boltzmann's constant), Eq. (5) reduces to

$$\langle a_l(t)a_i(t+\tau)\rangle-\langle a_l(t)a_i(t)\rangle=-k\tau L_{il}.$$

The symmetry of the autocorrelation matrix $\langle a_l(t)a_i \times(t+\tau)\rangle$, which follows from the principle of microscopic reversibility[5] then gives the symmetry of the $L_{il}$ matrix.

As far as the averaging process used in obtaining Eq. (5) is concerned, it is clear that $\tau$ is strictly a constant. Hence the logic leading to the reciprocity relations holds just as well for the case in which the $L_{ik}$ are functions of $\tau$. Thus, using a more explicit notation, Onsager's theorem may be taken more generally as the following. If the behavior of the system may be represented phenomenologically by

$$a_i(t+\tau)-a_i(t)=\tau \textstyle\sum_j L_{ij}(\tau)\gamma_j(t), \tag{3$'$}$$

then

$$L_{ij}(\tau)=L_{ji}(\tau) \tag{4$'$}$$

(with the previously mentioned restrictions as to magnetic and Coriolis fields). Whereas Eqs. (3) in the limit $\tau\to 0$ describe only Markoff or "relaxation" processes, Eqs. (3′) are able to describe any general type of linear process.

Note that an alternate form of these equations is

$$\dot{a}_i(t+\tau)=\textstyle\sum_j M_{ij}(\tau)\gamma_j(t), \tag{6}$$

where

$$M_{ij}(\tau)=\frac{d}{d\tau}[\tau L_{ij}(\tau)]. \tag{7}$$

Hence Eq. (4′) implies the symmetry of the $M_{ij}(\tau)$.

## B. The Reciprocal Relations of the Fluctuation Dissipation Theorem[3,4]

The reciprocal relations derived from the fluctuation-dissipation theorem provide symmetry relations for the following situation. Suppose a system $S$ to be in interaction with a reservoir $R$. Let the extensive parameters of the composite system be $x_i$ ($i=0, 1, \cdots, N_x$) and let the entropy language intensive parameters of the reservoir be $f_j$ ($j=0, 1, \cdots, N_f$). As an example, consider a system composed of a cylinder with two pistons (Fig. 1), intercepting volumes $V_1$ and $V_2$ (the extensive parameters $x_i$); the intensive parameter of the reservoir is the ratio of reservoir pressure to temperature, $P/T$. We shall consider that manipulations of the reservoir permit its intensive parameters to be made arbitrary functions of the time. Thus, in this connection we note that the very definition of a reservoir guarantees that all changes therein are quasi-static, so that the intensive parameters are at every moment determined by their equilibrium definitions.

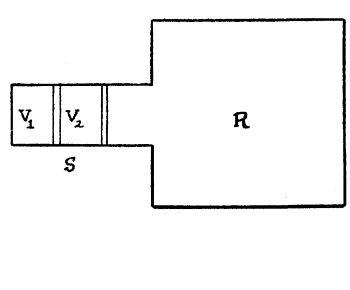


FIG. 1. System $S$ in contact with reservoir $R$.

[5] H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).
[6] H. B. Callen, thesis, Massachusetts Institute of Technology, 1947 (unpublished).

If $X_{i0}$ are the values of the $x_i$ in the equilibrium state for which $f_i(t)=f_{i0}$, and if $\lambda_i(t)\equiv f_i(t)-f_{i0}$ and $a_i(t)\equiv x_i(t)-X_{i0}$, then there will exist a range of values of the $\lambda_i(t)$ for which linearity will hold. That is, for sufficiently small $\lambda_i$, the Fourier transforms, $\Lambda_i(\omega)$ and $A_i(\omega)$, of $\lambda_i(t)$ and $a_i(t)$ will approximately satisfy

$$i\omega A_i(\omega)\equiv \dot{A}_i(\omega)=\sum_j Y_{ij}(\omega)\Lambda_j(\omega), \tag{8}$$

where the admittance matrix, $Y_{ij}(\omega)$, is independent of the applied forces $\lambda_j(t)$.

The fluctuation-dissipation theorem implies that, in the absence of magnetic or Coriolis fields,

$$Y_{ij}(\omega)=Y_{ji}(\omega). \tag{9}$$

In actuality only the inference of the symmetry of the real part of the admittance matrix has been previously drawn. The proof of the extension to the imaginary port (the reactance), as in Eq. (9), is given in the Appendix.

We shall have occasion to use certain properties of the $Y_{ij}(\omega)$ as discussed in reference 4. Namely, the $Y_{ij}(\omega)$ have no singularities in the lower-half complex plane and expansions of the $Y_{ij}(\omega)$ about $\omega=0$ yield

$$Y_{ij}(\omega)=i\omega c_{ij}+(i\omega)^2 d_{ij}+\cdots, \tag{10}$$

where $c_{ij}, d_{ij}, \cdots$ are constants. (Equation (10) is equivalent to the assumption, in electrical terminology, that the system be capacitive.) In particular,

$$c_{ij}=\left.\frac{\partial X_i}{\partial F_j}\right)_{\cdots F_k\cdots}(=c_{ji}), \tag{11}$$

the capital letters $X, F$ indicating that the equation applies to equilibrium states ($\cdots F_k\cdots$ are the reservoir intensive parameters).

Summarizing, we have two theorems which in some respects bear a strong resemblance. On the one hand, the generalized form of Onsager's theorem gives symmetry relations for the kinetic coefficients $L_{ij}(t)$ which describe phenomena occurring in closed systems after the removal of constraints. On the other hand, the reciprocity relations of the fluctuation-dissipation theorem give the symmetry of the admittance matrix $Y_{ij}(\omega)$ which represents phenomena associated with the interaction of a system with a reservoir when the latter exhibits sinusoidally varying forces.

A situation which can be treated by both theorems is the process resulting from the removal of constraints between a system and a reservoir. The suitability of the fluctuation-dissipation theorem to the analysis of such a process is evident. The Onsager theorem becomes applicable by the simple stratagem of considering the system plus reservoir as a closed system, as required in the Onsager formalism. By applying the two formalisms to such a situation, we shall determine in the next section the relationship between them.

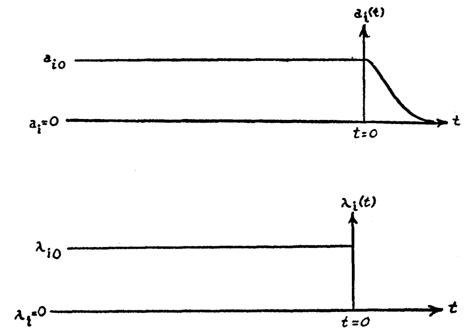


FIG. 2. Force $\lambda_i(t)$ and response $a_i(t)$ corresponding to the condition of constrained equilibrium for $t<0$, the constraints being removed at $t=0$.

## III. THE EQUIVALENCE OF THE TWO RECIPROCITY THEOREMS

We shall show in this section that the two reciprocity theorems are equivalent in the sense that the $L_{ij}(t)$ are essentially the Fourier transforms of the $Y_{ij}(\omega)$, bearing the relation of the step-function response and the admittance of circuit theory. This relationship has been demonstrated previously by Takahasi[7] for theorems very similar to those given by Eqs. (3′) and (4′) and Eqs. (8) and (9); the difference between the theorems of Takahasi and those discussed in the present paper lies essentially in the fact that certain processes, e.g., heat flow and the diffusion of matter, cannot be treated by the former. We might mention here that Takahasi's derivation is the classical analogue of the quantum mechanical theory presented as a recent paper by Callen, Barasch, and Jackson,[8] that theory apparently being limited in the same way as that of Takahasi.

Considering that constraints prevent interaction of the system $S$ with the reservoir $R$ for $t<0$, we shall calculate, by means of the formalism of the fluctuation-dissipation theorem, the quantities $a_i(t)$ if the constraints are removed at time $t=0$ (Fig. 2). To express analytically the condition of constrained equilibrium, we replace the constraints by constant values, $\lambda_{i0}$, of the reservoir forces for $t<0$,[9] the values of the extensive parameters being $a_{j0}$. The removal of the constraints at $t=0$ gains expression in requiring $\lambda_i(t)=0$ for $t>0$. Thus

$$\lambda_i(t)=\lambda_{i0}1(-t), \tag{12}$$

where $1(t)$ is the unit step function. We emphasize that the system $S-R$, in this case, is closed for all $t>0$.

Using the Cauchy principle value of the integral

$$\int_{-\infty}^{\infty} d\omega e^{i\omega t}\Lambda_i(\omega),$$

[7] Hidetosi Takahasi, J. Phys. Soc. (Japan) **7**, 439 (1952).

[8] Callen, Barasch, and Jackson, Phys. Rev. **88**, 1382 (1952).

[9] This is equivalent to replacing the microcanonical ensemble which describes the constrained state $\cdots a_{j0}\cdots$ of $S$, by a canonical ensemble, the average values of the $a_j$ in this ensemble being put equal to $a_{j0}$.

Eq. (12) gives

$$\Lambda_i(\omega)=\lambda_{i0}\left[\frac{-1}{2\pi i\omega}+\tfrac{1}{2}\delta(\omega)\right]. \tag{13}$$

From Eq. (8) then, using Eq. (10) and the other properties of $Y_{ij}$ discussed there, one obtains

$$a_i(t)=\sum_j h_{ij}(t)\lambda_{j0}+\tfrac{1}{2}\sum_j c_{ij}\lambda_{j0}, \tag{14}$$

where

$$h_{ij}(t)=-\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega e^{i\omega t}Y_{ij}(\omega)/(i\omega)^2. \tag{15}$$

Hence

$$a_i(t)-a_i(0)=t\sum_j l_{ij}(t)\lambda_{j0}, \tag{16}$$

where

$$l_{ij}(t)=\tfrac{1}{2}[h_{ij}(t)-h_{ij}(0)]. \tag{17}$$

We cannot yet compare the $l_{ij}(t)$ with Onsager's coefficients $L_{ij}$ since the forces $\lambda_j$ are in general different from the $\gamma_j$. However in this case the desired relationship between the forces is particularly trivial, namely,

$$\lambda_{j0}=\gamma_j(0). \tag{18}$$

This is so because in the first place we have

$$\gamma_j\equiv\lambda_j'-\lambda_j,$$

where $\lambda_j'$ are the forces of system $S$; secondly $\lambda_j'=\lambda_{j0}$ for $t\leq 0$ and $\lambda_j(+0)\equiv 0$. Obviously what is meant by $\gamma_j(0)$ in terms of this analysis is $\gamma_j(+0)$. Hence we have

$$a_i(t)-a_i(0)=t\sum_j l_{ij}(t)\gamma_j(0). \tag{19}$$

Comparing with Eq. (3′), it is clear that Onsager's coefficients are identical to the functions $l_{ij}(t)$ for $t>0$; the $L_{ij}(t)$ are undefined for $t<0$. We might mention here that it was Eq. (19) as derived here that suggested a possible time-dependence of the $L_{ij}$.

Equations (15) and (17) demonstrate the Fourier transform relationship between the $L_{ij}(t)$ and the $Y_{ij}(\omega)$. It is clear, then, that the symmetry of the $Y_{ij}(\omega)$ implies Onsager's theorem, the converse being true as well.

## IV. CONCLUSIONS

After generalizing the original Onsager theorem to the case wherein $L_{ij}=L_{ij}(t)$ and extending the original fluctuation-dissipation reciprocity relations so as to include the imaginary part of the admittance matrix, we have shown the two extended theorems to be equivalent.

## V. ACKNOWLEDGMENTS

I wish to thank Professor Herbert B. Callen for pointing out the need for an understanding of the relationship between these theorems and for his many valuable suggestions.

## APPENDIX: SYMMETRY OF THE ADMITTANCE MATRIX

The method for obtaining information as to the symmetry of the admittance matrix is basically the same as that used in deriving the symmetry of the $L_{ij}$ matrix. Namely, one obtains an expression for the statistical quantity $\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}$ by means of the phenomenological laws [which involve either the $L_{ij}(t)$ or the $Y_{ij}(\omega)$] and then applies the principle of microscopic reversibility which states that

$$\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}=\langle a_i(-t)\rangle_{\cdots a_j(0)\cdots}. \tag{A.1}$$

Since $\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}$ is the expectation value for $a_i$ a time $t$ after the release of constraints which had maintained the state $\cdots a_j(0)\cdots$, the right-hand side of Eq. (14) is the proper expression for $\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}$, for $t>0$. Using Eq. (A.1), we therefore obtain

$$\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}=\frac{1}{2\pi}\sum_j\gamma_{j0}\int_{-\infty}^{\infty}d\omega\frac{Y_{ij}(\omega)}{\omega^2}(e^{i\omega t}+e^{-i\omega t}),\quad \text{all } t. \tag{A.2}$$

(This may readily be checked by utilizing Eq. (10).) We may rewrite this as

$$\langle a_i(t)\rangle_{\cdots a_j(0)\cdots}=\frac{1}{\pi}\sum_j\gamma_{j0}\int_{-\infty}^{\infty}d\omega\frac{G_{ij}(\omega)}{\omega^2}e^{i\omega t},\quad \text{all } t, \tag{A.3}$$

where $G_{ij}(\omega)$ is the real part of $Y_{ij}(\omega)$.

Multiplying Eq. (A.3) by $a_k(0)$ and averaging over the equilibrium fluctuations, we see that

$$\begin{aligned}A_{ki}(t)&\equiv\langle a_k(0)a_i(t)\rangle\\&=-\frac{k}{\pi}\int_{-\infty}^{\infty}d\omega\frac{G_{ik}(\omega)}{\omega^2}e^{i\omega t},\quad \text{all } t,\\&=-\frac{k}{2\pi}\int_{-\infty}^{\infty}d\omega\frac{Y_{ik}(\omega)}{\omega^2}(e^{i\omega t}+e^{-i\omega t}),\quad \text{all } t.\end{aligned} \tag{A.4}$$

The symmetry relation $A_{ki}(t)=A_{ik}(t)$, (which follows from Eq. (A.1) and the assumption of a stationary random process) immediately gives the symmetry of the conductance matrix $G_{ij}(\omega)$ which has previously been obtained by Callen and Greene.[4] From Eqs. (A.4) and (10), it follows that

$$A_{ki}(t)=-\frac{k}{2\pi}\int_{-\infty}^{\infty}d\omega\frac{Y_{ik}(\omega)}{\omega^2}e^{i\omega t}-\frac{k}{2}c_{ik}\quad\text{for}\quad t>0.$$

Hence

$$T_{ij}(t)\equiv\int_{-\infty}^{\infty}d\omega\frac{Y_{ij}(\omega)}{\omega^2}e^{i\omega t}=T_{ji}(t)\quad\text{for}\quad t>0.$$

But

$$T_{ij}(t)=\pi c_{ij}=\pi c_{ji}=T_{ji}(t)\quad\text{for}\quad t<0.$$

In other words, the integral

$$\int_{-\infty}^{\infty}d\omega\frac{Y_{ij}(\omega)}{\omega^2}e^{i\omega t},$$

is symmetric in the indices $i$ and $j$ for all $t$. Thus the function $Y_{ij}(\omega)$ must be symmetric in $i$ and $j$.