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Irreversible Thermodynamics of Steady-State Processes

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An irreversible thermodynamic theory of steady-state processes is derived using quantum-statistical perturbation techniques. The modification of the conventional fluctuation-dissipation theorem of Callen and his co-workers and of the Onsager reciprocity is examined for a system in the nonequilibrium steady state. The principal results are as follows: (1) The instantaneous fluctuation $\Delta J(t)$ of the current from its steady-state average is decomposed into a thermal contribution $\Delta\dot{q}(t)$ characterizing the interaction of the system with a temperature reservoir and a contribution $\Delta j(t)$ characterizing the additional effects arising from the presence of a steady-state current. (2) The linear response $\phi(t)$ of the system to an applied force, referred to the steady state, and the stready-state current fluctuation moment $\langle\Delta J(0)\Delta J(t)\rangle$ are built up from different combinations of time correlation moments between $\Delta\dot{q}(t)$ and $\Delta j(t)$. (3) A tentative identification is made of the various contributions to the current fluctuations with thermal noise, shot noise, and generation-recombination noise. (4) The underlying time and magnetic field reversal symmetry of the motion can be destroyed by the presence of a steady-state current, so that the Onsager reciprocity need not, in general, be satisfied. Illustrative applications of the formalism to generation-recombination noise and warm electrons in semiconductors are discussed.

I. INTRODUCTION

It is the purpose of this paper to investigate the irreversible thermodynamics of steady-state processes, discussing how the presence of a steady-state current can significantly modify the conventional equilibrium theory.

Until quite recently, irreversible thermodynamics has been concerned primarily with linear processes referred to the equilibrium state of a system. The principal results, derived from both microscopic and macroscopic points of view, are (1) the Onsager reciprocity among the kinetic coefficients relating a number of simultaneously occurring processes,[1,2] and its extension to the full admittance matrix[3,4]; (2) the fluctuation-dissipation theorem (generalized Nyquist theorem), relating the linear response of a system to its spontaneous fluctuations in equilibrium[5,6]; and (3) various theorems pertaining to the nonequilibrium probability distributions and the production of entropy during a linear process.[7–9]

However, the increasing importance of nonlinear systems and the considerable interest concerning noise in driven systems demanded an extension of the existing theory of irreversible thermodynamics. Recently, the author and Callen[10] undertook the development of analogous thermodynamic relationships among the nonlinear response, the driven noise, and the spontaneous equilibrium fluctuations, using the quantum-statistical perturbation theory employed by Kubo.[11] As might be expected, these relationships were found to be generally quite complicated except in special cases such as that of a simple relaxation process. Further, although reference was made there to current-carrying systems, the formalism was developed primarily for closed thermodynamic systems incapable of supporting nonvanishing steady-state currents. In the present paper we employ quantum-statistical perturbation theory to investigate the irreversible thermodynamic behavior of open systems in the nonequilibrium steady state. Aside from its obvious importance in many situations of physical interest, the steady state has been selected for study because its simplicity compared to an arbitrary nonequilibrium state assures an adequate description in terms of a small number of variables, and because it represents a logical extension of the equilibrium state to which generalizations of many equilibrium concepts should be applicable.

Although it had been previously surmised that the fluctuation-dissipation theorem and the Onsager reciprocity were not generally valid for a system in the steady state, a precise formulation of the problem was recently given by Lax in his comprehensive treatment of the irreversible thermodynamics of Markoffian processes.[12] A portion of that work is devoted to pointing out that, even under the conventional identification of the linear response with the regression of a fluctuation, the fact that the existence of a steady-state current renders the customary equilibrium fluctuation theory invalid leads to a modification of both the Onsager reciprocity and the fluctuation-dissipation theorem. It is our purpose here to discuss this important question starting from first principles and to examine in detail the modifications introduced into the conventional fluctuation-dissipation theorem and the Onsager reci-

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procity by the presence of a nonvanishing steady-state current.

In Sec. II we derive the general expression for the linear response of a system, referred to the nonequilibrium steady state, in terms of appropriate steady-state operators. Invoking certain properties of these steady-state operators, the steady-state fluctuation-dissipation theorem is developed in Sec. III, and the distinction between the equilibrium and steady-state forms of this theorem is discussed. The additional current variables required to describe a steady-state system are also introduced. Section IV presents a discussion of the behavior of the steady-state system with respect to reversal of time and magnetic field and the resulting breakdown of the Onsager symmetry. In Sec. V we consider a simple physical system in which all fluctuating quantities are describable in terms of random fluctuations of the charge carriers among the various single-particle velocity states. This leads to a logical decomposition of the steady-state current fluctuations into thermal noise, generation-recombination noise, and (possibly) shot noise. Finally, in Sec. VI we consider the question of warm carriers in semiconductors, in order to illustrate the application of the formalism to systems in which an energy change accompanies the imposition of a steady-state current.

II. THE HAMILTONIAN AND THE STEADY-STATE CURRENTS

We consider a system, initially in equilibrium at some time in the distant past, which is brought into the steady state by application of an appropriate set of thermodynamic forces $F_i(t)$. In addition, at some time after the steady state has obtained, we superimpose a set of small forces $\Delta F_i(t)$ having arbitrary time dependence. The $\Delta F_i(t)$ give rise to a small displacement of the system with respect to the steady state. The Hamiltonian appropriate to a system driven in this manner is

$$\begin{aligned} H(t) &= H^{(0)} - \sum_i F_i(t) Q_i - \sum_i \Delta F_i(t) Q_i \\ &= H^{(F)}(t) - \sum_i \Delta F_i(t) Q_i, \end{aligned} \tag{1}$$

where $H^{(0)}$ is the unperturbed Hamiltonian of the driven system, Q_i is the thermodynamic extensive parameter conjugate to the force F_i, and $H^{(F)}(t) = H^{(0)} - \sum_i F_i(t) Q_i$ denotes the steady-state Hamiltonian. Thus, for example, in a homogeneous system driven by an applied voltage $V_i(t)$, the conjugate extensive parameter is $Q_i = e\sum_\mu x_{i\mu}/L_i$, where $x_{i\mu}$ is the ith displacement component of the μth particle and L_i is the corresponding linear dimension of the system.

If the system is in equilibrium, with temperature T, before the forces are applied, the expectation value of an operator A at time t is

$$\langle A(t)\rangle = \mathrm{Tr}\rho^{(0)} A(t) = \langle A(t)\rangle^{(0)}, \tag{2}$$

where $\rho^{(0)}$ is the initial canonical density operator

$$\rho^{(0)} = e^{-\beta H^{(0)}}/\mathrm{Tr} e^{-\beta H^{(0)}}, \quad \beta = 1/kT, \tag{3}$$

and where the driven Heisenberg operator $A(t)$ is defined by

$$A(t) = U^\dagger(t) A U(t). \tag{4}$$

The unitary time-evolution operator $U(t)$ satisfies the Schrödinger equation

$$\dot{U}(t) = (1/i\hbar)[H^{(F)}(t) - \sum_i \Delta F_i(t) Q_i] U(t). \tag{5}$$

Letting

$$U(t) = U^{(F)}(t) + \Delta U(t), \tag{6}$$

where the steady-state time-evolution operator $U^{(F)}(t)$ satisfies the equation

$$\dot{U}^{(F)}(t) = (1/i\hbar) H^{(F)}(t) U^{(F)}(t), \tag{7}$$

the linear term $\Delta U(t)$ in the solution of the Schrödinger equation with respect to the steady state is readily found to be

$$\Delta U(t) = -\frac{1}{i\hbar} U^{(F)}(t) \sum_i \int_{-\infty}^t dt_1\, \Delta F_i(t_1) Q_i^{(F)}(t_1). \tag{8}$$

$Q_i^{(F)}(t)$ is the steady-state Heisenberg operator

$$Q_i^{(F)}(t) = U^{(F)\dagger}(t) Q_i U^{(F)}(t). \tag{9}$$

We now consider the current operator J_j corresponding to the extensive quantity Q_j. The equilibrium Heisenberg operator $J_j^{(0)}(t)$ is given by

$$J_j^{(0)}(t) = -(1/i\hbar)[H^{(0)}, Q_j^{(0)}(t)]_-, \tag{10}$$

where the brackets denote a quantum-mechanical commutator. From Eqs. (4), (6), and (8) the linear term $\Delta J_j^{(F)}(t)$ in the deviation of the driven current operator from the steady state is found to be

$$\Delta J_j^{(F)}(t) = \frac{1}{i\hbar} \sum_i \int_{-\infty}^t dt_1\, \Delta F_i(t_1) \times [Q_i^{(F)}(t_1), J_j^{(F)}(t)]_-. \tag{11}$$

Thus, according to Eq. (2), the expectation value $\langle \Delta J_j(t)\rangle^{(F)}$ of the linear current response to the forces $\Delta F_i(t_1)$ becomes

$$\langle \Delta J_j(t)\rangle^{(F)} = \frac{1}{i\hbar} \sum_i \int_{-\infty}^t dt_1\, \Delta F_i(t_1) \times \langle [Q_i^{(F)}(t_1), J_j^{(F)}(t)]_-\rangle^{(0)}. \tag{12}$$

At this point in the development it seems worthwhile to comment briefly on the distinction between a closed thermodynamic system and an open system capable of supporting a nonvanishing steady-state current. A closed system is one for which no continuous paths exist for the transport of charge or energy and which is thus incapable of supporting steady-state thermo-

dynamic currents. When a force is applied to a closed system, the system readjusts itself so that a new, perturbed equilibrium state ultimately is obtained. On the other hand, an open system is one which does possess continuous paths around which thermodynamic currents can flow. When a force is applied to an open system in equilibrium, the system does not approach a new equilibrium state but, rather, some nonequilibrium steady state. For many open systems, the current-carrying property is formally introduced by imposing periodic boundary conditions. The interested reader will find a more detailed discussion of the distinction between open and closed systems in Appendix A.

It is convenient to characterize the linear current response by the after-effect function $\phi_{ij}^{(F)}(t_1,t)$, which is the response $\langle\Delta J_j(t)\rangle^{(F)}$ at time t to a δ-function force ΔF_i applied at time t_1. That is, by definition,

$$\langle\Delta J_j(t)\rangle^{(F)}=\sum_i \int_{-\infty}^{t} dt_1\, \Delta F_i(t_1)\phi_{ij}^{(F)}(t_1,t)\,; \quad (13)$$

from Eq. (12), we therefore identify

$$\phi_{ij}^{(F)}(t_1,t)=(1/i\hbar)\langle[Q_i^{(F)}(t_1),J_j^{(F)}(t)]_-\rangle^{(0)}. \quad (14)$$

Now in the equilibrium case,[10] it is clear that $\phi_{ij}^{(0)}(t_1,t)$ obeys time stationarity. That is, $\phi_{ij}^{(0)}(t_1,t)=\phi_{ij}^{(0)}(t-t_1)$ depends only on the quantity $(t-t_1)$. However, the time stationarity of the steady-state aftereffect function $\phi_{ij}^{(F)}(t_1,t)$ is not immediately evident. The question of time stationarity is intimately related to the problem of Joule heating of the system, and does not arise in the equilibrium case because the lowest nonvanishing term in the Joule heat is of second order in the applied forces.

By definition, it is necessary to require that a system in the steady state be time stationary. However, the imposition of time stationarity has a more fundamental implication. Although we assume the system to be in continual interaction with a temperature reservoir during the process, the Hamiltonian of Eq. (1) does not explicitly include such an interaction term. Hence, no specific provision is made for continuously eliminating the Joule heat generated in the system. However, a system which retains the accumulated Joule heat can never achieve a steady state, since the energy will increase without limit. A formal procedure for resolving this difficulty is simply to impose the requirement of time stationarity on the system. These matters are discussed further in Appendix B, where we consider the energy of a steady-state system.

In order to examine in detail the properties of the steady-state operators, we consider their perturbation expansion in powers of the steady-state forces $F_i(t)$. The nth-order term in the expansion of the current operator $J_j^{(F)}(t)$ is found to be[10]

$$^{(n)}J_j^{(F)}(t)=\left(\frac{1}{i\hbar}\right)^n \sum_{ik\cdots l}\int_{-\infty}^{t} dt_1\, F_i(t_1)\int_{-\infty}^{t_1} dt_2\, F_k(t_2)\cdots\int_{-\infty}^{t_{n-1}} dt_n\, F_l(t_n)$$
$$\times[Q_l^{(0)}(t_n),[\cdots,[Q_k^{(0)}(t_2),[Q_i^{(0)}(t_1),J_j^{(0)}(t)]_-]_-\cdots]_-]_-, \quad (15)$$

where the superscript (0) denotes an equilibrium Heisenberg operator. Since the precise details of the way in which the system is brought from its initial equilibrium state to the desired steady state must be of no importance, we assume step-function forces of the form

$$\begin{aligned} F_i(t)&=0 \text{ for } t<-T,\\ &=\text{constant } F_i \text{ for } t>-T, \end{aligned} \quad (16)$$

where T is sufficiently large and positive to insure attainment of the steady state prior to $t=0$ Then Eq. (15) becomes, letting $t_r\to t_r+t$,

$$^{(n)}J_j^{(F)}(t)=\left(\frac{1}{i\hbar}\right)^n \sum_{ik\cdots l} F_iF_k\cdots F_l\int_{-(t+T)}^{0} dt_1\int_{-(t+T)}^{t_1} dt_2\cdots\int_{-(t+T)}^{t_{n-1}} dt_n$$
$$\times e^{iH^{(0)}t/\hbar}[Q_l^{(0)}(t_n),[\cdots,[Q_k^{(0)}(t_2),[Q_i^{(0)}(t_1),J_j^{(0)}(0)]_-]_-\cdots]_-]_-e^{-iH^{(0)}t/\hbar}, \quad (17)$$

where we have removed the $e^{\pm iH^{(0)}t/\hbar}$ time dependence, common to all the Heisenberg operators, outside the multiple commutator brackets. As we shall see momentarily, time stationarity is imposed by requiring that the driven operator $^{(n)}J_j^{(F)}(t)$ be independent of the time $-T$ of application of the forces. Hence, taking $T\to\infty$, we have that

$$^{(n)}J_j^{(F)}(t)=e^{iH^{(0)}t/\hbar}\, {}^{(n)}J_j^{(F)}(0)e^{-iH^{(0)}t/\hbar}, \quad (18)$$

where

$$^{(n)}J_j^{(F)}(0)=\left(\frac{1}{i\hbar}\right)^n \sum_{ik\cdots l} F_iF_k\cdots F_l\int_{-\infty}^{0} dt_1\int_{-\infty}^{t_1} dt_2\cdots\int_{-\infty}^{t_{n-1}} dt_n$$
$$\times[Q_l^{(0)}(t_n),[\cdots,[Q_k^{(0)}(t_2),[Q_i^{(0)}(t_1),J_j^{(0)}(0)]_-]_-\cdots]_-]_- \quad (19)$$

is independent of t. A similar expression can be derived for the nth-order perturbation term of the steady-state operator $Q_i^{(F)}(t_1)$.

Synthesizing the steady-state operators $Q_i^{(F)}(t_1)$ and $J_j^{(F)}(t)$ from their respective perturbation terms, Eq. (18), the steady-state aftereffect function of Eq. (14) assumes the form

$$\phi_{ij}^{(F)}(t_1,t)=(1/i\hbar)\langle[e^{iH^{(0)}t_1/\hbar}Q_i^{(f)}(0)e^{-iH^{(0)}t_1/\hbar},e^{iH^{(0)}t/\hbar}J_j^{(F)}(0)e^{-iH^{(0)}t/\hbar}]_-\rangle^{(0)}. \tag{20}$$

Because the operators $e^{\pm iH^{(0)}t/\hbar}$ commute with the canonical density operator $\rho^{(0)}$, it is evident that $\phi_{ij}^{(F)}(t_1,t)=\phi_{ij}^{(F)}(t-t_1)$ is, in fact, time stationary. Thus, the linear response $\langle\Delta J_j(t)\rangle^{(F)}$ to the applied force $\Delta F_i(t)$ is characterized uniquely, according to Eq. (13), by the aftereffect function with $t_1=0$:

$$\phi_{ij}^{(F)}(t)=\frac{1}{i\hbar}\langle[Q_i^{(F)}(0),e^{iH^{(0)}t/\hbar}J_j^{(F)}(0)e^{-iH^{(0)}t/\hbar}]_-\rangle^{(0)}. \tag{21}$$

III. THE MODIFIED FLUCTUATION-DISSIPATION THEOREM

The conventional fluctuation-dissipation theorem is an expression of the intimate relationship which exists between the linear response of a system referred to its equilibrium state and the spontaneous equilibrium current fluctuations. In reference 10 it is shown that the equilibrium aftereffect function $\phi_{ij}^{(0)}(t)$ can be expressed in the form

$$\begin{aligned}\phi_{ij}^{(0)}(t)&=(1/i\hbar)\langle[Q_i^{(0)}(0),J_j^{(0)}(t)]_-\rangle^{(0)}\\&=\int_{-\infty}^{\infty}dt'\,\Gamma(t-t')\\&\quad\times\left\langle\frac{1}{2}\left[-\frac{1}{i\hbar}[H^{(0)},Q_i^{(0)}(0)]_-,J_j^{(0)}(t')\right]_+\right\rangle^{(0)},\end{aligned} \tag{22}$$

where

$$\Gamma(t)=\frac{2}{\pi\hbar}\ln\coth\frac{\pi|t|}{2\hbar\beta}\underset{\beta\to0}{\longrightarrow}\beta\delta(t). \tag{23}$$

Identifying the equilibrium current operator $J_j^{(0)}(0)$ according to Eq. (10), Eq. (22) can be rewritten as

$$\phi_{ij}^{(0)}(t)=\int_{-\infty}^{\infty}dt'\,\Gamma(t-t')\langle\tfrac{1}{2}[J_i^{(0)}(0),J_j^{(0)}(t')]_+\rangle^{(0)}. \tag{24}$$

The quantity $\langle\frac{1}{2}[J_i^{(0)}(0),J_j^{(0)}(t')]_+\rangle^{(0)}$ is the appropriately symmetrized (anticommutator) quantum mechanical expression for the equilibrium second correlation moment between the ith current component at time zero and the jth current component at time t'. This second moment is customarily employed to characterize the spontaneous current fluctuations, or noise, in the temporal representation.

In the classical limit of high temperature, the equilibrium fluctuation-dissipation theorem of Eq. (24) reduces, in virtue of Eq. (23), to

$$\phi_{ij}^{(0)}(t)\underset{\beta\to0}{\longrightarrow}\beta\langle J_i^{(0)}(0)J_j^{(0)}(t)\rangle^{(0)}\equiv\beta\langle J_i(0)J_j(t)\rangle^{(0)}, \tag{25}$$

where $\langle J_i(0)J_j(t)\rangle^{(0)}$ denotes the classical equilibrium correlation moment between J_i at time zero and J_j at time t.

Examination of the analysis[10] employed in arriving at Eq. (22) for $\phi_{ij}^{(0)}(t)$ shows that it is valid for any two operators $A(0)$ and $B(t)$, provided only that these operators have a time dependence of the form

$$A(t)=e^{iH^{(0)}t/\hbar}Ae^{-iH^{(0)}t/\hbar}. \tag{26}$$

Thus, the steady-state aftereffect function $\phi_{ij}^{(F)}(t)$, given in Eq. (21), can be written immediately in the form

$$\phi_{ij}^{(F)}(t)=(1/i\hbar)\langle[Q_i^{(F)}(0),J_j^{(F)}(t)]_-\rangle^{(0)}=\int_{-\infty}^{\infty}dt'\,\Gamma(t-t')\left\langle\frac{1}{2}\left[-\frac{1}{i\hbar}[H^{(0)},Q_i^{(F)}(0)]_-,J_j^{(F)}(t')\right]_+\right\rangle^{(0)}. \tag{27}$$

Equation (27) is the modified form which the fluctuation-dissipation theorem assumes which the system is operated in the steady state. Although this equation is formally identical to Eq. (22), except that $Q_i^{(0)}(0)$ and $J_j^{(0)}(t)$ have been replaced by the corresponding steady-state operators $Q_i^{(F)}(0)$ and $J_j^{(F)}(t)$, there is nevertheless a fundamental distinction between them. Whereas the equilibrium operator $-(1/i\hbar)[H^{(0)},Q_i^{(0)}(t)]_-$ *is identical with* the equilibrium Heisenberg current operator $J_i^{(0)}(t)$, the steady-state operator $-(1/i\hbar)[H^{(0)},Q_i^{(F)}(t)]_-$ *is not equivalent to* the steady-state current operator $J_i^{(F)}(t)$. This distinction can be readily seen by comparing Eq. (17) for the nth-order term ${}^{(n)}J_j^{(F)}(t)$ in the current operator $J_j^{(F)}(t)$ with the corresponding term in the steady-state operator $-(1/i\hbar)[H^{(0)},Q_j^{(F)}(t)]_-$:

$$\begin{aligned}-(1/i\hbar)[H^{(0)},Q_j^{(F)}(t)]_-^{(n)}&=-\left(\frac{1}{i\hbar}\right)^{n+1}\sum_{ik\cdots l}F_iF_k\cdots F_l\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_{n-1}}dt_n\\&\quad\times e^{iH^{(0)}t/\hbar}[H^{(0)},[Q_l^{(0)}(t_n),[\cdots,[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(0)]_-]_-\cdots]_-]_-]_-e^{-iH^{(0)}t/\hbar}.\end{aligned} \tag{28}$$

Recalling Eq. (10) for $J_j^{(0)}(t)$, it is apparent that the commutation with the unperturbed Hamiltonian $H^{(0)}$ occurs in a fundamentally different way in Eqs. (17) and (28). Therefore, in the steady state the aftereffect function $\phi_{ij}^{(F)}(t)$ is no longer simply related to the second correlation moment between the current J_i at time zero and the current J_j at time t, as in Eq. (24), but rather to the second correlation moment between a new operator $-(1/i\hbar)[H^{(0)},Q_i^{(F)}(0)]_-$ at time zero and the current $J_j^{(F)}(t)$ at time t, as given by Eq. (27).

In the classical limit of high temperature the steady-state fluctuation-dissipation theorem of Eq. (27) reduces, in virtue of Eq. (23), to

$$\phi_{ij}^{(F)}(t) \underset{\beta\to 0}{\longrightarrow} \beta\langle \dot{q}_i^{(F)}(0)J_j^{(F)}(t)\rangle^{(0)} \equiv \beta\langle \dot{q}_i(0)J_j(t)\rangle^{(F)}, \quad (29)$$

where we have defined

$$\dot{q}_i^{(F)}(t) = -(1/i\hbar)[H^{(0)},Q_i^{(F)}(t)]_- . \quad (30)$$

$\langle \dot{q}_i(0)J_j(t)\rangle^{(F)}$ denotes the classical steady-state correlation moment between $\dot{q}_i$ at time zero and J_j at time t.

In order to make the physical significance of the modified fluctuation-dissipation theorem more evident and to put this theorem into a form more suitable for application to specific physical models, it is convenient to decompose the steady-state current operator according to

$$J_i^{(F)}(t) = \dot{q}_i^{(F)}(t) + j_i^{(F)}(t), \quad (31)$$

where the component $\dot{q}_i^{(F)}(t)$ is defined by Eq. (30). Equation (31) thus defines the component operator $j_i^{(F)}(t)$. The properties exhibited by the component current operators are readily seen to be the following. From Eq. (2) for the expectation value of a driven operator and Eq. (30), it follows that the steady-state expectation value of $\dot{q}_i^{(F)}(t)$ vanishes identically.

$$\langle \dot{q}_i(t)\rangle^{(F)} \equiv \langle \dot{q}_i^{(F)}(t)\rangle^{(0)} = -(1/i\hbar)\ \mathrm{Tr}\rho^{(0)}[H^{(0)},Q_i^{(F)}(t)]_- = -(1/i\hbar)\ \mathrm{Tr}[\rho^{(0)},H^{(0)}]_- Q_i^{(F)}(t) \equiv 0, \quad (32)$$

since $[\rho^{(0)},H^{(0)}]_- \equiv 0$. Therefore, from the definition (31) of $j_i^{(F)}(t)$, the expectation value of this operator is found to be just the steady-state current:

$$\langle j_i(t)\rangle^{(F)} \equiv \langle j_i^{(F)}(t)\rangle^{(0)} = \langle J_i\rangle^{(F)}. \quad (33)$$

In the equilibrium state, $J_i(t)$ is identical to $\dot{q}_i(t)$, and the operator $j_i(t)$ is identically zero. An additional requirement on $\dot{q}_i(t)$ and $j_i(t)$ is intimately related to the energy associated with each of these component steady-state current operators. This requirement is discussed in Appendix B, where we consider the energy of a steady-state system, and in Sec. VI in connection with the warm carrier problem in semiconductors.

Substitution of Eq. (31) for $J_i(t)$ into Eq. (29) yields the (classical) steady-state fluctuation-dissipation theorem in the form

$$\phi_{ij}^{(F)}(t) \underset{\beta\to 0}{\longrightarrow} \beta\{\langle \Delta\dot{q}_i(0)\Delta\dot{q}_j(t)\rangle^{(F)} + \langle \Delta\dot{q}_i(0)\Delta j_j(t)\rangle^{(F)}\}. \quad (34)$$

For convenience we have written $\phi_{ij}^{(F)}(t)$ in terms of the instantaneous displacements $\Delta\dot{q}_i(t)$ and $\Delta j_j(t)$ of the component current variables from their steady-state expectation values.

$$\begin{aligned}\Delta\dot{q}_i(t) &= \dot{q}_i(t) - \langle \dot{q}_i\rangle^{(F)} = \dot{q}_i(t),\\ \Delta j_j(t) &= j_j(t) - \langle j_j\rangle^{(F)} = j_j(t) - \langle J_j\rangle^{(F)}.\end{aligned} \quad (35)$$

By way of contrast, we write down the classical form of the steady-state correlation moment $\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)}$ between the current J_i at time zero and the current J_j at time t in terms of the component variables $\Delta\dot{q}_i(t)$ and $\Delta j_j(t)$.

$$\begin{aligned}\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)} &\equiv \langle \Delta J_i^{(F)}(0)\Delta J_j^{(F)}(t)\rangle^{(0)} = \langle \Delta\dot{q}_i(0)\Delta\dot{q}_j(t)\rangle^{(F)}\\ &\quad + \langle \Delta\dot{q}_i(0)\Delta j_j(t)\rangle^{(F)} + \langle \Delta j_i(0)\Delta\dot{q}_j(t)\rangle^{(F)}\\ &\quad + \langle \Delta j_i(0)\Delta j_j(t)\rangle^{(F)}.\end{aligned} \quad (36)$$

Whereas in the case of equilibrium only one set of variables $\dot{q}_i(t)$ is necessary to completely describe or characterize both $\phi_{ij}(t)$ and $\langle \Delta J_i(0)\Delta J_j(t)\rangle$, the steady state is more complicated in that two sets of variables $\dot{q}_i(t)$ and $j_j(t)$ are required for a complete description. In addition, it is seen from Eqs. (34) and (36) that in the steady state the dependence on the various correlation moments between $\Delta\dot{q}$ and Δj is different for the quantities $\phi_{ij}^{(F)}(t)$ and $\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)}$. In the equilibrium state the variable $j_i(t)$, of course, vanishes, and Eqs. (34) and (36) reduce to the conventional fluctuation-dissipation theorem of Eq. (25).

Finally, there exists a fundamental thermodynamic distinction between the steady-state and equilibrium statements of the fluctuation-dissipation theorem. The equilibrium theorem of Eq. (25) constitutes a true thermodynamic relationship in the sense that both the after-effect function $\phi_{ij}^{(0)}(t)$ and the noise $\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(0)}$ are true macroscopic observables of the system. However, it is not clear that the steady-state fluctuation moments $\langle \Delta\dot{q}_i(0)\Delta\dot{q}_j(t)\rangle^{(F)}$ and $\langle \Delta\dot{q}_i(0)\Delta j_j(t)\rangle^{(F)}$, in terms of which the after-effect function $\phi_{ij}^{(F)}(t)$ is expressed by Eq. (34), are in fact macroscopic observables of the steady-state system. Thus, it is not evident that the steady-state fluctuation-dissipation theorem is a valid thermodynamic relationship. In order to demonstrate the validity of the modified theorem in this thermodynamic sense, it would be necessary, for example, to specify a unique prescription for experimentally sorting out the various contributions to the noise in Eq. (36). A possible classification of these noise contributions is discussed in Sec. V.

IV. SYMMETRY PROPERTIES

In a system which is simultaneously undergoing a number of irreversible processes, the linear response functions measured with respect to the equilibrium state and characterizing the mutual interference

among the processes exhibit important symmetry properties. These symmetry properties arise from the invariance of the system motion with respect to reversal of time and applied magnetic fields, and are known as the Onsager reciprocal relations. We might anticipate that the imposition of a nonequilibrium steady state on the system would in general destroy this underlying symmetry, so that the Onsager reciprocity need not be satisfied.

In order to present the modification of the Onsager symmetry by the existence of steady-state currents in context, it is of interest to recall briefly the symmetry properties appropriate to the equilibrium state.[10] The operators $Q_i^{(0)}$ are assumed to be even functions of the particle momenta, and the Hamiltonian $H^{(0)}$ is taken to be real, so that

$$Q_i^{(0)}(-t;\,-\mathfrak{H})=Q_i^{(0)*}(t;\,\mathfrak{H}), \tag{37}$$

and

$$J_i^{(0)}(-t;\,-\mathfrak{H})=-J_i^{(0)*}(t;\,\mathfrak{H}), \tag{38}$$

where $\mathfrak{H}$ is an applied magnetic field. Using these properties of the operators $Q_i^{(0)}(t)$ and $J_i^{(0)}(t)$, together with Eq. (22) for the equilibrium aftereffect function $\phi_{ij}^{(0)}(t)$, it follows that

$$\phi_{ji}^{(0)}(-t;\,\mathfrak{H})=\phi_{ij}^{(0)}(t;\,\mathfrak{H})=\phi_{ij}^{(0)}(-t;\,-\mathfrak{H}). \tag{39}$$

Equation (39) is the temporal statement of the (generalized) Onsager symmetry with respect to the equilibrium state of a system. These results can be rephrased in the more familiar terms afforded by the admittance matrix. The resulting spectral form of the Onsager symmetry is

$$Y_{ij}^{(0)}(\omega;\,-\mathfrak{H})=Y_{ji}^{(0)}(\omega;\,\mathfrak{H}), \tag{40}$$

where the ijth element $Y_{ij}(\omega)$ of the admittance matrix is given by

$$Y_{ij}(\omega)=\int_0^\infty dt\, e^{-i\omega t}\phi_{ij}(t). \tag{41}$$

Turning now to the steady state, we first consider the relationship between $\phi_{ij}^{(F)}(t)$ and $\phi_{ji}^{(F)}(-t)$ as contrasted with the equilibrium relationship expressed by the first equality of Eq. (39). Written in terms of the component operators $\dot{q}^{(F)}$ and $j^{(F)}$, Eq. (27) assumes the form

$$\phi_{ij}^{(F)}(t)=\int_{-\infty}^{\infty} dt'\,\Gamma(t-t')\{\langle\tfrac{1}{2}[\dot{q}_i^{(F)}(0),\dot{q}_j^{(F)}(t')]_+\rangle^{(0)} +\langle\tfrac{1}{2}[\dot{q}_i^{(F)}(0),j_j^{(F)}(t')]_+\rangle^{(0)}\}, \tag{42}$$

whereas, letting $t\rightarrow -t$ and interchanging i and j, we obtain

$$\phi_{ji}^{(F)}(-t)=\int_{-\infty}^{\infty} dt'\,\Gamma(t-t')\{\langle\tfrac{1}{2}[\dot{q}_i^{(F)}(0),\dot{q}_j^{(F)}(t')]_+\rangle^{(0)} +\langle\tfrac{1}{2}[j_i^{(F)}(0),\dot{q}_j^{(F)}(t')]_+\rangle^{(0)}\}. \tag{43}$$

In deriving Eq. (43) we have let $t'\rightarrow -t'$, made use of the symmetry of $\Gamma(t)$ evident from Eq. (23), and invoked the time stationarity of $\phi_{ij}^{(F)}(t)$. Since $j^{(F)}$ and $\dot{q}^{(F)}$ are fundamentally different operators, it is not clear from Eqs. (42) and (43) that $\phi_{ij}^{(F)}(t)=\phi_{ji}^{(F)}(-t)$ except in the event the correlation moment $\langle\frac{1}{2}[\dot{q}_i^{(F)}(0),j_j^{(F)}(t)]_+\rangle^{(0)}=0$. We have not yet succeeded in rigorously deriving the conditions under which a correlation may exist between $\dot{q}_i^{(F)}(0)$ and $j_j^{(F)}(t)$. However, in the following section the possibility is raised that the existence of this correlation moment is related to spatial nonhomogeneity of the system.

We now discuss the behavior of $\phi_{ij}^{(F)}(t;\,\mathfrak{H})$ under the simultaneous transformations $t\rightarrow -t$, $\mathfrak{H}\rightarrow -\mathfrak{H}$. Consider the nth-order term ${}^{(n)}J_i^{(F)}(t;\,\mathfrak{H})$ in the steady-state current operator given by Eq. (17). Letting $t\rightarrow -t$, $\mathfrak{H}\rightarrow -\mathfrak{H}$, and invoking Eqs. (37) and (38), this becomes

$$\begin{aligned}{}^{(n)}J_i^{(F)}(-t;\,-\mathfrak{H})=-\Bigg\{\left(\frac{1}{i\hbar}\right)^n \sum_{jk\cdots l} F_jF_k\cdots F_l\int_{-\infty}^{0} dt_1\int_{-\infty}^{t_1} dt_2\cdots\int_{-\infty}^{t_{n-1}} dt_n \\ \times e^{iH^{(0)}t/\hbar}[Q_l^{(0)}(-t_n;\,\mathfrak{H}),[\cdots,[Q_k^{(0)}(-t_2;\,\mathfrak{H}),[Q_j^{(0)}(-t_1;\,\mathfrak{H}),J_i^{(0)}(0;\,\mathfrak{H})]_-]_-\cdots]_-]_-e^{-iH^{(0)}t/\hbar}\Bigg\}^*.\end{aligned} \tag{44}$$

We see that ${}^{(n)}J_i^{(F)}(-t;\,-\mathfrak{H})$ differs from $-{}^{(n)}J_i^{(F)*}(t;\,\mathfrak{H})$ in that the variables of integration t_r have all been replaced by $-t_r$. Now in Appendix A, where we consider the distinction between closed systems and open systems capable of supporting steady-state currents, the evaluation of integrals such as those appearing in Eq. (44) is discussed. By rewriting the integrands in terms of appropriate summations over matrix elements in the unperturbed energy representation, each such integral can be reduced to the form

$$\int_{-\infty}^{0} dt\, f(E_m-E_n)e^{\pm i[(E_m-E_n)/\hbar]t}=\hbar\pi f(E_m-E_n)\delta(E_m-E_n)\mp i\hbar f(E_m-E_n)P\left(\frac{1}{E_m-E_n}\right). \tag{45}$$

The E_m are unperturbed energy eigenvalues of system, and $f(E_m-E_n)$ denotes an appropriate slowly varying function of (E_m-E_n). Hence, the effect of substituting $-t_r$ for t_r in the integrands is to reverse the sign of the principal value contribution of each integral. Therefore, in general, we must expect that

$$J_i^{(F)}(-t;\,-\mathfrak{H})\neq -J_i^{(F)*}(t;\,\mathfrak{H}), \tag{46}$$

in contrast to Eq. (38) for the equilibrium current operator $J_i^{(0)}(t;\mathcal{H})$. The same arguments will apply to the steady-state component operators $\dot{q}_i^{(F)}(t;\mathcal{H})$ and $j_i^{(F)}(t;\mathcal{H})$. Similarly, we find that in general

$$Q_i^{(F)}(-t;\,-\mathcal{H})\neq Q_i^{(F)*}(t;\mathcal{H}), \tag{47}$$

in contrast to Eq. (37).

Because the transformation properties stated in Eqs. (37) and (38) for the equilibrium Heisenberg operators $Q_i^{(0)}(t;\mathcal{H})$ and $J_i^{(0)}(t;\mathcal{H})$ need not be obeyed by the corresponding steady-state operators, we therefore expect that, in general,

$$\phi_{ij}^{(F)}(-t;\,-\mathcal{H})\neq\phi_{ij}^{(F)}(t;\mathcal{H}), \tag{48}$$

in contrast to the second equality of Eq. (39). It follows, from Eq. (41) for $Y_{ij}(\omega)$ that

$$Y_{ij}^{(F)}(\omega;\,-\mathcal{H})\neq Y_{ji}^{(F)}(\omega;\mathcal{H}), \tag{49}$$

regardless of whether or not $\phi_{ij}^{(F)}(t)=\phi_{ji}^{(F)}(-t)$. [See Eqs. (42) and (43) and the related discussion.] Further, we note that even the steady-state current fluctuations need no longer obey the principle of microscopic reversibility. That is,

$$\langle\tfrac{1}{2}[J_i(0;\,-\mathcal{H}),J_j(-t;\,-\mathcal{H})]_+\rangle^{(F)}\neq\langle\tfrac{1}{2}[J_i(0;\mathcal{H}),J_j(t;\mathcal{H})]_+\rangle^{(F)}. \tag{50}$$

It is not possible at present to suggest the conditions, if in fact any exist, under which a steady-state system can exhibit the conventional symmetry with respect to simultaneous reversal of time and magnetic field. We merely note in passing that principal value contributions to the perturbed energy of a statistical system are characteristically related to energy shifts in the eigenvalues of the system as contrasted with transitions between existing states.

V. GENERATION RECOMBINATION NOISE IN SEMICONDUCTORS

In this section we examine in somewhat greater detail the physical significance of the modification introduced into the conventional fluctuation-dissipation theorem by the existence of a steady-state current. The need for introducing the additional set of variables $j_i^{(F)}(t)$ in order to obtain an adequate description of a steady-state system will be further clarified. In addition, the formal decomposition of the steady-state current fluctuations presented in Eq. (36) will be tentatively identified with previously recognized noise contributions.

It is not difficult to see how the existence of a steady-state current requires in general the introduction of the additional variables $j_i^{(F)}(t)$ to obtain a complete description of the system. Consider first, for example, a one-dimensional system in equilibrium having a

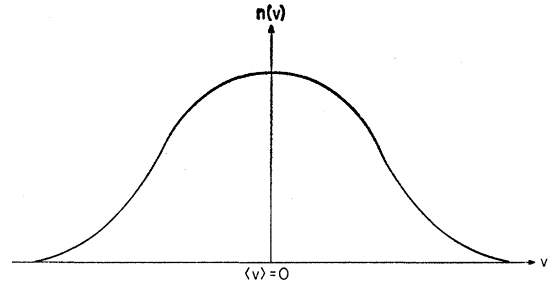

FIG. 1. Symmetric velocity distribution for a one-dimensional system in equilibrium.

symmetric population $n(v)$ of current-carrying velocity states shown in Fig. 1. $n(v)$ might represent the equilibrium electronic distribution in the conduction band of a semiconductor. For this case there exists a one-to-one correspondence between the decay of a small displacement from the equilibrium population and the decay of the accompanying current fluctuation. As pointed out by Lax,[12] it is precisely this one-to-one correspondence which permits the calculation of the equilibrium current fluctuations either from direct consideration of fluctuations in the current variable itself or by consideration of fluctuations in the distribution function over velocity states. In fact, the equilibrium fluctuation-dissipation theorem can be regarded as a consequence of this equivalence.

Now consider what happens when we impose a steady-state current on the system. In addition to the possibility of raising the "temperature" of the current carriers (warm carriers) or exciting additional conduction electrons, the steady-state velocity distribution is shifted in the direction of the imposed current. This situation is illustrated in Fig. 2. If we superimpose a displacement on the steady-state distribution in which the concentration of conducting particles is conserved, the one-to-one correspondence between the decay of the velocity distribution and that of the current may still be retained. (See Sec. VI for a discussion of warm carriers.) However, if we impose an initial displacement in which the concentration of conducting particles is not conserved, as a result of carrier generation

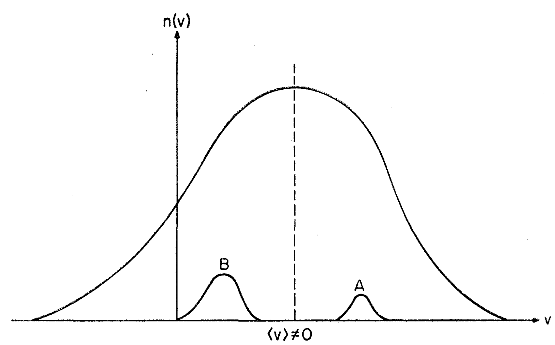

FIG. 2. Asymmetric velocity distribution for a one-dimensional system in the steady state.

recombination and/or diffusion,[13] for example, this one-to-one correspondence is destroyed. Thus, if A represents an initial addition of particles to the distribution, scattering and recombination will both contribute to the decay of the corresponding current displacement. However, if the initial population displacement is B, corresponding to the same initial current displacement, recombination will still tend to reduce the current, whereas scattering will now tend to increase the current deviation. As in the equilibrium case, the fluctuations in any current variable can still be computed from the fluctuations in the distribution function, although the behavior of the distribution function is now influenced by an additional process. However, in order to obtain an adequate description of the system motion in terms of fluctuating current variables, it appears necessary to consider both variables $\dot{q}_i^{(F)}(t)$ and $j^{(F)}(t)$. As specified in Eqs. (34) and (36), the fluctuations in these variables are combined in different ways to describe the linear response $\phi^{(F)}(t)$ and the noise $\langle\Delta J(0)\Delta J(t)\rangle^{(F)}$.

In view of the foregoing discussion and the properties of Eqs. (32) and (33) exhibited by the component variables $\dot{q}(t)$ and $j(t)$, we define the instantaneous displacement $\Delta\dot{q}(t)$ and $\Delta j(t)$ of these variables from their steady-state averages in terms of the corresponding instantaneous displacement $\Delta n(v,t)$ of the velocity distribution as

$$\Delta\dot{q}(t)=\frac{e}{L}\int dv\,(v-\langle v\rangle^{(F)})\Delta n(v,t), \tag{51}$$

and

$$\Delta j(t)=\frac{e}{L}\int dv\,\langle v\rangle^{(F)}\Delta n(v,t)=(e/L)\langle v\rangle^{(F)}\Delta N(t). \tag{52}$$

Since $\Delta n(v,t)$ is the displacement from the steady state of the number of particles having velocity v, $\Delta N(t)=\int dv\,\Delta n(v,t)$ is the corresponding displacement of the total number of particles. For simplicity of notation we have restricted ourselves to a one-dimensional system, where L is the length of the system. In the case of a spatially nonuniform system such as a semiconductor p–n junction, it would probably be necessary to introduce a spatial variable of integration into the definitions (51) and (52). Also, Eqs. (51) and (52) may not constitute complete definitions because the energy considerations governing the decomposition of the current variable, mentioned briefly in Sec. III and discussed again in Sec. VI, have not been introduced. However, it is likely that these definitions are adequate for systems in which the energy is unchanged by the imposition of a steady-state current, i.e., systems obeying a linear Boltzmann equation.

Substitution of Eqs. (51) and (52) into the various correlation moments appearing in Eqs. (34) and (36) for $\phi^{(F)}(t)$ and $\langle\Delta J(0)\Delta J(t)\rangle^{(F)}$ yields

$$\langle\Delta\dot{q}(0)\Delta\dot{q}(t)\rangle^{(F)}=\frac{e^2}{L^2}\int dv\int dv'\,(v-\langle v\rangle^{(F)})(v'-\langle v\rangle^{(F)})\times\langle\Delta n(v,0)\Delta n(v',t)\rangle^{(F)}, \tag{53}$$

$$\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}=\frac{e^2}{L^2}\langle v\rangle^{(F)}\int dv\int dv'\,(v-\langle v\rangle^{(F)})\times\langle\Delta n(v,0)\Delta n(v',t)\rangle^{(F)}, \tag{54}$$

$$\langle\Delta j(0)\Delta j(t)\rangle^{(F)}=(e^2/L^2)[\langle v\rangle^{(F)}]^2\times\langle\Delta N(0)\Delta N(t)\rangle^{(F)}. \tag{55}$$

Equation (53) for $\langle\Delta\dot{q}(0)\Delta\dot{q}(t)\rangle^{(F)}$ is identical in form to the expression for the equilibrium current fluctuation moment, except that here the fluctuations are referred to the nonvanishing average steady-state velocity, and are therefore identified as steady-state thermal fluctuations. The thermal character of these fluctuations will be further illustrated in the following section, when we discuss warm carrier noise.

It is evident that Eq. (55) for $\langle\Delta j(0)\Delta j(t)\rangle^{(F)}$ is an expression for the generation-recombination noise in solids. Consider, for example, a semiconductor in which there exist random thermal fluctuations of charge carriers between the conduction band and an impurity level in the forbidden energy gap. These fluctuations give rise to a random modulation of the conductivity and, consequently, of the current. The instantaneous current fluctuation due to a gross carrier fluctuation of this type is precisely the variable $\Delta j(t)$ defined in Eq. (52), so that Eq. (55) for $\langle\Delta j(0)\Delta j(t)\rangle^{(F)}$ constitutes the resulting generation-recombination noise. Since the fluctuation moment $\langle\Delta j(0)\Delta j(t)\rangle^{(F)}$ does not appear in Eq. (34) for $\phi^{(F)}(t)$, it is clear that generation-recombination noise cannot contribute to the linear response referred to the steady state, in agreement with experimental observation.

Although the origin of the correlation moment $\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}$ of Eq. (54) is less evident, this contribution can be readily shown to vanish in the case of simple generation-recombination noise. Performing the v' integration, Eq. (54) becomes

$$\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}=\frac{e^2}{L^2}\langle v\rangle^{(F)}\int dv\,(v-\langle v\rangle^{(F)})\times\langle\Delta n(v,0)\Delta N(t)\rangle^{(F)}. \tag{56}$$

The generation-recombination process is characteristically much slower than the transitions within the conduction band, so that a displaced thermal equilibrium within the band is always maintained regardless of the instantaneous total number of current-carrying particles present. Thus, we may write

$$\Delta n(v,0)=[n(v)/N]\Delta N(0), \tag{57}$$

[13] M. Lax and P. Mengert, J. Phys. Chem. Solids **14**, 248 (1960). These authors discuss the steady-state noise arising from the simultaneous generation-recombination and diffusion of carriers.

where $n(v)$ and N are the average number of particles with velocity v and the average total number of particles, respectively. Hence, Eq. (56) becomes

$$\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}=(e^2/L^2)\langle v\rangle^{(F)}\frac{\langle\Delta N(0)\Delta N(t)\rangle}{N}\times\int dv\,(v-\langle v\rangle^{(F)})n(v)\equiv 0, \quad (58)$$

and this contribution to the noise vanishes identically.

If the system were spatially nonhomogeneous, however, so that a fluctuation at one point affected the velocity distribution at another, or if the spatial extent of the system were sufficiently limited that the boundaries played an essential role in the random behavior of the system, we might anticipate that the correlation moment $\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}$ would contribute to the noise (and of course to $\phi^{(F)}(t)$ as well). Because of the possible dependence of $\langle\Delta\dot{q}(0)\Delta j(t)\rangle^{(F)}$ on the spatial nonuniformity of the system, together with the characteristic linear current dependence indicated in Eq. (54), we suggest that this contribution to the current fluctuations may be intimately related to the well-known shot noise.

According to the point of view developed in this section, it appears possible that, at least in some cases, valid thermodynamic significance can be attributed to the modified steady-state fluctuation-dissipation theorem. In the case of a semiconductor exhibiting both thermal and generation-recombination noise, for example, each of the noise contributions is clearly distinguishable experimentally in virtue of its characteristic time and current dependence, and consequently is a true macroscopic observable of the steady-state system. By suitable classification of the various noise components into generalizations of previously recognized contributions such as thermal noise, shot noise, and generation-recombination noise, it may prove possible to extend the thermodynamic validity of the formalism to more varied and complicated physical situations.

VI. WARM CARRIER FLUCTUATIONS IN SEMICONDUCTORS

In the previous section we considered a simple model of a steady-state system in which any energy changes brought about by the imposition of a steady-state current were not explicitly taken into account. However, for a general steady-state system, energy considerations, as well as the properties expressed in Eqs. (32) and (33), may be of importance in achieving the correct decomposition of the current operator $J_i^{(F)}(t)$ into the operators $\dot{q}_i^{(F)}(t)$ and $j_i^{(F)}(t)$. This question is examined in Appendix B, where it is proposed that fluctuations in $\dot{q}_i^{(F)}(t)$ can be associated only with that part of the system energy derived from the thermal interaction with the temperature reservoir, while any energy in excess of the true thermal energy must be associated with the variable $j_i^{(F)}(t)$. In order to illustrate this aspect of the steady-state problem, we devote the present section to a brief discussion of warm carriers in semiconductors.

The phenomenon of warm carriers has been intensively studied by numerous investigators, much of the early work being carried out by Shockley,[14] Conwell,[15,16] Ryder,[17,18] and Gunn.[19,20] In a semiconductor such as germanium or silicon, deviations from Ohm's law appear when the applied electric field exceeds that required to produce an electronic drift velocity appreciably greater than the sound velocity in the material. At low applied fields the interaction with the lattice is sufficiently strong that the energy gained from the electric field between collisions with the phonons can be readily dissipated by the lattice. Since the scattering is spherically symmetric, each collision randomizes the electron velocity, and the electrons remain at the temperature of the lattice. This situation is adequately described by the usual linear Boltzmann equation. As the applied field is increased, the scattering still randomizes the velocities, but the energy gained from the field between collisions is so great that it can no longer be as efficiently dissipated in the lattice. Assuming that the electrons interact with acoustical phonons only, the electronic energy thus increases until the rate of energy loss to the lattice becomes equal to the rate of energy gain from the field. This energy balance condition gives rise to a steady-state current proportional to the square root of the applied field, and the electron distribution can be roughly characterized by a "temperature" directly proportional to the applied field. As the field is further increased to the point where the considerably stronger interaction with the optical phonons becomes possible, the current saturates, and its voltage dependence disappears.

For the purpose of this discussion, we assume that the electron population of conduction band states in the intermediate range of acoustical phonon scattering can be described by a Boltzmann distribution at the excited temperature T', the total number of electrons in the conduction band being independent of T'. The problem of determining the true steady-state electronic distribution is an extremely difficult one, and the assumption of equilibrium statistics represents only a rough approximation. Further, we will neglect the slight displacement of the distribution in the direction of the steady-state current. Price[21] has examined the current fluctuations in a system of this type and concludes that

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[15] E. M. Conwell, Phys. Rev. **88**, 1379 (1952).
[16] E. M. Conwell, Phys. Rev. **90**, 769 (1953).
[17] E. J. Ryder and W. Shockley, Phys. Rev. **81**, 139 (1951).
[18] E. J. Ryder, Phys. Rev. **90**, 766 (1953).
[19] J. B. Gunn, J. Electronics **2**, 87 (1956).
[20] J. B. Gunn, *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1957), Vol. 2, p. 213.
[21] P. J. Price, IBM J. Research and Development **3**, 191 (1959).

an approximate fluctuation-dissipation theorem is valid in the form

$$\phi_{ij}^{(F)}(t) \simeq (1/kT')\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)}\delta_{ij} = (1/kT')\langle(\Delta J_i)^2\rangle^{(F)}e^{-t/\tau'}\delta_{ij}, \quad (59)$$

where the steady-state relaxation time τ' is given in terms of the mean free path l as

$$\tau' = l/v_{T'} = l(m^*/2kT')^{\frac{1}{2}}. \quad (60)$$

The approximate nature of Eq. (59) arises from the uncertainty in the true distribution function, and hence the exact definition of T'. In addition, the current fluctuations in the direction of the applied field are modified slightly by the corresponding displacement of the distribution. The δ_{ij}, where $i,j=x,y,z$, is a consequence of the assumed spherical symmetry of the system.

Whereas Price's steady-state fluctuation-dissipation theorem for the case of warm carriers is characterized by the excited electron temperature T', the general form of the theorem presented in Eq. (34) is characterized by the temperature T of the thermal reservoir with which the system is in contact, in this case the lattice. Neglecting the cross correlation term $\langle \Delta\dot{q}_i(0)\Delta j_j(t)\rangle^{(F)}$ because of the assumed spatial homogeneity of the system, Eq. (34) becomes

$$\phi_{ij}^{(F)}(t) = (1/kT)\langle \Delta\dot{q}_i(0)\Delta\dot{q}_j(t)\rangle^{(F)}\delta_{ij}. \quad (61)$$

We now proceed to show how our interpretation of the variables $\dot{q}_i^{(F)}(t)$ and $j_j^{(F)}(t)$ leads to a resolution of the apparent inconsistency between the two forms of the fluctuation-dissipation theorem given in Eqs. (59) and (61).

For the system of warm electrons considered here it is no longer meaningful to invoke Eqs. (32) and (33) in defining the component variables $\dot{q}_i^{(F)}(t)$ and $j_j^{(F)}(t)$, since there is no steady-state current in the directions transverse to the applied field, and any possible consideration of the relatively small average current along the field direction has been eliminated by the assumption of a spherically symmetric velocity distribution. Further, since the total number of electrons in the conduction band is assumed to be conserved as the electron temperature is raised, no current fluctuations can arise from a true generation-recombination process as in the previous section.

However, we can invoke the energy requirement discussed at the beginning of the present section, and again in Appendix B, by conceptually decomposing the steady-state velocity distribution $n_J(\mathbf{v})$ according to

$$n_J(\mathbf{v}) = n_{\dot{q}}(\mathbf{v}) + n_j(\mathbf{v}), \quad (62)$$

where

$$n_{\dot{q}}(\mathbf{v}) = f n_J(\mathbf{v}), \quad (63)$$

is that fraction f of the total distribution function for which the true thermal energy of the system is conserved and which we therefore associate with the variable $\dot{q}_i^{(F)}$. $n_j(\mathbf{v})$ is that part of $n_J(\mathbf{v})$ which contains the additional energy introduced by the interaction with the applied field. This particular type of decomposition may be justified on the grounds that the electrons are indistinguishable and are all subject to the same scattering mechanism in the steady state. The total distribution function is taken here to be

$$n_J(\mathbf{v}) = A e^{-m^*v^2/2kT'}, \quad (64)$$

where the constant A normalizes $n_J(\mathbf{v})$ to the total number of electrons N. Since the relaxation of the variable $\dot{q}_i^{(F)}(t)$ is assumed to proceed in the same manner as that of the total current $J_i^{(F)}(t)$, Eq. (61) for $\phi_{ij}^{(F)}(t)$ can be written, in analogy to Eq. (59),

$$\phi_{ij}^{(F)}(t) = (1/kT)\langle(\Delta\dot{q}_i)^2\rangle^{(F)}e^{-t/\tau'}\delta_{ij}. \quad (65)$$

According to Eqs. (62), (63), and (64) the steady-state fluctuation moments $\langle(\Delta J_i)^2\rangle^{(F)}$ and $\langle(\Delta\dot{q}_i)^2\rangle^{(F)}$ appearing in Eqs. (59) and (65) are computed to be

$$\langle(\Delta J_i)^2\rangle^{(F)} = \frac{e^2}{L_i^2}\int d\mathbf{v}\, v_i^2 n_J(\mathbf{v}) = \frac{e^2kT'N}{L_i^2m^*}, \quad (66)$$

and

$$\langle(\Delta\dot{q}_i)^2\rangle^{(F)} = \frac{e^2}{L_i^2}\int d\mathbf{v}\, v_i^2 n_{\dot{q}}(\mathbf{v}) = \frac{e^2 f}{L_i^2}\int d\mathbf{v}\, v_i^2 n_J(\mathbf{v}) = f\frac{e^2kT'N}{L_i^2m^*}. \quad (67)$$

But we also require that

$$\langle(\Delta\dot{q}_i)^2\rangle^{(F)} = \frac{2e^2}{3L_i^2m^*}\langle\epsilon_{\dot{q}}\rangle^{(F)} = \frac{e^2kTN}{L_i^2m^*}, \quad (68)$$

where $\langle\epsilon_{\dot{q}}\rangle^{(F)} = \frac{3}{2}NkT$ is the true thermal energy of the system as represented by the $n_{\dot{q}}(\mathbf{v})$ distribution. It follows from Eqs. (67) and (68) that $f=T/T'$, so that Eqs. (66) and (67) can be combined to yield the relationship

$$\langle(\Delta\dot{q}_i)^2\rangle^{(F)} = \frac{T}{T'}\frac{e^2kT'N}{L_i^2m^*} = \frac{T}{T'}\langle(\Delta J_i)^2\rangle^{(F)}. \quad (69)$$

Insertion of this result into Eqs. (59) and (65) for $\phi_{ij}^{(F)}(t)$ shows that these alternate forms of the fluctuation-dissipation theorem are indeed equivalent.

The significance of the foregoing discussion can perhaps be further illuminated if we inquire as to the essential distinction between the equilibrium state and the warm carrier steady state. In the equilibrium state the system gains its energy from interaction with a temperature reservoir, and the distribution function is a consequence of purely statistical considerations. Because dynamical considerations enter the description in no essential way, the equilibrium distribution function is unaffected by the spontaneous fluctuation of particles within it. When the "temperature" of the system is raised relative to that of the reservoir by the

application of an electric field, the system is no longer in statistical equilibrium, and dynamical considerations do enter the problem in an essential way. The function governing the steady-state warm carrier distribution is now very much affected by those fluctuations within it which change the energy of the system, since the "temperature" characterizing the distribution is a measure of the instantaneous system energy. That is, the average steady-state distribution function is itself a function of the particular state in which the system instantaneously finds itself. In view of this distinction. we tentatively postulate that the thermal distribution $n_{\dot{q}}(\mathbf{v})$ includes only those spontaneous fluctuations which do not contribute to fluctuations in the average distribution function and as such is a purely statistical quantity. The nonthermal distribution $n_j(\mathbf{v})$ on the other hand, governs all those fluctuations which do contribute to fluctuations in the steady-state distribution function through fluctuations in the electron "temperature" and is strongly influenced by dynamical considerations. We have not yet succeeded, however, in putting these ideas into suitable analytical form.

VII. DISCUSSION AND CONCLUSIONS

As a final note, it is of interest to consider the steady-state theory of irreversible thermodynamics presented in the foregoing sections in connection with Lax's formulation of the problem.[12] His basic assumption is that the linear term in the response to a step-function applied force (relaxation process) referred to a steady-state operating point can be identified with the average regression of a spontaneous steady-state fluctuation just as in the equilibrium case. (See also reference 3.) Thus, the expectation value $\langle \Delta J_j(t)\rangle_{\{\Delta Q_i(0)\}}^{(F)}$ of the current ΔJ_j at time t conditional on the set of displacements $\{\Delta Q_i(0)\}$ at time zero can be expressed in the form

$$\langle \Delta J_j(t)\rangle_{\{\Delta Q\cdot(0)\}}^{(F)} = \langle \Delta \dot{q}_j(t)\rangle_{\{\Delta Q_i(0)\}}^{(F)} = \sum_k \Delta F_k \Phi_{kj}^{(F)}(t)$$

$$= \sum_{kl} \frac{\partial F_k}{\partial \langle Q_l\rangle^{(F)}} \Delta Q_l \Phi_{kj}^{(F)}(t), \quad (70)$$

where $\Phi_{kj}^{(F)}(t)$ is the macroscopic linear response at time t to a unit step-function voltage $\Delta F_k(t)=1$ for $t<0$, $\Delta F_k(t)=0$ for $t>0$. Lax makes no distinction between the total current variable $\Delta J_j^{(F)}(t)$ and the variable $\Delta \dot{q}_j^{(F)}(t)$, so that they have been assumed equivalent in Eq. (70).

The steady-state fluctuation moment $\langle \Delta Q_i(0)\Delta J_j(t)\rangle^{(F)}$ is obtained from Eq. (70) by multiplying through by $\Delta Q_i(0)$ and averaging over the steady-state distribution of the set $\{\Delta Q_i(0)\}$:

$$\langle \Delta Q_i(0)\Delta J_j(t)\rangle^{(F)} = \langle \Delta Q_i(0)\Delta \dot{q}_j(t)\rangle^{(F)}$$

$$= \sum_{kl} \frac{\partial F_k}{\partial \langle Q_l\rangle^{(F)}} \langle \Delta Q_i \Delta Q_l\rangle^{(F)} \Phi_{kj}^{(F)}(t). \quad (71)$$

Now the aftereffect function $\phi_{kj}^{(F)}(t)$ is simply the time derivative of the relaxation function $\Phi_{kj}^{(F)}(t)$, while $\Delta \dot{q}_i(t) = (d/dt)\Delta Q_i(t)$. [See Eq. (30).] Hence, the time derivative of Eq. (71) is

$$\langle \Delta \dot{q}_i(0)\Delta \dot{q}_j(t)\rangle^{(F)} = \langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)}$$

$$= -\sum_{kl} \frac{\partial F_k}{\partial \langle Q_l\rangle^{(F)}} \langle \Delta Q_i \Delta Q_l\rangle^{(F)} \phi_{kj}^{(F)}(t). \quad (72)$$

In the equilibrium case conventional fluctuation theory[22] requires that

$$\sum_l \frac{\partial F_k}{\partial \langle Q_l\rangle^{(F)}} \langle \Delta Q_i \Delta Q_l\rangle^{(0)} = -\frac{1}{\beta}\delta_{ik}, \quad (73)$$

so that Eq. (72) reduces to

$$\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(0)} = (1/\beta)\phi_{ij}^{(0)}(t), \quad (74)$$

which is just the equilibrium fluctuation-dissipation theorem of Eq. (25).

Since the steady-state system is not in equilibrium, however, Lax suggests that Eq. (73) is no longer in general valid and defines the matrix

$$C_{ik} = -\beta \sum_l \frac{\partial F_k}{\partial \langle Q_l\rangle^{(F)}} \langle \Delta Q_i \Delta Q_l\rangle^{(F)}. \quad (75)$$

Thus, his modified fluctuation-dissipation theorem of Eq. (72) can be written

$$\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)} = (1/\beta)\sum_k C_{ik}\phi_{kj}^{(F)}(t). \quad (76)$$

Lax also assumes microscopic reversibility so that, in the absence of an applied magnetic field,

$$\langle \Delta J_i(0)\Delta J_j(t)\rangle^{(F)} = \langle \Delta J_j(0)\Delta J_i(t)\rangle^{(F)}.$$

Invoking Eq. (76), this yields a modified Onsager reciprocity of the form

$$\sum_k C_{ik}\phi_{kj}^{(F)}(t) = \sum_k \tilde{\phi}_{ik}^{(F)}(t)\tilde{C}_{kj}, \quad (77)$$

where the tilde denotes the transposed matrix. The spectral form of Eqs. (76) and (77) can be readily obtained by taking the appropriate Fourier transforms.

In the first place, we note from Eq. (50) that Lax's assumption of microscopic reversibility is not necessarily justified. Elimination of this assumption would, as he points out, complicate Eq. (77) for the modified Onsager symmetry.

Of greater fundamental significance, however, is the fact that the variable $\Delta \dot{q}_i(t)$ is not in general equivalent to the current variable $\Delta J_i(t)$ in a steady-state system. Hence, according to our point of view, the correct form of Lax's modified fluctuation-dissipation theorem, assuming the validity of identifying the relaxation function with the average regression of a steady-state

[22] R. F. Greene and H. B. Callen, Phys. Rev. 83, 1231 (1951).

fluctuation according to Eq. (70), would be

$$\langle \Delta\dot{q}_i(0)\Delta J_j(t)\rangle^{(F)} = (1/\beta)\sum_k C_{ik}\phi_{kj}^{(F)}(t). \qquad (78)$$

Comparison with Eq. (29) for $\phi_{kj}^{(F)}(t)$ would then require that even in the steady state

$$C_{ik} = -\beta\sum_l \frac{\partial F_k}{\partial\langle Q_l\rangle^{(F)}}\langle \Delta Q_i\Delta Q_l\rangle^{(F)} = \delta_{ik}, \qquad (79)$$

which is identical to the equilibrium expression of Eq. (73). Thus, any modification introduced by the presence of a steady-state current would be shifted from Lax's C_{ik} to a distinction between the fluctuation moments $\langle\Delta\dot{q}_i(0)\Delta J_j(t)\rangle^{(F)}$ and $\langle\Delta J_i(0)\Delta J_j(t)\rangle^{(F)}$ and the current variables $\Delta\dot{q}(t)$ and $\Delta J(t)$ from which they are constructed. It is by no means evident that these two forms of the steady-state fluctuation-dissipation theorem are equivalent.

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APPENDIX A

In this Appendix we consider in detail the distinction, mentioned in Sec. II, between a closed and open thermodynamic system. This distinction can be most simply illustrated using the first-order term $\langle J_i\rangle^{(1)}$ in the steady-state current, which is given according to Eqs. (2), (18), and (19) by

$$\langle J_i\rangle^{(1} = \frac{1}{i\hbar}\sum_i F_j\int_{-\infty}^{0} dt_1\,\langle[Q_j^{(0)}(t_1),J_i(0)]_-\rangle^{(0)}$$
$$= -\frac{1}{i\hbar}\sum_i F_j\int_{-\infty}^{0} dt_1\,\langle[J_j^{(0)}(t_1),Q_i^{(0)}(0)]_-\rangle^{(0)}. \qquad (A1)$$

In the last step we have transferred the time derivative from $Q_i^{(0)}(0)$ to $Q_j^{(0)}(t_1)$. Performing the indicated time integration, Eq. (A1) becomes

$$\langle J_i\rangle^{(1)} = \lim_{t_1\to-\infty}\frac{1}{i\hbar}\sum_i F_j\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(0)]_-\rangle^{(0)}, \qquad (A2)$$

the contribution from the $t_1=0$ limit vanishing because $[Q_i^{(0)}(0),Q_j^{(0)}(0)]_-=0$.

For a closed thermodynamic system the $t_1\to-\infty$ limit appearing in Eq. (A2) can be evaluated by computing the steady-state current directly from the density operator ρ corresponding to a system in perturbed canonical equilibrium with the constant forces F_j.

$$\rho = \exp[-\beta(H^{(0)}+\textstyle\sum_j F_jQ_j^{(0)})]/\operatorname{Tr}\exp[-\beta(H^{(0)}+\textstyle\sum_j F_jQ_j^{(0)})]. \qquad (A3)$$

Thus,

$$\langle J_i\rangle^{(F)} = \operatorname{Tr}\rho J_i^{(0)} = \operatorname{Tr}J_i^{(0)}\exp[-\beta(H^{(0)}+\textstyle\sum_j F_jQ_j^{(0)})]/\operatorname{Tr}\exp[-\beta(H^{(0)}+\textstyle\sum_j F_jQ_j^{(0)})]. \qquad (A4)$$

The first-order term in the well-known expansion of Eq. (A4) can be written[10]

$$\langle J_i\rangle^{(1)} = -(1/i\hbar)\textstyle\sum_j F_j\langle[Q_j^{(0)}(0),Q_i^{(0)}(0)]_-\rangle + \beta\textstyle\sum_j F_j\langle Q_j\rangle^{(0)}\langle J_i\rangle^{(0)}$$
$$= \beta\textstyle\sum_j F_j\langle Q_j\rangle^{(0)}\langle J_i\rangle^{(0)}. \qquad (A5)$$

Comparison of Eqs. (A2) and (A5) for $\langle J_i\rangle^{(1)}$ yields

$$\lim_{t_1\to-\infty}\frac{1}{i\hbar}\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(0)]_-\rangle^{(0)} = \beta\textstyle\sum_j F_j\langle Q_j\rangle^{(0)}\langle J_i\rangle^{(0)}. \qquad (A6)$$

Since the equilibrium current $\langle J_i\rangle^{(0)}=0$ by definition, the first-order steady-state current also vanishes. Similar considerations apply to the higher-order terms.

In the case of an open system, capable of supporting nonvanishing steady-state currents, it is no longer possible to invoke the expansion of Eq. (A4) for the steady-state current in interpreting the $t_1\to-\infty$ limit appearing in Eq. (A2) because the density operator (A3) is only valid for a system in canonical equilibrium with the applied forces F_j. In order to perform the integral appearing in Eq. (A1) directly, it is convenient to rewrite the integrand as a summation over matrix elements in the unperturbed energy representation

$$\langle J_i\rangle^{(1)} = -\frac{1}{i\hbar}\sum_i F_j\int_{\infty}^{0} dt\sum_{lm}\frac{e^{-\beta\epsilon_l}-e^{-\beta\epsilon_m}}{\operatorname{Tr}e^{-\beta H^{(0)}}}\times\langle l|J_j|m\rangle\langle m|Q_i|l\rangle e^{i(\epsilon_l-\epsilon_m)t/\hbar}, \qquad (A7)$$

where $\langle l|J_j|m\rangle$ is the matrix element of $J_j^{(0)}$ between the eigenstates ψ_l and ψ_m of $H^{(0)}$ having the energy eigenvalues ϵ_l and ϵ_m, respectively.

The time integral appearing in Eq. (A7) can be performed using the well-known asymptotic formula

$$\lim_{T\to-\infty}\int_T^0 dt\,e^{i(\epsilon_l-\epsilon_m)/\hbar} = \pi\hbar\delta(\epsilon_l-\epsilon_m) - i\hbar P\left(\frac{1}{\epsilon_l-\epsilon_m}\right), \qquad (A8)$$

where P denotes a Cauchy principal value. In general, the application of this formula to integrals such as that of Eq. (A7) requires that all quantities appearing in the integrand be smoothly varying functions of the quantum numbers l and m. This property in turn is intimately associated with the mechanism responsible for the irreversibility of the process[23] and is usually demon-

[23] L. van Hove, Physica 21, 517 (1955).

strated on the basis of some particular model.[24,25] We assume that Eq. (A8) can be legitimately applied to Eq. (A7), which yields

$$\langle J_i\rangle^{(1)}=\pi\hbar\beta\sum_j F_j\sum_{lm}\frac{e^{-\beta\epsilon_l}}{\mathrm{Tr}e^{-\beta H^{(0)}}}\langle l|J_j|m\rangle\langle m|J_i|l\rangle$$
$$\times\delta(\epsilon_l-\epsilon_m)+\sum_j F_j\sum_{lm}\frac{e^{-\beta\epsilon_l}}{\mathrm{Tr}e^{-\beta H^{(0)}}}P\left(\frac{1}{\epsilon_l-\epsilon_m}\right)$$
$$\times(\langle l|J_j|m\rangle\langle m|Q_i|l\rangle+\langle l|Q_i|m\rangle\langle m|J_j|l\rangle). \quad \text{(A9)}$$

In deriving Eq. (A9) we have made use in the δ-function term of the fact that

$$\langle m|Q_i|l\rangle=-i\hbar\langle m|J_i|l\rangle/(\epsilon_m-\epsilon_l)$$

and noted that

$$\lim_{\epsilon_l\to\epsilon_m}\frac{e^{-\beta\epsilon_l}-e^{-\beta\epsilon_m}}{\epsilon_m-\epsilon_l}=\beta e^{-\beta\epsilon_l}.$$

From Eq. (A9) it is seen that the existence of a nonvanishing steady-state current depends essentially upon the existence of nonvanishing matrix elements $\langle l|J_i|m\rangle$ for which ϵ_l is in the neighborhood of ϵ_m (note that the principal value contribution vanishes, at least for the case $i=j$). In order to achieve nonvanishing current matrix elements it is customary to impose periodic boundary conditions on the system. This is most simply illustrated by considering a free electron enclosed in a one-dimensional box of length L. A closed system is characterized by wave functions $\psi_k=(2/L)^{\frac{1}{2}}\sin(kx/2)$, which vanish at $x=0$, L. Thus, $\langle k|J|k'\rangle=0$, so that $\langle J\rangle^{(1)}=0$ for our closed system. On the other hand, an open system is characterized by periodic boundary conditions at $x=0$, L and consequently the wave functions $\psi_k=(1/L)^{\frac{1}{2}}e^{ikx}$. Thus, $\langle k|J|k'\rangle=(e\hbar k/mL)\delta_{kk'}$, so that $\langle J\rangle^{(1)}\neq0$ for our open system (actually, the conductivity is infinite for the case of plane waves or Bloch waves).

Similar considerations apply to more complicated systems, except that the dissipation mechanism limits the conductivity to a finite value. For the case of periodic boundary conditions the wave functions can be expanded according to $\psi_l=\sum_k a_l(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}$. Although the diagonal matrix elements $\langle l|J_i|m\rangle$ must vanish for a dissipative system, there will nevertheless be nonvanishing off-diagonal matrix elements $\langle l|J_i|m\rangle$ for which $\epsilon_l\sim\epsilon_m$.

APPENDIX B

In order to show the relationship between the imposition of time stationarity on a steady-state system in Sec. III and the Joule heating, we consider here the energy of such a system. Neglecting the interaction energy with the driving system, the zero-order term in the energy of the driven system is simply $\langle H^{(0)}\rangle^{(0)}$, while the first-order term vanishes. The second-order energy at time t is, according to Eqs. (2), (18), and (19) for a driven steady-state system,

$$\langle H(t)\rangle^{(2)}=\left(\frac{1}{i\hbar}\right)^2\sum_{ij}F_iF_j\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2$$
$$\times\langle[Q_i^{(0)}(t_2),[Q_j^{(0)}(t_1),H^{(0)}]_-]_-\rangle^{(0)}. \quad \text{(B1)}$$

We identify $(1/i\hbar)[Q_j^{(0)}(t_1),H^{(0)}]_-=J_j^{(0)}(t_1)$, so that Eq. (B1) becomes

$$\langle H(t)\rangle^{(2)}=\frac{1}{i\hbar}\sum_{ij}F_iF_j\int_{-\infty}^{t}dt_1\int_{-\infty}^{t_1}dt_2$$
$$\times\langle[Q_i^{(0)}(t_2),J_j^{(0)}(t_1)]_-\rangle^{(0)}. \quad \text{(B2)}$$

However, according to Eqs. (2), (18), and (19),

$$\frac{1}{i\hbar}\sum_i F_i\int_{-\infty}^{t_1}dt_2\,\langle[Q_i^{(0)}(t_2),J_j^{(0)}(t_1)]_-\rangle^{(0)}$$
$$=\langle J_j(t_1)\rangle^{(1)}. \quad \text{(B3)}$$

Hence,

$$\langle H(t)\rangle^{(2)}=\sum_j F_j\int_{-\infty}^{t}dt_1\,\langle J_j(t_1)\rangle^{(1)}. \quad \text{(B4)}$$

Since we have not explicitly included the interaction with the temperature reservoir, Eq. (B4) represents the second-order Joule heat generated in the system. If we evaluate the quantity $\langle J_j(t_1)\rangle^{(1)}$ for any current-carrying system and then perform the indicated time integration, it is clear that the resulting Joule heat is infinite.

However, we can also rewrite Eq. (B2) for $\langle H(t)\rangle^{(2)}$ by interchanging the order of integration.

$$\langle H(t)\rangle^{(2)}=\frac{1}{i\hbar}\sum_{ij}F_iF_j\int_{-\infty}^{t}dt_2\int_{t_2}^{t}dt_1$$
$$\times\langle[Q_i^{(0)}(t_2),J_j^{(0)}(t_1)]_-\rangle^{(0)}. \quad \text{(B5)}$$

Performing the t_1 integration and noting that

$$[Q_i^{(0)}(t_2),Q_j^{(0)}(t_2)]_-=0,$$

this becomes

$$\langle H(t)\rangle^{(2)}=\frac{1}{i\hbar}\sum_{ij}F_iF_j\int_{-\infty}^{t}dt_2\,\langle[Q_i^{(0)}(t_2),Q_j^{(0)}(t)]_-\rangle^{(0)}$$
$$=\sum_j F_j\langle Q_j(t)\rangle^{(1)}. \quad \text{(B6)}$$

If the cumulative effect of the Joule heating is retained in the system, $\langle Q_j(t)\rangle^{(1)}$ will grow indefinitely, and a true steady state will never be achieved. However, the requirement of time stationarity imposed in Sec. III yields a time dependence for the steady-state operator of the form given in Eq. (18). Thus, Eq. (B6) becomes

$$\langle H(t)\rangle^{(2)}=\sum_j F_j\langle Q_j\rangle^{(1)}, \quad \text{(B7)}$$

[24] W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).
[25] P. N. Argyres, Phys. Rev. **117**, 315 (1960).

which is independent of time and therefore characteristic of the true steady state. Similar considerations apply to the higher-order terms in the steady-state energy.

In a system driven in the steady state by the application of a set of external forces, there are in general two distinct contributions to the energy

$$\langle H\rangle^{(F)}=\sum_j F_j\langle Q_j\rangle^{(F)}+\langle H\rangle^{(0)}. \quad \text{(B8)}$$

One energy contribution is purely thermal in origin and would be present even if the system were closed, so that no steady-state currents could flow. In the electrical case, for example, such a change in energy might arise from a piling up of the charges at one end of the sample or a polarization of the atoms making up the system. However, the system would still be in canonical equilibrium at the temperature of the thermal reservoir. This thermal energy must be associated with the variable $\dot{q}_i^{(F)}$, since the current $j_i^{(F)}$ would not exist in the closed system. The second-energy contribution is purely dynamic in origin and can exist only in an open system. It would be determined, as in the warm carrier example discussed in Sec. VI, by the requirement that the rate of energy absorption from the applied forces equal the rate of energy dissipation into the thermal reservoir. This energy contribution must be regarded as residing in that part of the system characterized by the variable $j_i^{(F)}$, since this is the only respect in which the steady-state system formally differs from the perturbed equilibrium system.

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Remarks on the Electromagnetic Interactions of Massless Particles*

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A result recently obtained by Case and Gasiorowicz, that a massless particle of spin $s>\frac{1}{2}$ cannot have the usual type of coupling to the electromagnetic field, is examined from a point of view different from that taken by those authors. It is shown that such a particle may, in fact, have derivative couplings of order $2s+1$ or $2s-1$ with the electromagnetic field for s an integer or half-integer, respectively. These couplings cannot be generated by the usual requirement that the equations of motion be invariant under phase transformations, nor can they be present for dimensional reasons in a theory which contains no mass (or characteristic length), these conditions leading to the stated result. However, there is no reason in principle to expect such couplings to be absent if the massless particle interacts also with a charged massive field. An example is given for $s=1$, and the cross section for Coulomb scattering of a massless particle is given for arbitrary s.

I. INTRODUCTION

In a recent paper,[1] Case and Gasiorowicz showed that a massless particle of spin $s\geqslant 1$ cannot be charged in the usual sense. Their procedure was as follows. The field operator for a free massless particle of integer spin s may be represented by a symmetric traceless tensor $\phi_{\alpha\beta\cdots\sigma}(x)$ of rank s which satisfies the Klein-Gordon equation

$$\Box\phi_{\alpha\beta\cdots\sigma}(x)=0. \quad (1)$$

In addition, to insure that the field transforms according to the appropriate irreducible representation O_s of the inhomogeneous Lorentz group,[2] it is necessary that $\phi_{\alpha\beta\cdots\sigma}(x)$ satisfy the divergence condition

$$\partial_\alpha\phi_{\alpha\beta\cdots\sigma}(x)=0 \quad (2)$$

and a generalized gauge condition of the second kind.[1] The conventional (minimal) electromagnetic coupling for the particle may be generated by requiring that the equations of motion be invariant under the simultaneous coordinate-dependent transformations

$$\phi_{\alpha\beta\cdots\sigma}(x)\to e^{ie\chi(x)}\phi_{\alpha\beta\cdots\sigma}(x),$$
$$A_\mu(x)\to A_\mu(x)+\partial_\mu\chi(x),\quad \Box\chi=0. \quad (3)$$

Equation (1) is then replaced by the familiar result

$$[\partial_\mu-ieA_\mu(x)]^2\phi_{\alpha\beta\cdots\sigma}(x)=0. \quad (4)$$

Upon rewriting this equation in the form

$$\Box\phi_{\alpha\beta\cdots\sigma}=-j_{\alpha\beta\cdots\sigma}, \quad (4')$$

one can construct the formal retarded solution for $\phi_{\alpha\beta\cdots\sigma}$,

$$\phi_{\alpha\beta\cdots\sigma}(x)=\phi_{\alpha\beta\cdots\sigma}^{\text{in}}(x)+\int dx'\, D_R(x-x')\,j_{\alpha\beta\cdots\sigma}(x'), \quad (5)$$

where $D_R(x-x')$ is the retarded Green's function for zero mass, and $\phi_{\alpha\beta\cdots\sigma}^{\text{in}}(x)$ is the asymptotic (free) in-

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[1] K. M. Case and S. G. Gasiorowicz, Phys. Rev. **125**, 1055 (1962).

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