crystals, no such splitting could be detected. If present, the splitting must not be greater than 5 cm^{-1} in the trichlorobenzene and hexachlorobenzene and 3 cm^{-1} in the durene crystal. In the case of the hexachlorobenzene crystal, the energy of separation between the two $K=0$ levels in the exciton band has been calculated to be 0.7 cm^{-1}.

Thus it appears that at least one of the low-lying excited electronic states of the pyrene crystal has the nature of exciton states, though in the case of the 1,3,5-trichlorobenzene, hexachlorobenzene, and durene crystals any such conclusion would be too hasty in view of the paucity of experimental data.

Photoconductivity of organic crystals (Sec. 6).—In a recent paper[125] Northrop and Simpson have published values of photocurrents of pure hydrocarbon crystals. They observed that the impurity molecules embedded in pure crystals which quench the fluorescence of pure substance reduce the photocurrent in the same ratio. Their other observations regarding dependence of photocurrent with light intensity, applied voltage, etc., are in agreement with previous publications. From these observations they propose that the interaction of two excitons is required to produce a single ionized molecule. Thus the production of charge carriers is explained. Compton *et al.*[126] studied photocurrent of anthracene crystals before and after neutron bombardment and concluded that conductivity was greatly reduced on bombardment. They further observed that dependence of photocurrent on wavelength and intensity of incident light remained unaltered after bombardment. Before bombardment the photocurrent was markedly non-ohmic, after bombardment it was ohmic up to a field of 25 000 volts cm^{-1}. Before neutron bombardment the sample shows change of photocurrent when polarity of electrode is reversed, but this asymmetry disappears after irradiation. Kommandeur and Schneider[127] studied the photoconductivity in greater detail with very pure specimens of anthracene crystals and obtained results very different from previous ones. They observed that the maximum value of photocurrent corresponds to the minima of the absorption spectra. They also observed that the intensity dependence of photocurrent changes with wavelength, field direction, and even with magnitude of the applied field. These authors finally concluded that spectral response, voltage, and intensity dependence of photocurrent depend on the source and treatment of the crystals used, i.e., it depends on the density of imperfections of the crystals.

9. ACKNOWLEDGMENTS

We take this opportunity to express our sincere thanks to the Government of West Bengal for kindly extending a research grant to one of us (S.C.G.).

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Irreversible Thermodynamics of Nonlinear Processes and Noise in Driven Systems*

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1. INTRODUCTION

THIS paper reviews and extends the theory of irreversible thermodynamics. The irreversible behavior of a system driven by externally applied forces has been studied extensively, but attention has been focused primarily on the first-order term in the driven response. Here we also consider the higher-order terms in the driven response and the random fluctuations, or noise, occurring during an irreversible process. In addition to the well-known relations between the linear response and the equilibrium fluctuations, several new relations are proved involving the nonlinear response, the driven noise, and the equilibrium fluctuations.

The method of analysis is statistical mechanical and general, neither assuming a specific model nor postulating Markoffian behavior. The purposes of the analysis are thermodynamic; that is, to investigate interrelationships among macroscopically observable characteristics of systems undergoing irreversible processes. In this sense the aim should be clearly differentiated from those other approaches which might be characterized as kinetic or statistical mechanical rather than thermodynamic.

The most direct approach to the problem of irreversibility is the kinetic approach, in which a specific model is immediately introduced. The essential features of the model may be expressed in terms of molecular collision probabilities, giving rise to the Boltzmann equation, or to some similarly detailed kinetic equation. This is the standard method of "transport theory," and it is the method characteristic of the theory of the solid state.

A considerably more general approach is one which we term the irreversible statistical mechanical approach. The purpose there is to develop a general formalism, analogous to the partition sum algorithm of equilibrium statistical mechanics, which would provide a systematic recipe for the calculation of any macroscopically ob-

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servable characteristic of a system undergoing an irreversible process. No specific model is invoked; the aim is rather to provide a general formalism into which any particular model could be substituted to obtain explicit results. The irreversible statistical mechanical approach has not been completely successful as yet, but one type of partial result has been exploited widely. In this type of result the driven response of a system is obtained as a perturbation expansion in the applied forces. The various order response terms are typically expectation values of (multiple) commutators, taken with respect to the equilibrium system. It is, of course, hoped that a general algorithm for the computation of equilibrium commutator forms then will be developed to complete the general formalism.

The third approach is the thermodynamic approach which we adopt here. Although the statistical mechanical formalism is used to describe the motion, our purpose is not to compute either the response functions or the value of any quantities characterizing the equilibrium system. Our purpose is rather to explore the general interrelationships among different types of response functions and the equilibrium fluctuations, insisting, however, that the quantities so related each be macroscopically observable. Thus, for example, the equilibrium commutator forms in terms of which statistical mechanics expresses various response functions are not true observables of the equilibrium system. In order to give thermodynamic significance to statistical mechanical results, it is therefore necessary to re-express such quantities in terms of macroscopically observable symmetrized equilibrium forms, or anticommutators.

Three general classes of irreversible thermodynamic results have previously been obtained for first-order processes: (a) relationships between off-diagonal elements of the admittance—these are the Onsager reciprocity,[1,2] and its extension to non-Markoffian systems[3]; (b) the relationship between the first-order response and the second correlation moments of the equilibrium fluctuations—this is the so-called fluctuation-dissipation theorem[4,5]; (c) the relationship between the path distribution function for a driven system and the equilibrium fluctuations.[6–8]

The extensions of the theory which are developed here, and the general structure of irreversible thermodynamics, are summarized in the diagram in Fig. 1. The quantities appearing at the vertices of the diagrams denote the macroscopic observables, while the connecting lines indicate the existence of thermodynamic relationships. The arrowheads refer to the direction in

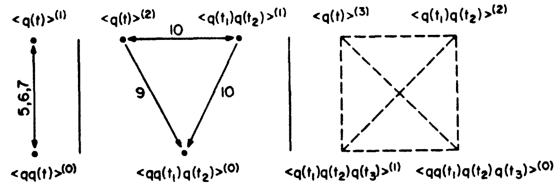

Fig. 1.

which specific relationships are developed in this paper, the numbers along the lines indicating the sections in which the various proofs appear.

The nature of the observables of interest can be made clear by the following considerations. Let $\langle q(t)\rangle$ denote the expectation value of the variable q at time t in a system driven by externally applied forces; that is, the driven response of the variable q. Further, let $\langle q(t)\rangle$ be expanded in powers of the applied forces. Then we label the first-order term in the response $\langle q(t)\rangle^{(1)}$, the second-order term $\langle q(t)\rangle^{(2)}$, etc. The zeroth-order term $\langle q(t)\rangle^{(0)} = \langle q\rangle^{(0)}$ is simply the average value of q in the equilibrium system. We similarly obtain a more detailed description of the driven system by introducing the expectation value $\langle q(t_1)q(t_2)\rangle$ of the product of the variable q at time t_1 with its value at time t_2; this is the second correlation moment of the random fluctuations, or noise, in the driven system. Again it is possible to expand $\langle q(t_1)q(t_2)\rangle$ in powers of the applied forces. We label the first-order term in the driven noise $\langle q(t_1)q(t_2)\rangle^{(1)}$, the second-order term $\langle q(t_1)q(t_2)\rangle^{(2)}$, and so on. The zeroth-order term $\langle q(t_1)q(t_2)\rangle^{(0)} = \langle qq(t_2-t_1)\rangle^{(0)}$ characterizes the spontaneous fluctuations in the equilibrium system. Similarly, it is possible to consider third- and high-order driven correlation moments.

There exists a definite hierarchy of irreversible thermodynamic relationships. The left-hand diagram represents the fluctuation-dissipation theorem, between the first-order response $\langle q(t)\rangle^{(1)}$ and the equilibrium second moment $\langle qq(t)\rangle^{(0)}$. The middle diagram indicates the triplet of relationships which exists among the second-order response $\langle q(t)\rangle^{(2)}$, the first-order term $\langle q(t_1)q(t_2)\rangle^{(1)}$ in the driven second moment (noise), and the third moment $\langle qq(t_1)q(t_2)\rangle^{(0)}$ of the spontaneous equilibrium fluctuations. The right-hand diagram indicates the cycle of interrelationships which may be presumed to exist among the next appropriate group of observables, although we do not consider this case explicitly.

In Secs. 2 to 4 the general statistical mechanical description of the time-evolution of a driven system is briefly reviewed. Sections 5 to 8 are devoted to a review of the existing first-order theory of irreversible thermodynamics. In Secs. 9 to 14 the general theory of irreversible thermodynamics is extended to the second-order response and the driven noise. Sections 13 and 14 are devoted to the irreversible thermodynamics of step-driven processes. In Secs. 15 and 16 the question of path distribution functions is considered, which may be regarded as the fundamental quantities of irreversible

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thermodynamics in the sense that all macroscopic quantities are derivable therefrom.

2. THE TIME EVOLUTION OF DRIVEN OPERATORS

We consider a system, of which the unperturbed Hamiltonian is $H^{(0)}$, in interaction with a number of external driving systems or signal generators. The Hamiltonian of the composite system may typically be represented by

$$H=H^{(0)}+\sum_i F_iQ_i+H_{sg}, \tag{1}$$

where $Q_i=Q_i(q,p)$ is a function of the coordinates q and momenta p of the system of interest, $F_i=F_i(q',p')$ is a function of the coordinates q' and momenta p' of the ith signal generator, and H_{sg} denotes the Hamiltonians of the signal generators.

Whereas the dissipative system possesses a large number of degrees of freedom and a quasi-continuous spectrum of energy eigenvalues, the signal generators have relatively few degrees of freedom and an extremely high degree of excitation. Thus, the coordinates of the signal generators, and consequently the $F_i(q',p')$, are essentially classical functions of the time. Ignoring the term H_{sg} as being irrelevant to the system of interest, the perturbed Hamiltonian assumes the form

$$H=H^{(0)}+\sum_i F_i(t)Q_i. \tag{2}$$

We adopt the interpretation that the Hermitian operators $Q_i(q,p)$ correspond to thermodynamic extensive parameters of the system of interest, while the $F_i(t)$ represent the conjugate intensive parameters imposed upon the system by the various signal generators. Thus, $Q_i(q,p)$ might be the operator corresponding to the position of a movable piston (volume), the total number of particles, or the magnetic moment of the system. The respective imposed intensive parameter would then be the pressure, the electrochemical potential, or the applied magnetic field.

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

$$\langle Q_i(t)\rangle=\text{Trace }\rho^{(0)}Q_i(t), \tag{3}$$

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

$$\rho^{(0)}=\exp[-\beta H^{(0)}]/\text{Tr}\exp[-\beta H^{(0)}],\quad \beta=1/kT, \tag{4}$$

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

$$Q_i(t)=U^\dagger(t)Q_iU(t). \tag{5}$$

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

$$\dot{U}(t)=\frac{1}{i\hbar}H(t)U(t)=\frac{i}{i\hbar}[H^{(0)}+\sum_i F_i(t)Q_i]U(t). \tag{6}$$

The differential equation (6) is equivalent to the integral equation

$$U(t)=\exp\left[-i\frac{H^{(0)}t}{\hbar}\right]\left[1+\frac{1}{i\hbar}\sum_i\int_{-\infty}^t dt_1F_i(t_1)Q_i^{(0)}(t_1)\times\exp\left[i\frac{H^{(0)}t_1}{\hbar}\right]U(t_1)\right] \tag{7}$$

the correctness of which can be verified by differentiation. $Q_i^{(0)}(t)$ represents the unperturbed Heisenberg operator

$$Q_i^{(0)}(t)=\exp\left[i\frac{H^{(0)}t}{\hbar}\right]Q_i\exp\left[-i\frac{H^{(0)}t}{\hbar}\right]. \tag{8}$$

The iterative solution of Eq. (7) is

$$U(t)=\exp\left[-i\frac{H^{(0)}t}{\hbar}\right]\sum_{n=0}^{\infty}\left(-\frac{1}{i\hbar}\right)^n\sum_{ij\cdots k}\int_{-\infty}^t dt_1\times\int_{-\infty}^{t_1}dt_2\cdots\int_{-\infty}^{t_{n-1}}dt_nF_i(t_1)F_j(t_2)\cdots\times F_k(t_n)Q_i^{(0)}(t_1)Q_j^{(0)}(t_2)\cdots Q_k^{(0)}(t_n). \tag{9}$$

The perturbation expansion of $Q_i(t)$ follows from Eqs. (5) and (9). The zeroth-order term is simply the unperturbed operator $Q_i^{(0)}(t)$. The first-order term $Q_i^{(1)}(t)$ is

$$Q_i^{(1)}(t)=-\frac{1}{i\hbar}\sum_i\int_{-\infty}^t dt_1F_j(t_1)[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-. \tag{10}$$

The second-order term $Q_i^{(2)}(t)$ is

$$Q_i^{(2)}(t)=\left(-\frac{1}{i\hbar}\right)^2\sum_{jk}\Bigg\{-\int_{-\infty}^t dt_1F_j(t_1)\times\int_{-\infty}^t dt_2F_k(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)Q_k^{(0)}(t_2)+\int_{-\infty}^t dt_1F_j(t_1)\int_{-\infty}^{t_1}dt_2F_k(t_2)\times[Q_k^{(0)}(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)+Q_i^{(0)}(t)Q_j^{(0)}(t_1)Q_k^{(0)}(t_2)]\Bigg\}. \tag{11}$$

In order to put the second-order term into a more suitable form, we decompose the t_2 integral of the first term, so that

$$\int_{\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t} dt_2F_k(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)Q_k^{(0)}(t_2)$$

$$=\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)Q_k^{(0)}(t_2)$$

$$+\int_{-\infty}^{t} dt_1F_j(t_1)\int_{t_1}^{t} dt_2F_k(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)Q_k^{(0)}(t_2)$$

$$=\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)Q_j^{(0)}(t_1)Q_i^{(0)}(t)Q_k^{(0)}(t_2)$$

$$+\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)Q_k^{(0)}(t_2)\times Q_i^{(0)}(t)Q_j^{(0)}(t_1). \quad (12)$$

In the last step we have inverted the order of integration in the second integral and interchanged the dummy indices i, j and the dummy times t_1, t_2. Using this result, Eq. (11) can be written in the form

$$Q_i^{(2)}(t)=\left(-\frac{1}{i\hbar}\right)^2\sum_{jk}\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)\times[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-]_-. \quad (13)$$

Examination of Eqs. (10) and (13) clearly indicates the general form of the nth-order term $Q_i^{(n)}(t)$ in the driven Heisenberg operator $Q_i(t)$. Thus, for example, the third-order term is

$$Q_i^{(3)}(t)=\left(-\frac{1}{i\hbar}\right)^3\sum_{jkl}\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)\times\int_{-\infty}^{t_2} dt_3F_l(t_3)[Q_l^{(0)}(t_3)\times[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-]_-]_-. \quad (14)$$

This section follows the perturbation formulation given by R. Kubo.[9] However, because we are later concerned with Q operators which are intrinsically time-dependent, we choose to examine the time evolution of $Q_i(t)$ rather than of $\rho(t)$.

3. THE MACROSCOPIC RESPONSE AND DRIVEN CORRELATION MOMENTS

The first-order term in the driven response $\langle Q_i(t)\rangle$ of the thermodynamic variable corresponding to the operator Q_i is

$$\langle Q_i(t)\rangle^{(1)}=\mathrm{Tr}\,\rho^{(0)}Q_i^{(1)}(t)=-\frac{1}{i\hbar}\sum_j\int_{-\infty}^{t} dt_1F_j(t_1)\times\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)} \quad (15)$$

where the bracket $\langle\ \rangle^{(0)}$ denotes an expectation value with respect to the equilibrium ensemble.

Similarly, the second-order term in the response is

$$\langle Q_i(t)\rangle^{(2)}=\left(-\frac{1}{i\hbar}\right)^2\sum_{jk}\int_{-\infty}^{t} dt_1F_j(t_1)\int_{-\infty}^{t_1} dt_2F_k(t_2)\times\langle[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-]_-\rangle^{(0)}. \quad (16)$$

The form of the higher-order terms is clear from Eqs. (15) and (16).

The spontaneous fluctuations in an equilibrium ensemble are characterized by the second correlation moments in time between each pair of variables, although all higher moments are required as well for a complete description. The second equilibrium correlation moment is

$$\Psi_{ij}^{(0)}(t)=\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)} \quad (17)$$

where the bracket $[\ ,\ ]_+$ denotes a symmetrized operator product, or anticommutator.

A driven ensemble also exhibits fluctuations about its average motion, which in general differ from the equilibrium fluctuations. The fluctuations in a driven ensemble are characterized by

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle=\mathrm{Tr}\,\rho^{(0)}\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+. \quad (18)$$

Using the result (10) for $Q_i^{(1)}(t)$, the first-order term $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ in the driven second moment (18) becomes

$$\langle\tfrac{1}{2}[Q_i(t),Q_j(t+\tau)]_+\rangle^{(1)}=\tfrac{1}{2}\langle[Q_i^{(0)}(t),\,Q_j^{(1)}(t+\tau)]_+ +[Q_i^{(1)}(t),\,Q_j^{(0)}(t+\tau)]_+\rangle^{(0)}$$

$$=-\frac{1}{2i\hbar}\sum_k\left\{\int_{-\infty}^{t+\tau} dt_1F_k(t_1)\langle[Q_i^{(0)}(t),\times[Q_k^{(0)}(t_1),\,Q_j^{(0)}(t+\tau)]_-]_+\rangle^{(0)}+\int_{-\infty}^{t} dt_1F_k(t_1)\langle[[Q_k^{(0)}(t_1),Q_i^{(0)}(t)]_-,\times Q_j^{(0)}(t+\tau)]_+\rangle^{(0)}\right\}. \quad (19)$$

Upon decomposition of the first integral according to

$$\int_{-\infty}^{t+\tau} dt_1=\int_{-\infty}^{t} dt_1+\int_{t}^{t+\tau} dt_1,$$

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

Eq. (19) becomes

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$$

$$=-\frac{1}{2i\hbar}\sum_k\Bigg\{\int_{-\infty}^{t}dt_1F_k(t_1)\langle[Q_k^{(0)}(t_1),$$

$$\times[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_-\rangle^{(0)}$$

$$+\int_t^{t+\tau}dt_1F_k(t_1)\langle[Q_i^{(0)}(t),$$

$$\times[Q_k^{(0)}(t_1),\,Q_j^{(0)}(t+\tau)]_-]_+\rangle^{(0)}\Bigg\}. \quad (20)$$

The higher-order terms in the perturbation expansion of the driven second moment can be written in analogous fashion, although the expressions involved become rapidly more complicated. The second-order term is

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(2)}$$

$$=\frac{1}{2}\left(-\frac{1}{i\hbar}\right)^2\sum_{kl}\Bigg\{\int_{-\infty}^{t}dt_1F_k(t_1)\int_{-\infty}^{t_1}dt_2F_l(t_2)$$

$$\times\langle[Q_l^{(0)}(t_2),\,[Q_k^{(0)}(t_1),$$

$$\times[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_-]_-\rangle$$

$$+\int_{-\infty}^{t}dt_1F_k(t_1)\int_t^{t+\tau}dt_2F_l(t_2)$$

$$\times\langle[Q_k^{(0)}(t_1),\,[Q_i^{(0)}(t),$$

$$\times[Q_l^{(0)}(t_2),\,Q_j^{(0)}(t+\tau)]_-]_+]_-\rangle^{(0)}\Bigg\}. \quad (21)$$

The nth-order term in the driven response can be written directly in terms of the $(n-1)$st-order term in the driven commutator $\langle[Q_j(t_1),Q_i(t)]_-\rangle^{(n-1)}$.

$$\langle Q_i(t)\rangle^{(n)}=\frac{1}{n}\left(-\frac{1}{i\hbar}\right)\sum_j\int_{-\infty}^{t}dt_1F_j(t_1)$$

$$\times\langle[Q_j(t_1),Q_i(t)]_-\rangle^{(n-1)}. \quad (22)$$

For $n=1$ this expression is identical to Eq. (15). For $n=2$ it can be obtained directly from Eq. (16) and the commutator analog of Eq. (19). For any order it is a direct consequence of the iterative nature of the perturbation expansion, and furnishes a clear picture of the essential structure of the motion.

4. STEP-DRIVEN PROCESSES

The preceding two sections were concerned with the motion of a driven system for which the forces are arbitrary functions of the time. In order to illustrate the formalism in a simple manner, we also consider step-driven processes in particular.

A step-driven process is defined as one for which the generalized forces in the distant past have increased slowly from zero to some constant value. This constant force remains applied until $t=0$, at which time it is suddenly removed and the system is allowed to relax into its equilibrium configuration. For a step-driven process the first- and second-order responses reduce to

$$\langle Q_i(t)\rangle^{(1)}=-\frac{1}{i\hbar}\sum_i F_j\int_{-\infty}^{0}dt_1\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)}, \quad (23)$$

$$\langle Q_i(t)\rangle^{(2)}=\left(-\frac{1}{i\hbar}\right)^2\sum_{jk}F_jF_k\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2$$

$$\times\langle[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-]_-\rangle^{(0)}. \quad (24)$$

When the indicated time integrations are performed in Eqs. (23) and (24), the contributions from the infinite time limits pose certain difficulties, which are related to the approach to equilibrium. This matter is examined in Appendix A. It is also possible to approach the question of step-driven processes from the following alternate point of view, which circumvents these difficulties. We expect the applied forces F_j to bring the system to a new equilibrium configuration at $t=0$, characterized by a density operator $\rho(0)$ having the generalized canonical form appropriate to an ensemble in contact with a set of reservoirs with constant intensive parameters F_j.

$$\rho(0)=\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}/\mathrm{Tr}\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}. \quad (25)$$

At $t=0$ the interaction with the external systems is removed. Since for $t>0$ the Hamiltonian is simply $H^{(0)}$, the response $\langle Q_i(t)\rangle$ during a step-driven process is given by

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

$$=\mathrm{Tr}\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}Q_i^{(0)}(t)/\mathrm{Tr}\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}. \quad (26)$$

In order to expand Eq. (26), we first perform the well-known expansion of the operator

$$A(\beta)\equiv\exp\{-\beta[H^{(0)}+\epsilon H^{(1)}]\},$$

where $H^{(1)}$ denotes the perturbation Hamiltonian. $A(\beta)$ satisfies the integral equation

$$A(\beta)=\exp[-\beta H^{(0)}]\times\left\{1-\epsilon\int_0^\beta d\lambda\,\exp[\lambda H^{(0)}]H^{(1)}A(\lambda)\right\}, \quad (27)$$

the iterative solution of which is

$$A(\beta)=\exp[-\beta H^{(0)}]\sum_{n=0}^{\infty}(-\epsilon)^n\int_0^{\beta}d\lambda_1 H^{(1)}(-i\hbar\lambda_1)\times\int_0^{\lambda_1}d\lambda_2 H^{(1)}(-i\hbar\lambda_2)\cdots\times\int_0^{\lambda_{n-1}}d\lambda_n H^{(1)}(-i\hbar\lambda_n) \quad (28)$$

where $H^{(1)}(-i\hbar\lambda_1)=\exp[\lambda_1 H^{(0)}]H^{(1)}\exp[-\lambda_1 H^{(0)}]$.

Replacing $\epsilon H^{(1)}$ by the perturbation Hamiltonian $\sum_j F_jQ_j$ in Eq. (28) yields the quantity appearing in the numerator of Eq. (26).

$$\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}=\exp[-\beta H^{(0)}]\sum_{n=0}^{\infty}(-1)^n\sum_{jk\cdots l}F_jF_k\cdots F_l\times\int_0^{\beta}d\lambda_1 Q_j^{(0)}(-i\hbar\lambda_1)\int_0^{\lambda_1}d\lambda_2 Q_k^{(0)}(-i\hbar\lambda_2)\cdots\times\int_0^{\lambda_{n-1}}d\lambda_n Q_l^{(0)}(-i\hbar\lambda_n). \quad (29)$$

The expansion of the denominator of Eq. (26) can be simplified by employing a technique, due to Nakajima,[10] which reduces all multiple temperature integrals by one order. Consider the trace of the operator $A(\beta)$ defined in the foregoing. Differentiating $\mathrm{Tr}\,A(\beta)=\mathrm{Tr}\exp\{-\beta[H^{(0)}+\epsilon H^{(1)}]\}$ with respect to ϵ, we obtain

$$\frac{\partial}{\partial\epsilon}\mathrm{Tr}\,A(\beta)=-\beta\,\mathrm{Tr}\exp\{-\beta[H^{(0)}+\epsilon H^{(1)}]\}H^{(1)}. \quad (30)$$

We now expand the quantity $\exp\{-\beta[H^{(0)}+\epsilon H^{(1)}]\}$ according to Eq. (27), integrate this expression with respect to ϵ, and substitute $\sum_j F_jQ_j$ for $\epsilon H^{(1)}$ to obtain the denominator of Eq. (25).

$$\mathrm{Tr}\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jQ_j]\}=\exp[-\beta H^{(0)}]\left\{1+\beta\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\sum_{j\cdots kl}F_j\cdots F_kF_l\times\int_0^{\beta}d\lambda_1\cdots\int_0^{\lambda_{n-2}}d\lambda_{n-1}Q_j^{(0)}(-i\hbar\lambda_1)\cdots\times Q_k^{(0)}(-i\hbar\lambda_{n-1})Q_l\right\}. \quad (31)$$

[10] S. Nakajima, *Advances in Physics* (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 363.

We now substitute the expansions (29) and (31) into Eq. (26) and collect terms corresponding to each order in the perturbation. The results for the first few orders in the expansion of $Q_i(t)$ are found to be

$$\langle Q_i(t)\rangle^{(1)}=-\sum_j F_j\left[\int_0^{\beta}d\lambda_1\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}-\beta\langle Q_i\rangle^{(0)}\langle Q_j\rangle^{(0)}\right], \quad (32)$$

$$\langle Q_i(t)\rangle^{(2)}=\sum_{jk}F_jF_k\left[\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\langle Q_j^{(0)}(-i\hbar\lambda_1)\times Q_k^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)}-\frac{\beta}{2}\int^{\beta}d\lambda_1\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k\rangle^{(0)}\langle Q_i\rangle^{(0)}\right]+\beta\sum_j F_j\langle Q_j\rangle^{(0)}\langle Q_i(t)\rangle^{(1)}, \quad (33)$$

$$\langle Q_i(t)\rangle^{(3)}=-\sum_{jkl}F_jF_kF_l\left[\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\int_0^{\lambda_2}d\lambda_3\times\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k^{(0)}(-i\hbar\lambda_2)\times Q_l^{(0)}(-i\hbar\lambda_3)Q_i^{(0)}(t)\rangle^{(0)}-\frac{\beta}{3}\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\times\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k^{(0)}(-i\hbar\lambda_2)Q_l\rangle^{(0)}\langle Q_i\rangle^{(0)}\right]+\beta\sum_j F_j\langle Q_j\rangle^{(0)}\langle Q_i(t)\rangle^{(2)}-\frac{\beta}{2}\sum_{jk}F_jF_k\times\int_0^{\beta}d\lambda_1\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k\rangle^{(0)}\langle Q_i(t)\rangle^{(1)}. \quad (34)$$

The classical forms of the foregoing equations are easily obtained and constitute a series of thermodynamic relationships. Letting $q_j(t)$ denote the time-dependent classical variable corresponding to the Heisenberg operator $Q_j(t)$ and replacing traces by integrals $\int d\Gamma$ over phase space, the classical step-driven response is, from Eq. (26),

$$\langle q_i(t)\rangle=\int d\Gamma\rho(t)q_i=\int d\Gamma\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jq_j]\}q_i(t)\Big/\times\int d\Gamma\exp\{-\beta[H^{(0)}+\textstyle\sum_j F_jq_j]\} \quad (35)$$

or

$$\langle q_i(t)\rangle = \langle \exp(-\beta \sum_j F_j q_j) q_i(t)\rangle^{(0)} / \times \langle \exp(-\beta \sum_j F_j q_j)\rangle^{(0)}. \quad (36)$$

Since all quantities appearing in Eq. (36) are now classical functions, the perturbation expansion can be carried out in a straightforward way. Thus, the first few order terms in the classical step-driven response $\langle q_i(t)\rangle$ are

$$\langle q_i(t)\rangle^{(1)} = -\beta \sum_j F_j[\langle q_j q_i(t)\rangle^{(0)} - \langle q_i\rangle^{(0)}\langle q_j\rangle^{(0)}], \quad (37)$$

$$\langle q_i(t)\rangle^{(2)} = \tfrac{1}{2}\beta^2 \sum_{jk} F_j F_k[\langle q_j q_k q_i(t)\rangle^{(0)} - \langle q_j q_k\rangle^{(0)}\langle q_i\rangle^{(0)}] + \beta \sum_j F_j \langle q_j\rangle^{(0)}\langle q_i(t)\rangle^{(1)}, \quad (38)$$

$$\langle q_i(t)\rangle^{(3)} = -\tfrac{1}{6}\beta^3 \sum_{jkl} F_j F_k F_l[\langle q_j q_k q_l q_i(t)\rangle^{(0)} - \langle q_j q_k q_l\rangle^{(0)}\langle q_i\rangle^{(0)}] - \tfrac{1}{2}\beta^2 \sum_{jk} F_j F_k \langle q_j q_k\rangle^{(0)}\langle q_i(t)\rangle^{(1)} + \beta \sum_j F_j \langle q_j\rangle^{(0)}\langle q_i(t)\rangle^{(2)}. \quad (39)$$

Equation (36) is the first truly thermodynamic relationship we have developed up to this point. It expresses the step-driven response $\langle q_i(t)\rangle$ in terms of the quantity $\langle \exp(-\beta \sum_j F_j q_j) q_i(t)\rangle^{(0)}$, which characterizes the spontaneous equilibrium fluctuations in an operationally significant way. In particular,

$$\langle \exp(-\beta \sum_j (F_j q_j) q_i(t)\rangle^{(0)}$$

represents the second equilibrium correlation moment between the quantity $\exp(-\beta \sum_j F_j q_j)$ at time zero and the quantity q_i at time t.

The first-order term (37) in the expansion of Eq. (36) will be recognized as a classical form of the so-called fluctuation-dissipation theorem,[4] which relates the first-order response $\langle q_i(t)\rangle^{(1)}$ to the equilibrium second correlation moment $\langle q_j q_i(t)\rangle^{(0)}$ between the variables q_j and $q_i(t)$. We discuss the quantum-mechanical form of the fluctuation-dissipation theorem in the following three sections, considering the step-driven case specifically in Sec. 7.

Similarly, Eqs. (38), (39), etc., relate the second- and higher-order terms in the classical step-driven response $\langle q_i(t)\rangle$ to appropriate higher equilibrium fluctuation moments. The quantum-mechanical form of these relationships is presented in Sec. 13.

5. EQUILIBRIUM FLUCTUATIONS AND THE FIRST-ORDER RESPONSE

The linear theory of irreversibility is reviewed in this and the two following sections, following quite closely the formulation of R. Kubo.[9] The pattern of this development suggests the method of extension to nonlinear processes, and yields a relation between commutators and anticommutators to which we make frequent reference.

It is convenient to characterize the first-order response by the aftereffect function $\phi_{ij}^{(1)}(t)$, which is the response $\langle Q_j(t)\rangle^{(1)}$ to a δ-function force F_i applied at $t=0$. That is, by definition,

$$\langle Q_j(t)\rangle^{(1)} = \sum_i \int_{-\infty}^{t} dt_1 F_i(t_1)\phi_{ij}^{(1)}(t-t_1). \quad (40)$$

Thus, writing the equilibrium commutator in Eq. (15) in the equivalent form $\langle [Q_i, Q_j^{(0)}(t-t_1)]_-\rangle^{(0)}$, we identify

$$\phi_{ij}^{(1)}(t) = -\frac{1}{i\hbar}\langle [Q_i, Q_j^{(0)}(t)]_-\rangle^{(0)}. \quad (41)$$

The aftereffect function $\phi_{ij}^{(1)}(t)$ exhibits significant symmetry properties with respect to reversal of the time t and of an applied magnetic vector potential $\mathbf{A}$. The classical quantities q_i are assumed to be even functions of the particle velocities; explicitly indicating the dependence on $\mathbf{A}$, the operators $Q_i(\mathbf{A})$ then satisfy the relationship

$$Q_i(-\mathbf{A}) = Q_i^*(\mathbf{A}). \quad (42)$$

The unperturbed Hamiltonian $H^{(0)}(\mathbf{A})$ and its eigenfunctions also satisfy Eq. (42).

Because the response $\langle Q_j(t)\rangle^{(1)}$ must itself be real, it follows that $\phi_{ij}^{(1)}(t)$ is real.

A second property of $\phi_{ij}^{(1)}(t)$ is

$$\phi_{ij}^{(1)}(-t) = -\phi_{ji}^{(1)}(t). \quad (43)$$

Introducing the transformation $t \to -t$ in Eq. (41), we have

$$\phi_{ij}^{(1)}(-t) = -\frac{1}{i\hbar}\langle [Q_i, Q_j^{(0)}(-t)]_-\rangle^{(0)}. \quad (44)$$

The t dependence can be transferred to the operator Q_i by performing a unitary transformation with

$\exp\{\pm i[H^{(0)}t/\hbar]\}$, proving Eq. (43).

$\phi_{ij}^{(1)}(t)$ is odd under reversal of time and magnetic field.

$$\phi_{ij}^{(1)}(-t; -\mathbf{A}) = -\phi_{ij}^{(1)}(t; \mathbf{A}). \quad (45)$$

According to Eq. (42) $Q_j^{(0)}(-t; -\mathbf{A}) = Q_j^{(0)*}(t; \mathbf{A})$, similarly $\rho^{(0)}(-\mathbf{A}) = \rho^{(0)*}(\mathbf{A})$, so that $\phi_{ij}^{(1)}(-t; -\mathbf{A}) = -\phi_{ij}^{(1)*}(t; \mathbf{A})$. Invoking the reality of $\phi_{ij}^{(1)}(t; \mathbf{A})$ yields the property (45).

Properties (43) and (45) also imply

$$\phi_{ij}^{(1)}(t; -\mathbf{A}) = \phi_{ji}^{(1)}(t; \mathbf{A}). \quad (46)$$

We now establish the fundamental relationship which exists between the equilibrium commutator

$$\phi_{ij}^{(1)}(t) = -(1/i\hbar)\langle [Q_i, Q_j^{(0)}(t)]_-\rangle^{(0)},$$

characterizing the first-order response, and the equilibrium anticommutator $\Psi_{ij}^{(0)}(t)=\langle\frac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$, characterizing the spontaneous equilibrium fluctuations. The motivation for so doing is that the latter quantity is a true macroscopic observable of the equilibrium system, while the former is not.

Consider the equilibrium second moment $\Psi_{ij}^{(0)}(t)$. Since the analysis is carried out in the spectral representation, it is convenient to define the operators Q_i such that $\Psi_{ij}^{(0)}(t)$ has no constant component, thus avoiding the attendant δ-function singularity appearing in its Fourier transform. As discussed in Appendix A, the time-independent portion of $\Psi_{ij}^{(0)}(t)$ is

$$\lim_{t\to\infty}\Psi_{ij}^{(0)}(t)=\lim_{t\to\infty}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}=\langle Q_i\rangle^{(0)}\langle Q_j\rangle^{(0)}. \quad (47)$$

Consequently, we assume that the operators Q_i are defined such that $\langle Q_i\rangle^{(0)}=0$.

$\Psi_{ij}^{(0)}(t)$ can be written

$$\Psi_{ij}^{(0)}(t)=\tfrac{1}{2}\langle Q_iQ_j^{(0)}(t)+Q_j^{(0)}(t)Q_i\rangle^{(0)}=\tfrac{1}{2}\langle Q_iQ_j^{(0)}(t)+Q_i^{(0)}(-i\hbar\beta)Q_j^{(0)}(t)\rangle^{(0)}. \quad (48)$$

The second term on the right has been obtained by inserting $\exp[\pm\beta H^{(0)}]$ in front of Q_i and cyclically permuting the operators in the trace. That is,

$$\langle Q_j^{(0)}(t)Q_i\rangle^{(0)}=\mathrm{Tr}\,\rho^{(0)}Q_j^{(0)}(t)\exp[\pm\beta H^{(0)}Q_i=\mathrm{Tr}\,\rho^{(0)}\exp[\beta H^{(0)}Q_i\exp[-\beta H^{(0)}]Q_j^{(0)}(t), \quad (49)$$

and invoking the definition (8) for $Q_i^{(0)}(-i\hbar\beta)$ gives Eq. (48). We decompose Eq. (48) into a double summation over matrix elements in the unperturbed energy representation

$$\Psi_{ij}^{(0)}(t)=\tfrac{1}{2}\sum_{lm}\rho(E_l)\{1+\exp[\beta(E_l-E_m)]\}\times\langle E_l|Q_i|E_m\rangle\langle E_m|Q_j|E_l\rangle\exp\left[i\frac{(E_m-E_l)t}{\hbar}\right] \quad (50)$$

where $\rho(E_l)=e^{-\beta E_l}/\sum_l e^{-\beta E_l}$, and $\langle E_l|Q_i|E_m\rangle$ is the matrix element of Q_i between the eigenstates of $H^{(0)}$ having the eigenvalues E_l and E_m. In virtue of the quasi-continuous spectrum of energy eigenvalues, the double summation appearing in Eq. (50) can be replaced by a double integration over energy eigenvalues.

$$\Psi_{ij}^{(0)}(t)=\frac{1}{2}\int_{-\infty}^{\infty}dE_l\int_{-\infty}^{\infty}dE_m\rho(E_l)\eta(E_l)\eta(E_m)\times\{1+\exp[\beta(E_l-E_m)]\}\langle E_l|Q_i|E_m\rangle\times\langle E_m|Q_j|E_l\rangle\exp\left[i\frac{(E_m-E_l)t}{\hbar}\right] \quad (51)$$

where $\eta(E_l)$ is the energy density-of-states function.

We obtain the Fourier transform $G_{ij}^{(0)}(\omega)$ of $\Psi_{ij}^{(0)}(t)$ by introducing

$$E_m=E_l+\hbar\omega. \quad (52)$$

Thus Eq. (51) becomes

$$\Psi_{ij}^{(0)}(t)=\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega e^{i\omega t}G_{ij}^{(0)}(\omega) \quad (53)$$

where

$$G_{ij}^{(0)}(\omega)=\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\hbar[1+\exp(-\hbar\beta\omega)]\int_{-\infty}^{\infty}dE\rho(E)\times\eta(E)\eta(E+\hbar\omega)\langle E|Q_i|E+\hbar\omega\rangle\times\langle E+\hbar\omega|Q_j|E\rangle; \quad (54)$$

$G_{ij}^{(0)}(\omega)$ is the spectrum of the spontaneous equilibrium fluctuations.

We obtain the Fourier transform of the aftereffect function $\phi_{ij}^{(1)}(t)$ in an analogous way. Equation (41) can be rewritten

$$\phi_{ij}^{(1)}(t)=-\frac{1}{i\hbar}\langle Q_iQ_j^{(0)}(t)-Q_j^{(0)}(t)Q_i\rangle^{(0)}=-\frac{1}{i\hbar}\langle Q_iQ_j^{(0)}(t)-Q_i^{(0)}(-i\hbar\beta)Q_j^{(0)}(t)\rangle^{(0)}. \quad (55)$$

Decomposing the equilibrium expectation value into a double integral over matrix elements in the unperturbed energy representation and introducing the transformation (52), we obtain the result

$$\phi_{ij}^{(1)}(t)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega e^{i\omega t}L_{ij}^{(1)}(\omega) \quad (56)$$

where

$$L_{ij}^{(1)}(\omega)=(2\pi)^{\frac{1}{2}}i[1-\exp(-\hbar\beta\omega)]\int_{-\infty}^{\infty}dE\rho(E)\eta(E)\times\eta(E+\hbar\omega)\langle E|Q_i|E+\hbar\omega\rangle\langle E+\hbar\omega|Q_j|E\rangle \quad (57)$$

is clearly the Fourier transform of $\phi_{ij}^{(1)}(t)$.

Comparison of Eqs. (54) and (57) shows that the Fourier transform $G_{ij}^{(0)}(\omega)$ of the equilibrium second moment $\Psi_{ij}^{(0)}(t)$ is related to the Fourier transform $L_{ij}^{(1)}(\omega)$ of the aftereffect function $\phi_{ij}^{(1)}(t)$ according to

$$i\omega G_{ij}^{(0)}(\omega)=E^{(1)}(\omega;\beta)L_{ij}^{(1)}(\omega) \quad (58)$$

where

$$E^{(1)}(\omega;\beta)=\frac{\hbar\omega}{2}\coth\frac{\hbar\beta\omega}{2}\underset{\beta\to 0}{\longrightarrow}\frac{1}{\beta}. \quad (59)$$

The universal function $E^{(1)}(\omega;\beta)$ is uniquely quantum-mechanical in origin and corresponds to a slight smearing out of the microscopic contributions to the macroscopic response at extremely high frequencies ($\gtrsim 10^{12}$ cps at room temperature). In the classical limit $\beta \to 0$, $E^{(1)}(\omega;\beta) \to (1/\beta)$ as indicated.

Equation (58) is the spectral statement of the fundamental relationship which exists between the first-order response and the spontaneous equilibrium fluctuations. It provides directly the basis for the fluctuation-dissipation theorem, several alternate forms of which have been developed.[3,4,9] We discuss these in the following two sections.

The result (58) has also been obtained by Kubo[9] using function-theoretical arguments rather than the matrix approach employed here.

6. THE ADMITTANCE AND THE FLUCTUATION-DISSIPATION THEOREM

We rephrase the results of the preceding section in the familiar terms afforded by the admittance matrix. We define $\alpha_j(\omega)$ and $\gamma_i(\omega)$ as the Fourier transforms of the first-order "current" and force, respectively,

$$\frac{d}{dt}\langle Q_j(t)\rangle^{(1)} = \langle \dot{Q}_j(t)\rangle^{(1)} = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega e^{i\omega t}\alpha_j(\omega), \quad (60)$$

$$F_i(t) = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega e^{i\omega t}\gamma_i(\omega). \quad (61)$$

We further define the admittance matrix elements $Y_{ij}(\omega)$ by

$$\alpha_j(\omega) = \sum_i \gamma_i(\omega) Y_{ij}(\omega) \quad (62)$$

whence, from the definition (40), it follows that

$$Y_{ij}(\omega) = i\omega \int_0^{\infty} dt e^{-i\omega t}\phi_{ij}^{(1)}(t). \quad (63)$$

By Eq. (63) the symmetry properties appropriate to $Y_{ij}(\omega)$ follow immediately from the symmetry properties of $\phi_{ij}^{(1)}(t)$. The reality of $\phi_{ij}^{(1)}(t)$ implies that the real and imaginary parts of $Y_{ij}(\omega)$ are even and odd, respectively, under the transformation $\omega \to -\omega$.

$$\left.\begin{matrix}\mathrm{Re}\\ \mathrm{Im}\end{matrix}\right\} Y_{ij}(-\omega) = \left\{\begin{matrix}+\mathrm{Re}\\ -\mathrm{Im}\end{matrix}\right\} Y_{ij}(\omega). \quad (64)$$

The symmetry property (46) of $\phi_{ij}^{(1)}(t)$ with respect to reversal of the applied magnetic field implies a corresponding symmetry of $Y_{ij}(\omega)$.

$$Y_{ij}(\omega; -\mathbf{A}) = Y_{ji}(\omega; \mathbf{A}). \quad (65)$$

Equation (65) represents the extension of the original Onsager reciprocity[1,2] to all frequency components of the admittance matrix elements.

We now rewrite the spectral relationship between the first order response and the equilibrium fluctuations in terms of the $Y_{ij}(\omega)$ by decomposing Eq. (58) into its symmetric and antisymmetric parts with respect to the indices ij.

$$^{(s)(a)}G_{ij}^{(0)}(\omega) = \frac{E^{(1)}(\omega;\beta)}{i\omega}\tfrac{1}{2}[L_{ij}^{(1)}(\omega) \pm L_{ji}^{(1)}(\omega)] \quad (66)$$

where the superscripts (s) and (a) denote the symmetric and antisymmetric parts, respectively. However, using the time-reversal symmetry property (43) of $\phi_{ij}^{(1)}(t)$, it follows from Eq. (63) for $Y_{ij}(\omega)$ and Eq. (58) for $L_{ij}^{(1)}(\omega)$ that these quantities are related according to

$$\tfrac{1}{2}[L_{ij}^{(1)}(\omega) + L_{ji}^{(1)}(\omega)] = -\frac{2i}{(2\pi)^{\frac{1}{2}}}\frac{\mathrm{Re}^{(s)}Y_{ij}(\omega)}{\omega}, \quad (67)$$

$$\tfrac{1}{2}[L_{ij}^{(1)}(\omega) - L_{ji}^{(1)}(\omega)] = \frac{2}{(2\pi)^{\frac{1}{2}}}\frac{\mathrm{Im}^{(a)}Y_{ij}(\omega)}{\omega}. \quad (68)$$

$\mathrm{Re}^{(s)}Y_{ij}(\omega)$ is the real (symmetric) part of $Y_{ij}(\omega)$ and $\mathrm{Im}^{(a)}Y_{ij}(\omega)$ the imaginary (antisymmetric part). We note from Eq. (65) that $\mathrm{Re}^{(s)}Y_{ij}(\omega)$ and $\mathrm{Im}^{(a)}Y_{ij}(\omega)$ are even and odd, respectively, with respect to reversal of the vector potential $\mathbf{A}$.

Substituting the relations (67) and (68) into Eq. (66), we obtain the results

$$^{(s)}G_{ij}^{(0)}(\omega) = -\left(\frac{2}{\pi}\right)^{\frac{1}{2}} E^{(1)}(\omega;\beta)\frac{\mathrm{Re}^{(s)}Y_{ij}(\omega)}{\omega^2}, \quad (69)$$

$$^{(a)}G_{ij}^{(0)}(\omega) = -i\left(\frac{2}{\pi}\right)^{\frac{1}{2}} E^{(1)}(\omega;\beta)\frac{\mathrm{Im}^{(a)}Y_{ij}(\omega)}{\omega^2}. \quad (70)$$

Since $G_{ij}^{(0)}(\omega)$ is the spectrum of the equilibrium second moment $\langle\frac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$, the Fourier transforms of Eqs. (69) and (70) are

$$^{(s)}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)} = -\frac{2}{\pi}\int_0^{\infty} d\omega \cos\omega t E^{(1)}(\omega;\beta)\frac{\mathrm{Re}^{(s)}Y_{ij}(\omega)}{\omega^2}, \quad (71)$$

$$^{(a)}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)} = \frac{2}{\pi}\int_0^{\infty} d\omega \sin\omega t E^{(1)}(\omega;\beta)\frac{\mathrm{Im}^{(a)}Y_{ij}(\omega)}{\omega^2}. \quad (72)$$

The symmetric part $^{(s)}\langle\frac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$ of the equilibrium second moment with respect to ij is even with respect to reversal of the vector potential $\mathbf{A}$, while the antisymmetric part $^{(a)}\langle\frac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$ is an odd function of $\mathbf{A}$. Further, $^{(a)}\langle\frac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$ vanishes in the absence of an applied magnetic field.

Equations (69) and (70) or (71) and (72) constitute the familiar spectral statement of the fluctuation-dissipation theorem.[4] In the classical limit $\beta \to 0$ [see Eq. (59)], Eqs. (70) and (71) reduce to the familiar

Nyquist forms

$$^{(s)}\langle q_i q_j(t)\rangle^{(0)} = -\frac{2}{\pi\beta}\int_0^\infty d\omega \cos\omega t \frac{\mathrm{Re}^{(s)} Y_{ij}(\omega)}{\omega^2}, \quad (73)$$

$$^{(a)}\langle q_i q_j(t)\rangle^{(0)} = \frac{2}{\pi\beta}\int_0^\infty d\omega \sin\omega t \frac{\mathrm{Im}^{(a)} Y_{ij}(\omega)}{\omega^2}. \quad (74)$$

If we put $t=0$ in the Nyquist relation (73), the left-hand member represents the total noise intensity. It is of interest to note that this form of the equation for $t=0$ also follows from the Kramers-Krönig or dispersion relations, together with the results of equilibrium fluctuation theory. The Kramers-Krönig formulas relate the real and imaginary parts of the admittance matrix element $Y_{ij}(\omega)$ in consequence of the general requirement of causality. In Appendix B we consider this connection between the dispersion relations and the spectral form of the fluctuation-dissipation theorem.

It is sometimes convenient to characterize the spontaneous equilibrium fluctuations in terms of a set of hypothetical intensive quantities F_i rather than the extensive quantities Q_i. These hypothetical forces are associated with the fluctuating Q_i in the same formal way as real forces are associated with the average first-order driven response. That is, by analogy with Eq. (62), the fluctuating force is so defined that the product of its Fourier transform with $Y(\omega)/i\omega$ yields the Fourier transform of the fluctuating extensive parameter.

Consider a one-dimensional system with a single force $F(t)$ and corresponding operator Q. The spectrum $\mathcal{G}^{(0)}(\omega)$ of the second moment $\langle FF(t)\rangle^{(0)}$ of the equilibrium force fluctuation is defined by

$$\langle FF(t)\rangle^{(0)} = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega e^{i\omega t}\mathcal{G}^{(0)}(\omega). \quad (75)$$

Using Eq. (62), together with Eq. (69) for $G^{(0)}(\omega)$, we obtain

$$\mathcal{G}^{(0)}(\omega) = \frac{\omega^2 G^{(0)}(\omega)}{|Y(\omega)|^2} = -\left(\frac{2}{\pi}\right)^{\frac{1}{2}} E^{(1)}(\omega;\beta)\frac{\mathrm{Re}\, Y(\omega)}{|Y(\omega)|^2}$$

$$= -\left(\frac{2}{\pi}\right)^{\frac{1}{2}} E^{(1)}(\omega;\beta)\,\mathrm{Re}\, Z(\omega) \quad (76)$$

where $\mathrm{Re}\, Z(\omega) = \mathrm{Re}\, Y(\omega)/|Y(\omega)|^2$ is the real, or dissipative, part of the complex impedance function. Thus, $\langle FF(t)\rangle^{(0)}$ is given by

$$\langle FF(t)\rangle^{(0)} = -\frac{2}{\pi}\int_0^\infty d\omega \cos\omega t E^{(1)}(\omega;\beta)\mathrm{Re}\, Z(\omega) \quad (77)$$

which corresponds to the one-dimensional form of the fluctuation-disspation theorem (71) for

$$\langle \tfrac{1}{2}[Q, Q^{(0)}(t)]_+\rangle^{(0)}.$$

Similarly, it is shown that the symmetric and antisymmetric parts of the second moment $\langle F_i F_j(t)\rangle^{(0)}$ of the equilibrium force fluctuations for a multidimensional system are given by

$$^{(s)}\langle F_i F_j(t)\rangle^{(0)} = -\frac{2}{\pi}\int_0^\infty d\omega \cos\omega t E^{(1)}(\omega;\beta) \times \mathrm{Re}^{(s)} Z_{ij}(\omega), \quad (78)$$

$$^{(a)}\langle F_i F_j(t)\rangle^{(0)} = \frac{2}{\pi}\int_0^\infty d\omega \sin\omega t E^{(1)}(\omega;\beta) \times \mathrm{Im}^{(a)} Z_{ij}(\omega). \quad (79)$$

The symmetry properties of the elements $Z_{ij}(\omega)$ of the complex impedance matrix are identical to those of $Y_{ij}(\omega)$.

The fluctuation-disspation theorem of Eqs. (71) and (72) or (78) and (79), which establishes a quantitative relationship between a dissipative process and appropriate equilibrium fluctuations, can be given the following intuitive interpretation. A dissipative process can be conveniently considered to involve the interaction between the dissipative system and a source system or signal generator. As mentioned at the beginning of Sec. 2, the dissipative system is characterized by a large number of degrees of freedom and is capable of absorbing energy when acted upon by an imposed force. In equilibrium it exhibits random fluctuations of its variables.

The source system, on the other hand, which provides the imposed forces and delivers energy to the dissipative system, is characterized by relatively few degrees of freedom and a high degree of excitation. Examples of such systems might be a classical pendulum or polyatomic molecule. When isolated from the dissipative system and given some internal energy, the source system may be regarded as having a sort of internal coherence.

If the source system is now connected to the dissipative system, this internal coherence is destroyed, the periodic motion vanishes, and the energy is sapped away, until finally the source system is left with only the random disordered energy $1/\beta$ characteristic of thermal equilibrium. This loss of coherence within the source system may be regarded as being caused by the random fluctuations generated by the dissipative system and acting back upon the source system itself. The disspation therefore appears as the macroscopic consequence of the disordering effect of the random equilibrium fluctuations, and, as such, is necessarily quantitatively related to the fluctuations.

An interesting analogy is furnished by the historical development of the theory of spontaneous radiation from excited atoms. After the initial development of quantum mechanics, it was found impossible to compute the spontaneous transition probabilities for an isolated excited atom, and this dissipative process appeared to be outside the existing structure of dynamics. With the advent of quantum electrodynamics, however, the dissipation could be computed, and it was found that the spontaneous transitions could be consistently considered to be induced by the random fluctuations of the electromagnetic field in the vacuum. In this case, the excited atom plays the role of the source system, and the vacuum plays the role of the dissipative system.

7. THE FIRST-ORDER RESPONSE—TEMPORAL REPRESENTATION

A particularly useful temporal form of the fluctuation-dissipation theorem, due to R. Kubo,[9] is obtained by taking the Fourier transform of the basic spectral relationship (58) between $L_{ij}^{(1)}(\omega)$ and $G_{ij}^{(0)}(\omega)$. According to Eq. (56) this yields the aftereffect function $\phi_{ij}^{(1)}(t)$ in the form

$$\phi_{ij}^{(1)}(t)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega e^{i\omega t}\frac{1}{E^{(1)}(\omega;\beta)}i\omega G_{ij}^{(0)}(\omega). \quad (80)$$

Letting

$$1/E^{(1)}(\omega;\beta)=\int_{-\infty}^{\infty}dte^{-i\omega t}\Gamma(t)$$

and noting from Eq. (53) that

$$i\omega G_{ij}^{(0)}(\omega)=[1/(2\pi)^{\frac{1}{2}}]\int_{-\infty}^{\infty}dte^{-i\omega t}\langle\tfrac{1}{2}[Q_i,\dot{Q}_j^{(0)}(t)]_+\rangle^{(0)},$$

Eq. (80) becomes

$$\phi_{ij}^{(1)}(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}dt'\Gamma(t')$$
$$\times\int_{-\infty}^{\infty}dt''\langle\tfrac{1}{2}[Q_i,\dot{Q}_j^{(0)}(t'')]_+\rangle^{(0)}e^{i\omega(t-t'-t'')}. \quad (81)$$

Invoking the δ-function property of

$$\int_{-\infty}^{\infty}d\omega e^{i\omega(t-t'-t'')},$$

we obtain the result

$$\phi_{ij}^{(1)}(t)=-\frac{1}{i\hbar}\langle[Q_i,Q_j^{(0)}(t)]_-\rangle^{(0)}$$
$$=\int_{-\infty}^{\infty}dt'\Gamma(t-t')\langle\tfrac{1}{2}[Q_i,\dot{Q}_j^{(0)}(t')]_+\rangle^{(0)} \quad (82)$$

where

$$\Gamma(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega e^{i\omega t}\frac{1}{E^{(1)}(\omega;\beta)}$$
$$=\frac{2}{\pi\hbar}\ln\coth\frac{\pi|t|}{2\hbar\beta}\underset{\beta\to 0}{\longrightarrow}\beta\delta(t). \quad (83)$$

The evaluation of the function $\Gamma(t)$ has previously been carried out by R. Kubo,[9] and is presented in Appendix C.

Equation (82) constitutes the temporal statement of the fluctuation-dissipation theorem. Although equivalent to the spectral form of Eq. (58), it presents the basic relationship between equilibrium commutators and anticommutators in a more explicit fashion.

The result (82) can of course be substituted back into Eq. (40) for $\langle Q_j(t)\rangle^{(1)}$ to yield the first-order response directly in terms of the equilibrium correlation moment.

$$\langle Q_j(t)\rangle^{(1)}=-\sum_i\int_{\infty}^{t}dt_1F_i(t_1)\int_{-\infty}^{\infty}dt_1'\Gamma(t_1-t_1')$$
$$\times\langle\tfrac{1}{2}[\dot{Q}_i^{(0)}(t_1'),Q_j^{(0)}(t)]_+\rangle^{(0)}. \quad (84)$$

In obtaining (84) from (40) and (82), we have introduced the transformation $t_1'=t-t'$ and made use of the identity

$$\langle\tfrac{1}{2}[Q_i,\dot{Q}_j^{(0)}(t_1-t_1')]_+\rangle^{(0)}=-\langle\tfrac{1}{2}[\dot{Q}_i^{(0)}(t_1'),Q_j^{(0)}(t)]_+\rangle^{(0)}.$$

In the classical limit $\beta\to 0$, Eq. (84), in virtue of the δ-function property of $\Gamma(t)$, reduces to

$$\langle q_j(t)\rangle^{(1)}=-\beta\sum_i\int_{-\infty}^{t}dt_1F_i(t_1)\langle\dot{q}_i(t_1)q_j(t)\rangle^{(0)}. \quad (85)$$

The first-order response during a step-driven process can be obtained directly from Eq. (84) by introducing the step-function forces defined in Sec. 4.

$$\langle Q_j(t)\rangle^{(1)}=-\sum_i F_i\int_{-\infty}^{0}dt_1\int_{-\infty}^{\infty}dt_1'\Gamma(t_1-t_1')$$
$$\times\langle\tfrac{1}{2}[\dot{Q}_i^{(0)}(t_1'),Q_j^{(0)}(t)]_+\rangle^{(0)}. \quad (86)$$

Integrating by parts and putting $\langle Q_i\rangle^{(0)}=0$ gives

$$\langle Q_j(t)\rangle^{(1)}=\sum_i F_i\int_{-\infty}^{0}dt_1\int_{-\infty}^{\infty}dt_1'\frac{\partial\Gamma(t_1-t_1')}{\partial t_1'}$$
$$\times\langle\tfrac{1}{2}[Q_i^{(0)}(t_1'),Q_j^{(0)}(t)]_+\rangle^{(0)} \quad (87)$$

or, performing the t_1-integration,

$$\langle Q_j(t)\rangle^{(1)}=-\sum_i F_i\int_{-\infty}^{\infty}dt_1'\Gamma(t_1')$$
$$\times\langle\tfrac{1}{2}[Q_i^{(0)}(t_1'),Q_j^{(0)}(t)]_+\rangle^{(0)}. \quad (88)$$

In the classical limit $\beta\to 0$, it reduces to Eq. (37) (with $\langle q_i\rangle^{(0)}=0$).

Throughout this and the preceding two sections we have been explicitly concerned with the driven response of standard thermodynamic variables such as volume, number of particles, magnetic moment, etc. However,

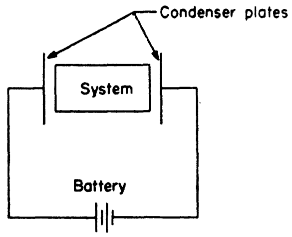

FIG. 2.

in the important case of transport processes one is interested in driven generalized currents rather than in conventional thermodynamic parameters. The special considerations required to treat currents, and particularly to treat the steady state, have been carefully discussed elsewhere.[11] Before concluding the discussion of the linear theory of irreversibility, we indicate briefly the manner of formulation of the theory in terms of driven currents.

We consider the case of electrical conduction, for example, by assuming the specific Hamiltonian

$$H(t)=H^{(0)}+\sum_{i=1}^{3}\mathcal{E}_i(t)Q_i=H^{(0)}+e\sum_{i=1}^{3}\mathcal{E}_i(t)\sum_{\mu}x_{i\mu} \quad (89)$$

where $\mathcal{E}_i(t)$ is the applied electric field in the ith direction, and $x_{i\mu}$ is the ith displacement component of μth charged particle. The component J_i of the current operator $\mathbf{J}$ is simply the time derivative of the operator Q_i.

$$J_i=\dot{Q}_i=e\sum_{\mu}\dot{x}_{i\mu}. \quad (90)$$

In our interpretation heretofore we would have visualized the Hamiltonian (89) as applying to the physical situation illustrated in Fig. 2. The field is applied to the sample by condenser plates which are *not* in physical contact with the sample. The state asymptotically approached after imposition of a step-function force is one with zero current. An alternative interpretation arises if we formally impose periodic boundary conditions on the particle wave functions in the system. A step-function applied force then leads asymptotically to a steady-state current. The formalism is essentially unchanged, but the trace of any operator implies a summation over an entirely different Hilbert space than has been implied heretofore.

The first-order current response $\langle J_j(t)\rangle^{(1)}$ is given, from Eq. (15), by

$$\langle J_j(t)\rangle^{(1)}=-\frac{1}{i\hbar}\sum_{i=1}^{3}\int_{-\infty}^{t}dt_1\mathcal{E}_i(t_1)\langle[Q_i^{(0)}(t_1),J_j^{(0)}(t)]_-\rangle^{(0)}$$

$$=-\frac{1}{i\hbar}\sum_{i=1}^{3}\int_{-\infty}^{t}dt_1\mathcal{E}_i(t_1)\,{}^J\phi_{ij}^{(1)}(t-t_1) \quad (91)$$

[11] See W. Kohn and J. M. Luttinger, Phys. Rev. **108**, 590 (1957).

where the current after-effect function ${}^J\phi_{ij}^{(1)}(t)$ is

$${}^J\phi_{ij}^{(1)}(t)=-\frac{1}{i\hbar}\langle[Q_i,J_j^{(0)}(t)]_-\rangle^{(0)}. \quad (92)$$

The fluctuation-dissipation theorem relating e first-order current response to the second mo t $\langle\frac{1}{2}[J_i,J_j^{(0)}(t)]_+\rangle^{(0)}$ of the spontaneous equilib n current fluctuations is readily obtained using the niques employed previously in connection with e extensive parameter displacements Q_i. The result n the spectral and temporal representations, respectiv, are

$${}^{(s)}\langle\tfrac{1}{2}[J_i,J_j^{(0)}(t)]_+\rangle^{(0)}$$

$$=-\frac{2}{\pi}\int_0^\infty d\omega\,\cos\omega t E^{(1)}(\omega;\beta)\,\mathrm{Re}^{(s)}Y_{ij}(\omega), \quad (93)$$

$${}^{(a)}\langle\tfrac{1}{2}[J_i,J_j^{(0)}(t)]_+\rangle^{(0)}$$

$$=\frac{2}{\pi}\int_0^\infty d\omega\,\sin\omega t E^{(1)}(\omega;\beta)\,\mathrm{Im}^{(a)}Y_{ij}(\omega), \quad (94)$$

$${}^J\phi_{ij}^{(1)}(t)=\int_{-\infty}^{\infty}dt'\Gamma(t-t')\langle\tfrac{1}{2}[J_i,J_j^{(0)}(t')]_+\rangle^{(0)}. \quad (95)$$

Equations (93) and (94) follow immediately from s. (71) and (72), if we replace the operators Q_i by r time derivatives J_i, which simply removes the f r $(1/\omega)^2$ in the integrand. Similarly, Eq. (95) c sponds to Eq. (82) for $\phi_{ij}^{(1)}(t)$.

Finally, the above analysis of driven currents ca e justified by another consideration, which is pe s more physical than the artifice of periodic boun y conditions applied to the system in Fig. 2. We con r a time-dependent magnetic field $\mathcal{H}(t)$ imposed a y through a toroidal conductor, as shown in Fig. 3. e induced current in the toroid will be driven by a gential electric field $\boldsymbol{\mathcal{E}}(t)=-\dot{\mathbf{A}}(t)$, $\mathbf{A}(t)$ being the v r potential associated with $\mathcal{H}(t)$. The Hamiltonian appriate to this situation is

$$H(t)=H^{(0)}+A(t)J \quad (96)$$

where J is the operator corresponding to the elect l current around the toroid.

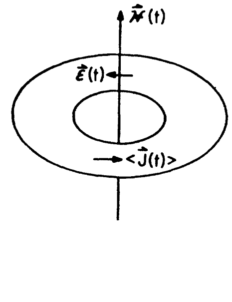

FIG. 3.

The first-order response $\langle J(t)\rangle^{(1)}$ to the perturbation $A(t)J$ is then

$$\langle J(t)\rangle^{(1)}=-\frac{1}{i\hbar}\int_{-\infty}^{t}dt_1A(t_1)\langle[J^{(0)}(t_1),J^{(0)}(t)]_-\rangle^{(0)}. \quad (97)$$

$\langle J(t)\rangle^{(1)}$ can be rewritten in terms of the induced electric field $\mathcal{E}(t)$ by integrating Eq. (97) by parts.

$$\langle J(t)\rangle^{(1)}=-\frac{1}{i\hbar}A(t)\int_{-\infty}^{t}dt_1\langle[J^{(0)}(t_1),J^{(0)}(t)]_-\rangle^{(0)}$$
$$-\frac{1}{i\hbar}\int_{-\infty}^{t}dt_1\mathcal{E}(t_1)\int_{-\infty}^{t_1}dt_1'\langle[J^{(0)}(t_1'),J^{(0)}(t)]_-\rangle^{(0)} \quad (98)$$

where we have let $\dot{A}(t_1)=-\mathcal{E}(t_1)$.

The term involving $\mathcal{E}(t)$ is the physically interesting one, the integrated term corresponding simply to the accumulation of magnetic field required to sustain the driving electric field. By ignoring the latter term, the physical situation is precisely that which would obtain if the process were driven by a battery placed in the circuit rather than by the magnetic field $\mathfrak{H}(t)$. For this case, $\langle J(t)\rangle^{(1)}$ reduces to

$$\langle J(t)\rangle^{(1)}=-\frac{1}{i\hbar}\int_{-\infty}^{t}dt_1\mathcal{E}(t_1)$$
$$\times\int_{-\infty}^{t_1}dt_1'\langle[J^{(0)}(t_1'),J^{(0)}(t)]_-\rangle^{(0)}. \quad (99)$$

By Eq. (90) we identify

$$Q_i^{(0)}(t_1)=\int_{-\infty}^{t_1}dt_1'J^{(0)}(t_1'). \quad (100)$$

Therefore,

$$\langle J(t)\rangle^{(1)}=-\frac{1}{i\hbar}\int_{-\infty}^{t}dt_1\mathcal{E}(t_1)\langle[Q^{(0)}(t_1),J^{(0)}(t)]_-\rangle^{(0)} \quad (101)$$

which is identical with Eq. (91) for the case of one-dimensional electrical conduction.

8. APPLICATIONS OF THE FIRST-ORDER THEORY

Several applications of the foregoing first-order theory are now mentioned briefly.

In their original paper on the fluctuation-dissipation theorem, Callen and Welton[4] discussed the relation of that theorem to the energy density in an isotropic radiation field. The impedance of a charged particle driven by a periodic electric field exhibits a dissipative term arising from the radiation damping force. According to the fluctuation-dissipation theorem (78), this implies the existence of a random fluctuating electric field exerted by the vacuum on the free particle. The energy density of this fluctuating field is found to be just the familiar Planck radiation density.

Van Vliet[12] has recently employed the fluctuation-dissipation theorem to discuss the equilibrium charge carrier fluctuations in semiconducting materials. A simple admittance matrix corresponding to a linear RC network is introduced, the resistances being expressed in terms of transition rates between different groups of carrier levels. The fluctuation-dissipation theorem thereby yields the second moments of the equilibrium carrier fluctuations in terms of the thermal generation-recombination process. The charge carrier fluctuations in turn give rise to a contribution to the driven noise, to which further reference is made in Sec. 12.

In addition to the fluctuation-dissipation theorem and the spectral reciprocity, Kubo[9] points out that general proofs of certain sum rules can be obtained from irreversible thermodynamic considerations. Thus, for the case of electrical conductivity in a system of interacting particles in an applied magnetic field, he finds that the frequency integrals of $\mathrm{Re}^{(s)}Y_{ij}(\omega)$ and $\omega\,\mathrm{Im}^{(a)}Y_{ij}(\omega)$ are given by

$$\frac{2}{\pi}\int_0^{\infty}d\omega\,\mathrm{Re}^{(s)}Y_{ij}(\omega)=\sum_r\frac{e^2n_r}{m_r}\delta_{ij}, \quad (102)$$

$$\frac{2}{\pi}\int_0^{\infty}d\omega\,\omega\,\mathrm{Im}^{(a)}Y_{ij}(\omega)=\sum_r\frac{e_r^3n_r}{m_r^2c}\mathfrak{H}_z. \quad (103)$$

n_r, m_r, and e_r are the number, mass, and charge, respectively, of the rth type of particle, and $\mathfrak{H}_z$ is the z-directed applied magnetic field. Analogous sum rules can be derived for the magnetic susceptibility matrix.

H. Mori[13] has applied the fluctuation-disspation theorem to the analysis of transport processes in fluids. The coupling between the slow macroscopic relaxation of the system and the rapid microscopic fluctuations is shown to be responsible for the dissipation. Thus, the coefficients of viscosity, thermal conductivity, and diffusion can be computed in terms of the equilibrium fluctuations of the thermodynamic fluxes.

9. THE SECOND-ORDER RESPONSE IN A GENERAL PROCESS

In Secs. 5 through 8 the first-order theory of irreversible thermodynamics was reviewed, showing the relationship of $\langle Q_i(t)\rangle^{(1)}$ to the equilibrium fluctuations. Sections 9 through 14 are devoted to an extension of the fluctuation-dissipation concept to the driven second moment $\langle\frac{1}{2}[Q_i(t),Q_j(t+\tau)]_+\rangle$ and to the second- and higher-order terms in the driven response $\langle Q_i(t)\rangle$. A number of interrelationships among these quantities and the equilibrium fluctuations are established.

[12] K. M. Van Vliet, Phys. Rev. **110**, 50 (1958).
[13] H. Mori, Phys. Rev. **112**, 1829 (1958).

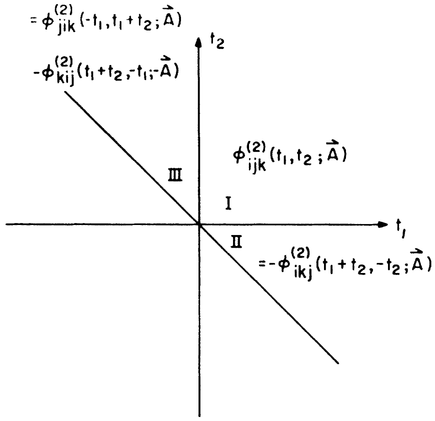

FIG. 4.

Consider the second-order response $\langle Q_i(t)\rangle^{(2)}$. From Eq. (16),

$$\langle Q_i(t)\rangle^{(2)}=\frac{1}{2}\left(-\frac{1}{i\hbar}\right)^2\sum_{jk}\left\{\int_{-\infty}^{t}dt_1F_j(t_1)\int_{-\infty}^{t_1}dt_2F_k(t_2)\times\langle[Q_k^{(0)}(t_2),[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-]_-\rangle^{(0)}+\int_{-\infty}^{t}dt_1F_j(t_1)\int_{t_1}^{t}dt_2F_k(t_2)\langle[Q_j^{(0)}(t_1),\times[Q_k^{(0)}(t_2),Q_i^{(0)}(t)]_-]_-\rangle^{(0)}\right\} \quad (104)$$

where we have inverted the order of integration in the second term. The second-order after-effect function $\phi_{ijk}^{(2)}(t_1,t_2)$ is defined by rewriting Eq. (104) as

$$\langle Q_i(t)\rangle^{(2)}=\frac{1}{2}\sum_{jk}\left\{\int_{-\infty}^{t}dt_1F_j(t_1)\int_{-\infty}^{t_1}dt_2F_k(t_2)\times\phi_{kji}^{(2)}(t_1-t_2,\,t-t_1)+\int_{-\infty}^{t}dt_1F_j(t_1)\int_{t_1}^{t}dt_2F_k(t_2)\times\phi_{jki}^{(2)}(t_2-t_1,\,t-t_2)\right\} \quad (105)$$

whence

$$\phi_{ijk}^{(2)}(t_1,t_2)=\left(-\frac{1}{i\hbar}\right)^2\langle[Q_i,\,[Q_j^{(0)}(t_1),\,Q_k^{(0)}(t_1+t_2)]_-]_-\rangle^{(0)}. \quad (106)$$

$\phi_{ijk}^{(2)}(\tau,\,t-\tau)$ is the response $\langle Q_k(t)\rangle^{(2)}$ at time $t(>0)$ to a δ-function force F_i applied at time zero, and a δ-function force F_j applied at time $\tau(>0)$. Consequently, the first term in Eq. (105) characterizes the contribution to $\langle Q_i(t)\rangle^{(2)}$ arising from the application of $F_k(t_2)$ prior to $F_j(t_1)$, while the second term characterizes the contribution arising from the application of $F_k(t_2)$ subsequent to $F_j(t_1)$.

Although Eq. (105) defines $\phi_{ijk}^{(2)}(t_1,t_2)$ only for positive t_1 and t_2, we accept Eq. (106) as the formal definition of $\phi_{ijk}^{(2)}(t_1,t_2)$ for arbitrary values of t_1 and t_2. The symmetry properties of $\phi_{ijk}^{(2)}(t_1,t_2)$ permit us to evaluate this function for arbitrary times in terms of its measured values for positive times.

We first observe that $\phi_{ijk}^{(2)}(t_1,t_2)$ is invariant with respect to simultaneous reversal of all times and the applied magnetic vector potential $\mathbf{A}$, the argument being identical to that given below Eq. (45).

$$\phi_{ijk}^{(2)}(-t_1,\,-t_2;\,-\mathbf{A})=\phi_{ijk}^{(2)}(t_1,t_2;\mathbf{A}). \quad (107)$$

Further, $\phi_{ijk}^{(2)}(t_1,t_2)$ can be written in either of the following forms.

$$\phi_{ijk}^{(2)}(t_1,t_2)=\left(-\frac{1}{i\hbar}\right)^2\{-\langle[Q_j^{(0)}(t_1),\times[Q_k^{(0)}(t_1+t_2),\,Q_i]_\mp]_\mp\rangle^{(0)}+\langle[[Q_i,\,Q_j^{(0)}(t_1)]_\mp,\times Q_k^{(0)}(t_1+t_2)]_\mp\rangle^{(0)}\}. \quad (108)$$

These forms follow by writing out all terms in the double commutator of Eq. (106) and appropriately regrouping. Consider the double commutator form of Eq. (108), which states that

$$\phi_{ijk}^{(2)}(t_1,t_2)+\phi_{jki}^{(2)}(t_2,\,-t_1-t_2)+\phi_{kij}^{(2)}(-t_1-t_2,\,t_1)=0. \quad (109)$$

This cyclic relationship corresponds to Eq. (43) for $\phi_{ij}^{(1)}(t)$.

We now return to our observation that the symmetries (107) and (109) permit us to evaluate $\phi_{ijk}^{(2)}(t_1,t_2)$ for arbitrary times from its measured value for positive times. Consider the t_1t_2 plane shown in Fig. 4, which we have divided into sectors. The value of $\phi_{ijk}^{(2)}(t_1,t_2;\mathbf{A})$ in sector I is obtained by direct measurement.

The value in sector II (for which $t_1>-t_2>0$) is obtained by noting that

$$\phi_{ijk}^{(2)}(t_1,t_2;\mathbf{A})=-\phi_{ijk}^{(2)}(t_1+t_2;\,-t_2;\mathbf{A}).$$

Sector III is determined by rewriting Eq. (109), interchanging the indice ik in the second term and reversing the vector potential $\mathbf{A}$ in the third term.

$$\phi_{ijk}^{(2)}(t_1,t_2;\mathbf{A})-\phi_{jik}^{(2)}(-t_1,\,t_1+t_2;\mathbf{A})+\phi_{kij}^{(2)}(t_1+t_2,\,-t_1;\,-\mathbf{A})=0. \quad (110)$$

Then for $t_2>-t_1>0$ the second and third terms are measurable, thereby determining the value of the first term in sector IV.

Equation (107) reflects the known values into the remaining half-plane.

We now discuss the relationship which exists between $\phi_{ijk}^{(2)}(t_1,t_2)$ and the equilibrium fluctuations. Consider the form of Eq. (108), for $\phi_{ijk}^{(2)}(t_1,t_2)$, involving the double anticommutators. This can be rewritten

$$\phi_{ijk}^{(2)}(t_1,t_2)=4\left(-\frac{1}{i\hbar}\right)^2[\Psi_{kij}^{(0)}(-t_1-t_2,\,t_1)-\Psi_{jki}^{(0)}(t_2,\,-t_1-t_2)] \quad (111)$$

where

$$\Psi_{ijk}^{(0)}(t_1,t_2)=\tfrac{1}{4}\langle[Q_i,\,[Q_j^{(0)}(t_1),\,Q_k^{(0)}(t_1+t_2)]_+]_+\rangle^{(0)}. \quad (112)$$

Since $\Psi_{ijk}^{(0)}(t_1,t_2)$ is the equilibrium expectation value of a symmetrized product of the operators Q_i, $Q_j^{(0)}(t_1)$, and $Q_k^{(0)}(t_1+t_2)$, it is a third correlation moment among the equilibrium fluctuations of the variables corresponding to these operators.

However, referring back to Eq. (108) to identify the two third equilibrium correlation moments in Eq. (111), we see that each involve precisely the same operators at precisely the same times, although the order of symmetrization is different! The two distinct third moments correspond in principle to different ways of measuring the correlation, as can be seen from the following general considerations.

Since there is only one way of symmetrizing a product of two non-commuting operators, it is possible to write a unique quantum-mechanical expression for the second equilibrium correlation moment [see Eq. (17)]. However, quantum mechanics furnishes no such unique *a priori* prescription for symmetrizing a product of three (or more) operators.[14] Thus, for example, in Eq. (112) we introduced the equilibrium symmetrized quantity $\Psi_{ijk}^{(0)}(t_1,t_2)$ containing four permutations of the operator product $Q_iQ_j^{(0)}(t_1)Q_k^{(0)}(t_1,t_2)$, while we can also construct the fully symmetrized form $\bar{\Psi}_{ijk}^{(0)}(t_1,t_2)$ containing all six permutations.

$$\begin{aligned}\bar{\Psi}_{ijk}^{(0)}(t_1,t_2)&\\ =\tfrac{1}{6}\langle Q_iQ_j^{(0)}(t_1)Q_k^{(0)}(t_1+t_2)&\\ +Q_j^{(0)}(t_1)Q_k^{(0)}(t_1+t_2)Q_i&\\ +Q_k^{(0)}(t_1+t_2)Q_iQ_j^{(0)}(t_1)\rangle^{(0)}&\\ +(\text{complex conjugate}).& \quad (113)\end{aligned}$$

Each possible symmetrized arrangement corresponds to some particular experimental measurement. Consider an experiment in which three detectors monitor the variables Q_i, Q_j, and Q_k, and feed their signals into a counter. Appropriate time delay circuits are inserted between the Q_i and Q_j detectors and the counter such that the counter makes a single measurement of the desired product. Since all three signals are handled in a completely symmetrical fashion, this experiment measures the fully symmetrized operator product $\bar{\Psi}_{ijk}^{(0)}(t_1,t_2)$.

Alternately, suppose the Q_k signal and the delayed Q_j signal are fed into a multiplier, and the multiplied signal is fed into the counter along with the delayed Q_i signal. The counter makes a simultaneous measurement of the product of its two inputs. In this case Q_j and Q_k are treated symmetrically, as are their product and Q_i, and the experiment measures the quantity $\Psi_{ijk}^{(0)}(t_1,t_2)$ of Eq. (112).

In the classical limit (zero order in β) the two correlation moments become identical, as discussed later in Sec. 13.

Returning to Eq. (111), we see that this expression constitutes a thermodynamic relationship between the second-order response, characterized by the second-order aftereffect function $\phi_{ijk}^{(2)}(t_1,t_2)$, and the equilibrium fluctuations, characterized by the difference between the two operationally distinct third correlation moments $\Psi_{kij}^{(0)}(-t_1-t_2,\,t_1)$ and $\Psi_{jki}^{(0)}(t_2,\,-t_1-t_2)$.

10. FIRST-ORDER NOISE IN A GENERAL PROCESS

In this section we consider the first-order term $\langle[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ in the driven second moment, establishing its relationship to the equilibrium fluctuations. The relationship between the first-order driven noise and the second-order response is also discussed.

The relationship of the first-order driven second moment to the equilibrium fluctuations is conveniently approached using Eq. (20) for $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$. The quantity

$$-(1/2i\hbar)\langle[Q_k^{(0)}(t_1),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_-\rangle^{(0)}$$

appearing in the first term of Eq. (20) is the noise response $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ to an applied force $F_k(t)=\delta(t-t_1)$, $t_1<t<t+\tau$. As such, it characterizes the noise contribution arising from the application of $F_k(t_1)$ prior to time t. This noise response function can be readily symmetrized and is the quantity of primary physical interest.

On the other hand, the quantity

$$-(1/2i\hbar)\langle[Q_i^{(0)}(t),\,[Q_k^{(0)}(t_1),\,Q_j^{(0)}(t+\tau)]_-]_+\rangle^{(0)}$$

appearing in the second term of Eq. (20) is the noise response to the force $F_k(t)=\delta(t-t_1)$, $t<t_1<t+\tau$. As such it characterizes the noise contribution arising from the application of $F_k(t_1)$ in the time interval t to $t+\tau$, during which the noise is being measured. We denote this function by $\theta_{ikj}^{(1)}(t_1-t,\,t+\tau-t_1)$. Thus,

$$\theta_{ijk}^{(1)}(t_1,t_2)=-\frac{1}{2i\hbar}\langle[Q_i,\,[Q_j^{(0)}(t_1),\,Q_k^{(0)}(t_1+t_2)]_-]_+\rangle^{(0)}. \quad (114)$$

As we shall see, $\theta_{ijk}^{(1)}(t_1,t_2)$ is not of particular physical interest; we discuss it briefly at the end of this section in connection with the second-order response.

The first equilibrium expectation value appearing on the right-hand side of Eq. (20) can be symmetrized by

[14] J. R. Shewell, Am. J. Phys. 27, 16 (1959).

invoking the basic relationship (82) between commutators and anticommutators. Replacing t by $(t-t_1)$ and introducing the transformation $t_1'=t-t'$ gives Eq. (82) in the form

$$-\frac{1}{i\hbar}\langle[Q_k^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)} = -\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1')\langle\tfrac{1}{2}[\dot{Q}_k^{(0)}(t_1'),Q_i^{(0)}(t)]_+\rangle^{(0)}. \quad (115)$$

If we replace the operator Q_i by the anticommutator $\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+$, this becomes

$$-\frac{1}{2i\hbar}\langle[Q_k^{(0)}(t_1),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_-\rangle^{(0)} = -\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1')\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'), \times[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)}. \quad (116)$$

The result (116) can be substituted directly into Eq. (20), along with the definition (114) of $\theta_{ijt}^{(1)}(t_1,t_2)$, to yield the first-order driven noise in the form

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)} = -\sum_k\int_{-\infty}^{t} dt_1F_k(t_1)\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1') \times\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)} +\sum_k\int_t^{t+\tau} dt_1F_k(t_1)\theta_{ikj}^{(1)}(t_1-t,\,t+\tau-t_1). \quad (117)$$

As discussed in the preceding section, the symmetrized equilibrium expectation value

$$\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)}$$

is one macroscopically observable form of the third correlation moment among the spontaneous equilibrium fluctuations of the variables corresponding to the operators $\dot{Q}_k^{(0)}(t_1')$, $Q_i^{(0)}(t)$, and $Q_j^{(0)}(t+\tau)$.

A thermodynamic relationship between the intensity of the first-order driven noise and the equilibrium fluctuations follows immediately from Eq. (117). Letting $\tau=0$, the second term in Eq. (117) vanishes, leaving

$$\langle\tfrac{1}{2}[Q_i(t),Q_j(t)]_+\rangle^{(1)} = -\sum_k\int_{-\infty}^{t} dt_1F_k(t_1)\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1') \times\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),Q_j^{(0)}(t)]_+]_+\rangle^{(0)}. \quad (118)$$

Equation (118) expresses the first-order driven noise intensity $\langle\frac{1}{2}[Q_i(t),Q_j(t)]_+\rangle^{(1)}$ in terms of the equilibrium third fluctuation moment

$$\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),[Q_i^{(0)}(t),Q_j^{(0)}(t)]_+]_+\rangle^{(0)}.$$

Returning to the more general quantity

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)},$$

for most purposes one is interested in measuring this driven noise only for processes in which the imposed forces are slowly varying over the time interval during which the noise is being measured. We therefore assume that $F_k(t_1)\simeq\text{constant}\equiv F_k$ in the interval t to $(t+\tau)$ although, of course, $F_k(t_1)$ is arbitrary for $t_1<t$. Further, we decompose $F_k(t_1)$ into two components according to

$$F_k(t_1)=F_k+\Delta F_k(t_1). \quad (119)$$

The contribution to $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ arising from the time-dependent force component $\Delta F_k(t_1)$ is

$$-\sum_k\int_{-\infty}^{t} dt_1\Delta F_k(t_1)\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1') \times\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)} \quad (120)$$

since the integral $\int_t^{t+\tau} dt_1\Delta F_k(t_1)$ vanishes. It is therefore directly expressible in terms of the equilibrium fluctuations.

The contribution arising from the constant force component F_k, on the other hand, is just the first-order term in the perturbation expansion of the driven second moment with respect to a constant applied force. However, the application of a constant force F_k implies simply a change in the corresponding (equilibrium) intensive parameter associated with the system. Hence, this contribution can also be regarded as a macroscopically observable characteristic of the equilibrium system. We denote it by

$$\sum_k F_k\frac{\partial}{\partial F_k}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)}$$

where the derivative is evaluated at $F_k=0$.

Inserting the quantities (120) and (121) into Eq. (117), we obtain the result

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)} = \sum_k\Big\{-\int_{-\infty}^{t} dt_1\Delta F_k(t_1)\int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1') \times\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)} +F_k\frac{\partial}{\partial F_k}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)}\Big\}. \quad (122)$$

Equation (122) constitutes a thermodynamic relationship between $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ and the indicated macroscopically observable characteristics of the equilibrium fluctuations.

We further note that $(\partial/\partial F_k)\langle\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)}$ can be re-expressed in terms of the nonlinear behavior of the system by invoking the fluctuation-dissipation theorem, Eqs. (71) and (72). In order to keep the notation simple, we consider explicitly the case of no applied magnetic field, for which $\langle\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)}$ reduces to

$$\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)} = -\frac{2}{\pi}\int_0^\infty d\omega\,\cos\omega\tau E^{(1)}(\omega;\beta)\frac{\mathrm{Re}\,Y_{ij}(\omega)}{\omega^2}. \quad (123)$$

Just as $\langle\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+\rangle^{(0)}$ is a function of the applied forces F_k, $Y_{ij}(\omega)$ also in general depends upon F_k. Consequently, Eq. (122) can be written as

$$\begin{aligned}\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(0)} &= \sum_k\Big\{-\int_{-\infty}^t dt_1\Delta F_k(t_1)\int_{-\infty}^\infty dt_1'\Gamma(t_1-t_1') \\ &\quad\times\langle\tfrac{1}{4}[\dot{Q}_k^{(0)}(t_1'),\,[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)} \\ &\quad-\frac{2}{\pi}\int_0^\infty d\omega\,\cos\omega\tau E^{(1)}(\omega;\beta)\frac{1}{\omega^2}\,\mathrm{Re}\frac{\partial Y_{ij}(\omega)}{\partial F_k}\Big\}. \quad (124)\end{aligned}$$

The physical significance of the derivative $\partial Y_{ij}(\omega)/\partial F_k$ can be regarded as arising from the nonlinearity of the system in the following way. Most physical systems are nonlinear. Nevertheless, for sufficiently small deviations from a given "operating point" (corresponding to a constant applied force F_k) the linear approximation is adequate. As a consequence of the nonlinearity of the system, however, the admittance matrix must in general be a function of the "operating point." The quantity $\partial Y_{ij}(\omega)/\partial F_k$ specifies the first-order contribution to this dependence on F_k.

Equation (124) is an alternate thermodynamic expression for $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ to that given in Eq. (122), expressing the first-order driven noise in terms of the equilibrium third moment $\langle\frac{1}{4}[\dot{Q}_k^{(0)}(t_1'),$ $\times[Q_i^{(0)}(t),\,Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)}$ and the second-order response function $\partial Y_{ij}(\omega)/\partial F_k$.

In the classical limit, Eqs. (122) and (124) reduce, respectively, to

$$\langle q_i(t)q_j(t+\tau)\rangle^{(1)} = \sum_k\Big\{-\beta\int_{-\infty}^t dt_1\Delta F_k(t_1)\langle\dot{q}_k(t_1)q_i(t)q_j(t+\tau)\rangle^{(0)} + F_k\frac{\partial}{\partial F_k}\langle q_iq_j(\tau)\rangle^{(0)}\Big\}, \quad (125)$$

$$\langle q_i(t)q_j(t+\tau)\rangle^{(1)} = \sum_k\Big\{-\beta\int_{-\infty}^t dt_1\Delta F_k(t_1)\langle\dot{q}_k(t_1)q_i(t)q_j(t+\tau)\rangle^{(0)} -\frac{2}{\pi\beta}F_k\int_0^\infty d\omega\,\cos\omega\tau\frac{1}{\omega^2}\,\mathrm{Re}\,\frac{\partial Y_{ij}(\omega)}{\partial F_k}\Big\}. \quad (126)$$

We return finally to a brief discussion of the relationship of the noise response function $\theta_{ijk}^{(1)}(t_1,t_2)$, defined in Eq. (114), to the second-order response. This relationship also stems from the basic relationship between equilibrium commutators and anticommutators given in Eq. (82). Replacing the operator Q_j in Eq. (82) by the commutator $-(1/i\hbar)[Q_j,Q_k^{(0)}(t_2)]_-$ and noting Eqs. (106) and (114) for $\phi_{ijk}^{(2)}(t_1,t_2)$ and $\theta_{ijk}^{(1)}(t_1,t_2)$, respectively, we find that

$$\phi_{ijk}^{(2)}(t_1,t_2)=\int_{-\infty}^\infty dt_1'\Gamma(t_1-t_1')\frac{\partial}{\partial t_1'}\theta_{ijk}^{(1)}(t_1',t_2). \quad (127)$$

The spectral form of Eq. (127) is found to be

$$\theta_{ijk}^{(1)}(t_1,t_2)=\frac{1}{2\pi}\int_{-\infty}^\infty d\omega_1\int_{-\infty}^\infty d\omega_2 e^{i\omega_1t_1}e^{i\omega_2t_2} \times E^{(1)}(\omega;\beta)\frac{L_{ijk}^{(2)}(\omega_1,\omega_2)}{i\omega_1} \quad (128)$$

where $L_{ijk}^{(2)}(\omega_1,\omega_2)$ is the double Fourier transforms of $\phi_{ijk}^{(2)}(t_1,t_2)$ defined by

$$\phi_{ijk}^{(2)}(t_1,t_2)=\frac{1}{2\pi}\int_{-\infty}^\infty d\omega_1\int_{-\infty}^\infty d\omega_2 e^{i\omega_1t_1}e^{i\omega_2t_2} \times L_{ijk}^{(2)}(\omega_1,\omega_2). \quad (129)$$

Equations (128) and (129) have the following formal implications. Using Eq. (114) for $\theta_{ijk}^{(1)}(t_1,t_2)$, Eq. (19) for $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)}$ can be written in the form

$$\langle\tfrac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(1)} = \sum_k\Big\{\int_{-\infty}^t dt_1F_k(t_1)\theta_{jki}^{(1)}(t_1-t-\tau,\,t-t_1) + \int_{-\infty}^{t+\tau} dt_1F_k(t_1)\theta_{ikj}^{(1)}(t_1-t,\,t+\tau-t_1)\Big\}. \quad (130)$$

Since Eqs. (127) and (128) express the function $\theta_{ijk}^{(1)}(t_1,t_2)$ in terms of the macroscopically observable second-order aftereffect function $\phi_{ijk}^{(2)}(t_1,t_2)$, Eq. (130) permits us to compute $\langle\frac{1}{2}[Q_i(t),\,Q_j(t+\tau)]_+\rangle^{(0)}$ from suitable measurements of the second-order response.

11. FLUCTUATION SYMMETRY

In the preceding two sections we have established the basic interrelationship among the second-order response, the first-order second moment, and the equilibrium third moment.

In order better to appreciate this basic interrelationship, it is of interest to examine its consistency from the point of view of symmetry. For this purpose it is convenient to represent the response $\langle Q_i(t)\rangle$ to a set of applied forces $F_j(t)$ by the symbolic expansion

$$\langle Q_i(t)\rangle = \chi_i^{(0)} + \sum_j \mathfrak{F}_j \chi_{ji}^{(0)} + \tfrac{1}{2}\sum_{jk} \mathfrak{F}_j \mathfrak{F}_k \chi_{jki}^{(2)} + \cdots. \quad (131)$$

The response functions χ are suitable combinations of the aftereffect functions defined previously, while the $\mathfrak{F}_j$ are integral operators, linear functionals of the forces $F_j(t)$ acting on the χ's. $\chi_i^{(0)}$ denotes the equilibrium expectation value $\langle Q_i\rangle^{(0)}$. Similarly, the driven second moment $\langle \frac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle$ can be represented by the expansion

$$\langle \tfrac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle = \xi_{ij}^{(0)} + \sum_k \mathfrak{F}_k' \xi_{kij}^{(1)} + \tfrac{1}{2}\sum_{kl} \mathfrak{F}_k' \mathfrak{F}_l' \xi_{klij} + \cdots \quad (132)$$

where the ξ are suitable noise response functions, and the $\mathfrak{F}_k'$ are appropriate integral operators.

The physical symmetry of many systems is such that reversal of all forces simply reverses all responses $\langle Q_i(t)\rangle - \langle Q_i\rangle^{(0)}$. For such systems only the odd terms in Eq. (131), and only the even terms in Eq. (132) can exist.

The physical symmetry referred to above also has obvious implications for the equilibrium fluctuations. Consider particularly the third equilibrium correlation moment $\langle q_i q_j(t_1) q_k(t_2)\rangle^{(0)}$. This moment is defined in terms of an integral involving the equilibrium joint probability distribution $W_3^{(0)}(q_i; q_j,t_1; q_k,t_2)$. For many systems the physical symmetry implies that this joint probability distribution is unchanged if each of the q's is replaced by its negative. For such a "fluctuation-symmetric" system, all odd equilibrium correlation moments vanish.

The relations which were proven among the second-order response, the first-order noise, and the equilibrium third moments indicate that the physical symmetries referred to in the two preceding paragraphs are equivalent, as we might intuitively expect. A system which is fluctuation-symmetric, with no odd equilibrium moments, exhibits no second-order response, and no first-order noise.

A homogeneous system, symmetric under spatial inversion, is fluctuation-symmetric with respect to its transport properties. In such systems, electron, phonon, or other currents can exhibit no first-order noise.

With fluctuation-symmetric systems, it is necessary to go to second order to obtain a contribution to the driven noise. Such second-order driven noise can be appreciable in magnitude, and, in fact, is easily observed in semiconductors. By analogy with Eqs. (111), (124), and (127), the second-order noise may be presumed to depend generally in some complicated way upon the third-order response and the equilibrium fourth moment. In Sec. 12, we give a limited discussion of one contribution to second-order noise.

On the other hand, there are many systems which do not obey fluctuation-symmetry and which therefore may exhibit first-order driven noise. Rectifiers, for example, because of their pronounced asymmetry with respect to current flow, necessarily possess significant equilibrium third moments.

Finally, it is possible for a system to be fluctuation-symmetric with respect to some of its variables but not with respect to others. Thus, for example, a *p-n* junction is fluctuation-symmetric with respect to current in the plane of the junction but fluctuation-asymmetric with respect to current perpendicular to this plane. Another example would be a bulk solid, which we have previously mentioned as being fluctuation-symmetric with respect to its transport properties. Such a system would not in general be fluctuation symmetric with respect to its thermodynamic extensive variables such as energy, volume, or the number of particles in the conduction band.

12. SECOND-ORDER DRIVEN NOISE

Although we do not undertake a complete discussion of the second-order noise in this paper, it is of interest to indicate how the general theory would apply in a specific physical situation. As an example, we consider the steady-state thermal generation-recombination noise in semiconductors.

We consider explicitly the second-order driven current noise $\langle \frac{1}{2}[J_i(t), J_j(t+\tau)]_+\rangle^{(2)}$. In accordance with the recipe developed in Sec. 3 for computing driven second moments in terms of the equilibrium system, we have that

$$\begin{aligned}\langle \tfrac{1}{2}[J_i(t), J_j(t+\tau)]_+\rangle^{(2)} &= \tfrac{1}{2}\{\langle [J_i^{(0)}(t), J_j^{(2)}(t+\tau)]_+\rangle^{(0)} \\ &\quad + \langle [J_i^{(1)}(t), J_j^{(1)}(t+\tau)]_+\rangle^{(0)} \\ &\quad + \langle [J_i^{(2)}(t), J_j^{(0)}(t+\tau)]_+\rangle^{(0)}\}. \quad (133)\end{aligned}$$

Although the first and third terms also contribute to $\langle \frac{1}{2}[J_i(t), J_j(t+\tau)]_+\rangle^{(2)}$, we focus attention on the term $\langle \frac{1}{2}[J_i^{(1)}(t), J_j^{(1)}(t+\tau)]_+\rangle^{(0)}$, which is subject to clear physical interpretation.

The first-order driven current operator $J_i^{(1)}(t)$ is obtained in accordance with the discussion at the end of Sec. 7.

$$J_i^{(1)}(t) = -\frac{1}{i\hbar}\sum_k \int_{-\infty}^{t} dt_1 \mathcal{E}_k(t_1)[Q_k^{(0)}(t_1), J_i^{(0)}(t)]_-. \quad (134)$$

In the steady state, the electric field $\mathcal{E}_k(t)$ is constant, and Eq. (134) reduces to

$$J_i^{(1)}(t)=-\frac{1}{i\hbar}\sum_k \mathcal{E}_k \exp\left[i\frac{H^{(0)}t}{\hbar}\right] \times\int_{-\infty}^{0} dt_1[Q_k^{(0)}(t_1),J_i]_- \exp\left[-i\frac{H^{(0)}t}{\hbar}\right] \quad (135)$$

where we have let $t_1'=t-t_1$ and extracted the resulting t dependence of the commutator as indicated.

We define the unperturbed Heisenberg operator $\sigma_{ki}^{(0)}(t)$ corresponding to the kith element of the conductivity matrix by rewriting Eq. (135) as

$$J_i^{(1)}(t)=\sum_k \mathcal{E}_k\sigma_{ki}^{(0)}(t) \quad (136)$$

whence

$$\sigma_{ki}^{(0)}(t)=-\frac{1}{i\hbar}\exp\left[i\frac{H^{(0)}t}{\hbar}\right] \times\int_{-\infty}^{0} dt_1[Q_k^{(0)}(t),J_i]_- \exp\left[-i\frac{H^{(0)}t}{\hbar}\right]. \quad (137)$$

Using Eq. (136) for $J_i^{(1)}(t)$, the contribution $\langle\frac{1}{2}[J_i^{(1)}(t), J_j^{(1)}(t+\tau)]_+\rangle^{(0)}$ to the second-order steady-state current noise becomes

$$\langle\tfrac{1}{2}[J_i^{(1)},J_j^{(1)}(\tau)]_+\rangle^{(0)} =\sum_{kl} \mathcal{E}_k\mathcal{E}_l\langle\tfrac{1}{2}[\sigma_{ki},\sigma_{lj}^{(0)}(\tau)]_+\rangle^{(0)} \quad (138)$$

where we have set $t=0$ in virtue of time stationarity. The quantity $\langle\frac{1}{2}[\sigma_{ki},\sigma_{lj}^{(0)}(\tau)]_+\rangle^{(0)}$ can be interpreted as the second correlation moment between the spontaneous equilibrium fluctuations of the conductivity matrix elements σ_{ki} and $\sigma_{jl}^{(0)}(\tau)$.

The correlation function $\langle\frac{1}{2}[\sigma,\sigma^{(0)}(t)]_+\rangle^{(0)}$ is easily calculated in the case of a simple semiconductor for which the conductivity is given by $\sigma=ne^2\tau_s/m^*$,[15] where n is the equilibrium carrier concentration, m^* is the effective mass, and τ_s denotes a simple relaxation time for the scattering mechanisms. Assuming that

$$n(t)=n_0e^{-t/\tau_\beta} \quad (139)$$

where τ_β denotes a relaxation time associated with thermal charge carrier generation and recombination, the second-order term $\langle J^{(1)}J^{(1)}(t)\rangle^{(0)}$ in the steady-state current noise $\langle JJ(t)\rangle$ is

$$\langle J^{(1)}J^{(1)}(t)\rangle^{(0)}=\frac{e^4\tau_s^2}{m^{*2}}\langle nn(t)\rangle^{(0)}\mathcal{E}^2 =\frac{e^4\tau_s^2}{m^{*2}}\langle n^2\rangle^{(0)}e^{-t/\tau_\beta}\mathcal{E}^2 \quad (140)$$

which is a well-known result.[12]

[15] See for example W. Shockley, *Holes and Electrons in Semiconductors* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950).

There exist in general other contributions to the second-order steady-state noise, as can be seen from Eq. (133). Here we have sought only to establish the connection of the general formalism with the usual model treatment of semiconductor noise.

13. HIGHER-ORDER STEP-DRIVEN RESPONSE

Whereas we have previously shown that the second-order response in a general process is characterized by the *difference* of two equilibrium third moments, the classical result of Eq. (38) suggests the possibility of establishing a more conventional quantum relationship in the case of step-driven processes. Although measurement of two distinct equilibrium third moments is still required to determine the second-order step-driven response, we shall find that for this simple class of processes the relationship is in close formal analogy to the first-order fluctuation-dissipation theorem. Further, the uniquely quantum-mechanical effects are more easily visualized in this case.

It is convenient to consider $\langle Q_i(t)\rangle^{(2)}$ as given in the form of Eq. (33). Rewriting this expression so as to indicate explicitly both contributions from a given pair of forces F_j, F_k, and assuming that $\langle Q_i\rangle^{(0)}=0$,

$$\langle Q_i(t)\rangle^{(2)}=\tfrac{1}{2}\sum_{jk} F_jF_k\int_0^\beta d\lambda_1\int_0^{\lambda_1} d\lambda_2 \times[\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)} +\langle Q_k^{(0)}(-i\hbar\lambda_1)Q_j^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)}]. \quad (141)$$

Inserting $\exp[\pm\beta H^{(0)}]$ in front of the operator $Q_i^{(0)}(t)$ and permuting the operators cyclicly, the integrand of the second term in Eq. (141) can be rewritten

$$\langle Q_k^{(0)}(-i\hbar\lambda_1)Q_j^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)} =\langle Q_i^{(0)}(t)Q_k^{(0)}(-i\hbar\lambda_1+i\hbar\beta)Q_j^{(0)} \times(-i\hbar\lambda_2+i\hbar\beta)\rangle^{(0)}. \quad (142)$$

Thus, inverting the order of integration, and making the successive transformations $\lambda_2'=\beta-\lambda_1$, $\lambda_1'=\beta-\lambda_2$,

$$\int^\beta d\lambda_1\int_0^{\lambda_1} d\lambda_2\langle Q_k^{(0)}(-i\hbar\lambda_1)Q_j^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)} =\int_0^\beta d\lambda_1\int_0^{\lambda_1} d\lambda_2\langle Q_i^{(0)}(t)Q_k^{(0)}(+i\hbar\lambda_2) \times Q_j^{(0)}(+i\hbar\lambda_1)\rangle^{(0)}. \quad (143)$$

Inserting (143) into Eq. (141), we thereby obtain $\langle Q_i(t)\rangle^{(2)}$ in the form

$$\langle Q_i(t)\rangle^{(2)}=\tfrac{1}{2}\sum_{jk} F_jF_k\int_0^\beta d\lambda_1\int_0^{\lambda_1} d\lambda_2 \times[\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_k^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)} +\langle Q_i^{(0)}(t)Q_k^{(0)}(i\hbar\lambda_2)Q_j^{(0)}(i\hbar\lambda_1)\rangle^{(0)}]. \quad (144)$$

It is further convenient to define the second-order step-response function $\Phi_{jki}^{(2)}(t)$ by rewriting Eq. (144) as

$$\langle Q_i(t)\rangle^{(2)}=\tfrac{1}{2}\sum_{jk}F_jF_k\Phi_{jki}^{(2)}(t)$$

whence

$$\Phi_{jki}^{(2)}(t)=\int^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2[\langle Q_j^{(0)}(-i\hbar\lambda_1)\times Q_k^{(0)}(-i\hbar\lambda_2)Q_i^{(0)}(t)\rangle^{(0)}+(\text{c.c.})]. \quad (146)$$

The notation (c.c.) is used to indicate the complex conjugate of the first term. $\Phi_{jki}^{(2)}(t)$ represents the second-order response to unit step-function forces F_j and F_k.

We now proceed to analyze $\Phi_{jki}^{(2)}(t)$ by decomposing the equilibrium expectation values appearing in Eq. (146) into appropriate summations over matrix elements in the unperturbed energy representation. This technique is similar to that employed in Sec. 5 in connection with $\phi_{ij}^{(1)}(t)$, and yields

$$\Phi_{jki}^{(2)}(t)=\int_0^{\beta}d\lambda_1\int_0^{\lambda_1}d\lambda_2\sum_{lmn}\rho(E_l)\langle E_l|Q_j|E_m\rangle\times\langle E_m|Q_k|E_n\rangle\langle E_n|Q_i|E_l\rangle e^{\lambda_1(E_l-E_m)}\times e^{\lambda_2(E_m-E_n)}\exp\left[i\frac{(E_n-E_l)t}{\hbar}\right]+(\text{c.c.}) \quad (147)$$

where $\langle E_l|Q_j|E_m\rangle$ is the matrix element of Q_j between the eigenstates of $H^{(0)}$ having the energy eigenvalues E_l and E_m, and $\rho(E_l)=e^{-\beta E_l}/\sum_l e^{-\beta E_l}$.

Performing the indicated temperature integration, and replacing the triple summation by a triple integral over energy eigenvalues, this becomes

$$\Phi_{jki}^{(2)}(t)=\int_{-\infty}^{\infty}dE_l\int_{-\infty}^{\infty}dE_m\int_{-\infty}^{\infty}dE_n\rho(E_l)\eta(E_l)\times\eta(E_m)\eta(E_n)\left[\frac{1}{(E_l-E_n)(E_l-E_m)}-\frac{e^{\beta(E_l-E_m)}}{(E_m-E_n)(E_l-E_m)}+\frac{e^{\beta(E_l-E_n)}}{(E_m-E_n)(E_l-E_n)}\right]\times\langle E_l|Q_j|E_m\rangle\langle E_m|Q_k|E_n\rangle\langle E_n|Q_i|E_l\rangle\times\exp\left[i\frac{(E_n-E_l)t}{\hbar}\right]+(\text{c.c.}) \quad (148)$$

where $\eta(E_l)$ is the energy density-of-states function. Introducing the transformations

$$E_m=E_l+\hbar\omega_1,\quad E_n=E_l+\hbar\omega_2 \quad (149)$$

and letting $\omega_1\rightarrow-\omega_1$, $\omega_2\rightarrow-\omega_2$ in the (c.c.) term, we finally obtain $\Phi_{jki}^{(2)}(t)$ in the form

$$\Phi_{jki}^{(2)}(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2e^{i\omega_2 t}N_{jki}^{(2)}(\omega_1,\omega_2) \quad (150)$$

where

$$N_{jki}^{(2)}(\omega_1,\omega_2)=\left[\frac{1}{\omega_1\omega_2}+\frac{\exp(-\hbar\beta\omega_1)}{\omega_1(\omega_1-\omega_2)}+\frac{\exp(-\hbar\beta\omega_2)}{\omega_2(\omega_2-\omega_1)}\right]\times g_{jki}(\omega_1,\omega_2)+\left[\frac{1}{\omega_1\omega_2}+\frac{\exp(+\hbar\beta\omega_1)}{\omega_1(\omega_1-\omega_2)}+\frac{\exp(+\hbar\beta\omega_2)}{\omega_2(\omega_2-\omega_1)}\right]g_{jki}^*(-\omega_1,-\omega_2) \quad (151)$$

and

$$g_{jki}(\omega_1,\omega_2)=g_{ikj}^*(\omega_2,\omega_1)=2\pi\int_{-\infty}^{\infty}dE\rho(E)\eta(E)\eta(E+\hbar\omega_1)\times\eta(E+\hbar\omega_2)\langle E|Q_j|E+\hbar\omega_1\rangle\times\langle E+\hbar\omega_1|Q_k|E+\hbar\omega_2\rangle\langle E+\hbar\omega_2|Q_i|E\rangle. \quad (152)$$

In order to relate the second-order step-driven response to the equilibrium fluctuations, we undertake a similar spectral analysis of the equilibrium correlation moment of the variables corresponding to the operators Q_j, $Q_k^{(0)}(t_1)$, and $Q_i^{(0)}(t_1+t_2)$. However, as discussed at the end of Sec. 9, there exist several equally valid, operationally distinct quantum-mechanical expressions for a given equilibrium third moment. Thus, the quantity $\Psi_{jki}^{(0)}$ defined in Eq. (112) corresponds to one particular set of experimental conditions, while the fully symmetrized equilibrium form $\bar{\Psi}_{jki}^{(0)}$ defined in Eq. (113) is appropriate to a different experimental arrangement. We find, in fact, that measurement of both $\Psi_{jki}^{(0)}(t_1,t_2)$ and $\bar{\Psi}_{jki}^{(0)}(t_1,t_2)$ is required for a complete experimental determination of $\Phi_{jki}^{(2)}(t)$, except in the classical limit.

Equation (113) for $\bar{\Psi}_{jki}^{(0)}(t_1,t_2)$ is conveniently rewritten

$$\bar{\Psi}_{jki}^{(0)}(t_1,t_2)=\tfrac{1}{6}\langle Q_jQ_k^{(0)}(t_1)Q_i^{(0)}(t_1+t_2)+Q_j^{(0)}(-i\hbar\beta)Q_k^{(0)}(t_1)Q_i^{(0)}(t_1+t_2)+Q_j^{(0)}(-i\hbar\beta)Q_k^{(0)}(t_1-i\hbar\beta)\times Q_i^{(0)}(t_1+t_2)\rangle^{(0)}+(\text{c.c.}) \quad (153)$$

where we have inserted $\exp[\pm\beta H^{(0)}]$ at suitable positions in the second and third terms and permuted the operators cyclicly.

As in the case of $\Phi_{jki}^{(2)}(t)$, the quantity $\bar{\Psi}_{jki}^{(0)}(t_1,t_2)$ can be decomposed into a triple integral over matrix elements in the unperturbed energy representation. Introducing the transformations (149) and letting

$\omega_1 \to -\omega_1$, $\omega_2 \to -\omega_2$ in the (c.c.) term, we obtain the expression

$$\Psi_{jki}^{(0)}(t_1,t_2)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2 e^{i\omega_1 t_1}e^{i\omega_2 t_2}\times\bar{G}_{jki}^{(0)}(\omega_1,\omega_2) \quad (154)$$

where

$$\bar{G}_{jki}^{(0)}(\omega_1,\omega_2) =\frac{\hbar^2}{6}\{[1+\exp(-\hbar\beta\omega_1)+\exp(-\hbar\beta\omega_2)]\times g_{jki}(\omega_1,\omega_2)+[1+\exp(+\hbar\beta\omega_1)+\exp(+\hbar\beta\omega_2)]g_{jki}^*(-\omega_1,-\omega_2)\}, \quad (155)$$

$g_{jki}(\omega_1,\omega_2)$ having been given previously in Eq. (152). $\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)$ is the double Fourier transform of the equilibrium third moment $\bar{\Psi}_{jki}^{(0)}(t_1,t_2)$.

Similar analysis of the equilibrium third moment $\Psi_{jki}^{(0)}(t_1,t_2)$ of Eq. (112) yields the result

$$\Psi_{jki}^{(0)}(t_1,t_2)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega_1\int_{-\infty}^{\infty}d\omega_2 e^{i\omega_1 t_1}e^{i\omega_2 t_2}\times G_{jki}^{(0)}(\omega_1,\omega_2) \quad (156)$$

where

$$G_{jki}^{(0)}(\omega_1,\omega_2) =\frac{\hbar^2}{4}\{[1+\exp(-\hbar\beta\omega_1)]g_{jki}(\omega_1,\omega_2)+[1+\exp(+\hbar\beta\omega_1)]g_{jki}^*(-\omega_1,-\omega_2)\}. \quad (157)$$

We now discuss the relation of the second-order step-driven response to the equilibrium fluctuations using the spectral quantities $N_{jki}^{(2)}(\omega_1,\omega_2)$, $\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)$, and $G_{jki}^{(0)}(\omega_1,\omega_2)$ obtained above. In order to indicate the formal analogy of this relationship to the first-order fluctuation-dissipation theorem, it is convenient to define the functions $r_{jki}^{(2)}(\omega_1,\omega_2)$ and $f_{jki}^{(0)}(\omega_1,\omega_2)$.

$$r_{jki}^{(2)}(\omega_1,\omega_2)=\left[\frac{1}{\omega_1\omega_2}+\frac{\exp(-\hbar\beta\omega_1)}{\omega_1(\omega_1-\omega_2)}+\frac{\exp(-\hbar\beta\omega_2)}{\omega_2(\omega_2-\omega_1)}\right]\times g_{jki}(\omega_1,\omega_2), \quad (158)$$

$$f_{jki}^{(0)}(\omega_1,\omega_2)=\frac{\hbar^2}{6}[1+\exp(-\hbar\beta\omega_1)+\exp(-\hbar\beta\omega_2)]\times g_{jki}(\omega_1,\omega_2), \quad (159)$$

in terms of which Eqs. (159) and (155) can be rewritten

$$N_{jki}^{(2)}(\omega_1,\omega_2)=r_{jki}^{(2)}(\omega_1,\omega_2)+r_{jki}^{(2)*}(-\omega_1,-\omega_2), \quad (160)$$

$$\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)=f_{jki}^{(0)}(\omega_1,\omega_2)+f_{jki}^{(0)*}(-\omega_1,-\omega_2). \quad (161)$$

Comparison of Eqs. (158) and (159) shows that $r_{jki}^{(2)}(\omega_1,\omega_2)$ and $f_{jki}^{(0)}(\omega_1,\omega_2)$, which characterize the second-order step-driven response and the equilibrium fluctuations, respectively, in the sense of Eqs. (160) and (161), are related according to

$$r_{jki}^{(2)}(\omega_1,\omega_2)=\frac{1}{E^{(2)}(\omega_1,\omega_2;\beta)}f_{jki}^{(0)}(\omega_1,\omega_2) \quad (162)$$

where

$$E^{(2)}(\omega_1,\omega_2;\beta) =\frac{\hbar^2}{6}\frac{1+\exp(-\hbar\beta\omega_1)+\exp(-\hbar\beta\omega_2)}{\dfrac{1}{\omega_1\omega_2}+\dfrac{\exp(-\hbar\beta\omega_1)}{\omega_1(\omega_1-\omega_2)}+\dfrac{\exp(-\hbar\beta\omega_2)}{\omega_2(\omega_2-\omega_1)}}\underset{\beta\to 0}{\longrightarrow}\frac{1}{\beta^2}. \quad (163)$$

Equation (162) strongly suggests itself as a direct extension to second-order processes of the fluctuation-dissipation theorem of Eq. (58), which relates the Fourier transform $L_{ij}^{(1)}(\omega)$ of the first-order aftereffect function $\phi_{ij}^{(1)}(t)$ to the Fourier transform $G_{ij}^{(0)}(\omega)$ of the equilibrium second fluctuation moment. The universal function $E^{(2)}(\omega_1,\omega_2;\beta)$ is the second-order analog of $E^{(1)}(\omega;\beta)$. It is uniquely quantum-mechanical in origin, corresponding to a slight smearing out of the microscopic contributions to the macroscopic response at extremely high frequencies. In the classical limit, $E^{(2)}(\omega_1,\omega_2;\beta)\to(1/\beta^2)$ as indicated.

Whereas Eq. (58) constitutes a true thermodynamic relationship, however, Eq. (162) does not. That is, the function $f_{jki}^{(0)}(\omega_1,\omega_2)$ is not macroscopically observable, although its sum with $f_{jki}^{*(0)}(-\omega_1,-\omega_2)$ is, as indicated by Eq. (161).

The specific way in which quantum-mechanical effects enter the picture is evident by first considering what happens in the classical limit. For this case, Eqs. (151), (155), and (157) reduce to

$$N_{jki}^{(2)}(\omega_1,\omega_2)=\frac{\hbar^2\beta^2}{6}[g_{jki}(\omega_1,\omega_2)+g_{jki}^*(-\omega_1,-\omega_2)] =\beta^2\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)=\beta^2 G_{jki}^{(0)}(\omega_1,\omega_2). \quad (164)$$

The functions $\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)$ and $G_{jki}^{(0)}(\omega_1,\omega_2)$ have become equivalent, and measurement of either completely determines $N_{jki}^{(2)}(\omega_1,\omega_2)$. The temporal form of Eq. (164) is obtained immediately from Eqs. (150), (154), and (156).

$$\Phi_{jki}^{(2)}(t)\underset{\beta\to 0}{\longrightarrow}\beta^2\langle q_j q_k q_i(t)\rangle^{(0)}. \quad (165)$$

Substitution of this result into Eq. (145) for $\langle Q_i(t)\rangle^{(2)}$ yields the classical result given previously in Eq. (38).

We decompose $g_{jki}(\omega_1,\omega_2)$ into its real and imaginary, even and odd parts with respect to simultaneous reversal of ω_1 and ω_2.

$$g_{jki}(\omega_1,\omega_2) =\mathrm{Re}^{(+)}g_{jki}(\omega_1,\omega_2)+i\,\mathrm{Im}^{(+)}g_{jki}(\omega_1,\omega_2)+\mathrm{Re}^{(-)}g_{jki}(\omega_1,\omega_2)+i\,\mathrm{Im}^{(-)}g_{jki}(\omega_1,\omega_2). \quad (166)$$

The superscripts (+) and (−) denote the even and odd part, respectively, under the transformation $\omega_1 \to -\omega_1$, $\omega_2 \to -\omega_2$. Using this decomposition, the classical relationship (164) becomes

$$N_{jki}^{(2)}(\omega_1,\omega_2) = \frac{\hbar^2\beta^2}{3}[\mathrm{Re}^{(+)}g_{jki}(\omega_1,\omega_2) + i\,\mathrm{Im}^{(-)}g_{jki}(\omega_1,\omega_2)] = \beta^2\bar{G}_{jki}^{(0)}(\omega_1,\omega_2). \quad (167)$$

Thus, in the classical limit we are concerned only with $\mathrm{Re}^{(+)}g_{jki}(\omega_1,\omega_2)$ and $\mathrm{Im}^{(-1)}g_{jki}(\omega_1,\omega_2)$, both of which are determined by experimental knowledge of the complex quantity $\bar{G}_{jki}^{(0)}(\omega_1,\omega_2) = G_{jki}^{(0)}(\omega_1,\omega_2)$.

In the general quantum case, however, $N_{jki}^{(2)}(\omega_1,\omega_2)$ depends upon all four components of $q_{jki}(\omega_1,\omega_2)$ because of the uniquely quantum-mechanical spreading introduced by the quantities

$$\left[\frac{1}{\omega_1\omega_2} + \frac{\exp(\pm\hbar\beta\omega_1)}{\omega_1(\omega_1-\omega_2)} + \frac{\exp(\pm\hbar\beta\omega_2)}{\omega_2(\omega_2-\omega_1)}\right]$$

appearing in Eq. (151). For this case $\bar{G}_{jki}^{(0)}(\omega_1,\omega_2)$ and $G_{jki}^{(0)}(\omega_1,\omega_2)$ are no longer equivalent, and Eq. (155) and (157) constitute two independent complex expressions which can be solved for the four components of $g_{jki}(\omega_1,\omega_2)$. Because of the quantum-mechanical interference among the components of $g_{jki}(\omega_1,\omega_2)$, measurement of both equilibrium third moments $\bar{\Psi}_{jki}^{(0)}(t_1,t_2)$ and $\Psi_{jki}^{(0)}(t_1,t_2)$ is necessary to determine completely the function $N_{jki}^{(2)}(\omega_1,\omega_2)$ and, consequently, by Eq. (150), the second-order step-driven response, $\Phi_{jki}^{(2)}(t)$.

It may be presumed that an analogous quantum-mechanical analysis of the third- and higher-order terms in the step-driven response can be made, although we do not attempt to carry out this laborious program here. Instead we simply refer to the classical relation between the step-driven response and the equilibrium fluctuations, given previously in Eqs. (36) through (39).

14. STEP-DRIVEN NOISE

For step-driven processes, the perturbation expansion of the driven noise $\langle\frac{1}{2}[Q_i(t),Q_j(t+\tau)]_+\rangle$ simplifies considerably, exhibiting a strong formal similarity to the step-driven response $\langle Q_i(t)\rangle$. We can, therefore, use the techniques employed previously for analyzing the step-driven response to discuss the relationship between the step-driven noise and the equilibrium fluctuations.

Consider Eq. (117) for the first-order driven noise $\langle\frac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle^{(1)}$. For step-function forces, the unsymmetrized term vanishes, and Eq. (117) reduces, upon integration, to

$$\langle\tfrac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle^{(1)} = -\sum_k F_k\int_{-\infty}^{\infty} dt_1\Gamma(t_1)\langle\tfrac{1}{4}[Q_k^{(0)}(t_1), \times[Q_i^{(0)}(t), Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)}. \quad (168)$$

Equation (168) can also be obtained from Eq. (88) for the first-order step-driven response $\langle Q_i(t)\rangle^{(1)}$ by replacing the operator Q_j by the anticommutator $\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+$. Equation (168) relates the first-order step-driven noise $\langle\frac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle^{(1)}$ to the third equilibrium correlation moment

$$\langle\tfrac{1}{4}[Q_k^{(0)}(t_1), [Q_i^{(0)}(t), Q_j^{(0)}(t+\tau)]_+]_+\rangle^{(0)}.$$

In the classical limit it reduces to

$$\langle q_i(t)q_j(t+\tau)\rangle^{(1)} = -\beta\sum_k F_k\langle q_kq_i(t)q_j(t+\tau)\rangle^{(0)}. \quad (169)$$

The formal similarity between Eqs. (88) and (168) also carries over into the higher-order terms. Thus, in the case of step-function forces, Eq. (21) for $\langle\frac{1}{2}[Q_i(t,)$ $Q_j(t+\tau)]_+\rangle^{(2)}$ reduces to

$$\langle\tfrac{1}{2}[Q_i(t), Q_j(t+\tau)]_+\rangle^{(2)} = \left(-\frac{1}{i\hbar}\right)^2\sum_{kl}F_kF_l\int_{-\infty}^{0}dt_1\int_{-\infty}^{t_1}dt_2\langle[Q_l^{(0)}(t_2), \times[Q_k^{(0)}(t_1), \tfrac{1}{2}[Q_i^{(0)}(t), Q_j^{(0)}(t+\tau)]_+]_-]_-\rangle^{(0)} \quad (170)$$

which also follows from Eq. (24) for the second-order step-driven response $\langle Q_i(t)\rangle^{(2)}$, if we replace Q_i by $\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+$. Consequently, the analysis of the previous section for the second-order step-driven response can be applied directly to the second-order step-driven noise. Similarly, it may be assumed that the third- and higher-order terms can also be treated on an equivalent basis.

The consequences of the above formal resemblance can be most simply demonstrated in the classical limit. Consider Eq. (36) for the full step-driven response $\langle q_i(t)\rangle$. Replacing the operator Q_i by the anticommutator $\frac{1}{2}[Q_i,Q_j^{(0)}(\tau)]_+$, which corresponds to replacing the classical variable q_i by the product $q_iq_j(\tau)$, Eq. (36) becomes

$$\langle q_i(t)q_j(t+\tau)\rangle = \langle\exp(-\beta\sum_k F_kq_k)q_i(t)q_j(t+\tau)\rangle^{(0)} / \langle\exp(-\beta\sum_k F_kq_k)\rangle^{(0)}. \quad (171)$$

Equation (171) expresses the step-driven noise $\langle q_i(t)q_j(t+\tau)\rangle$ wholly in terms of the third correlation moment $\langle\exp(-\beta\sum_k F_kq_k)q_i(t)q_j(t+\tau)\rangle^{(0)}$ of the spontaneous equilibrium fluctuations.

It is possible to summarize the results of this section and the preceding one in the following intuitively appealing way. We first differentiate Eq. (36) for $\langle q_i(t)\rangle$ with respect to F_j, evaluating the result at F_1, F_2, $\cdots = 0$.

$$\frac{\partial}{\partial F_j}\langle q_i(t)\rangle = -\beta\langle q_jq_i(t)\rangle^{(0)} \quad (172)$$

which is equivalent to Eq. (37).

Taking the second derivative of $\langle q_i(t)\rangle$ with respect to F_j and F_k, we obtain

$$\frac{\partial^2}{\partial F_j \partial F_k}\langle q_i(t)\rangle = \beta^2 \langle q_j q_k q_i(t)\rangle^{(0)} \tag{173}$$

which is equivalent to Eq. (38).

On the other hand, differentiating Eq. (171) for $\langle q_j(t) q_i(t+\tau)\rangle$ with respect to F_k, we obtain

$$\frac{\partial}{\partial F_k}\langle q_j(t) q_i(t+\tau)\rangle = -\beta \langle q_k q_j(t) q_i(t+\tau)\rangle^{(0)} \tag{174}$$

which is equivalent to Eq. (169). Letting $t=0$ and replacing τ by t, this becomes

$$\frac{\partial}{\partial F_k}\langle q_j q_i(t)\rangle = -\beta \langle q_k q_j q_i(t)\rangle^{(0)}. \tag{175}$$

Equations (173) and (175) can be combined in the form

$$\frac{\partial^2}{\partial F_j \partial F_k}\langle q_i(t)\rangle = -\beta \frac{\partial}{\partial F_k}\langle q_j q_i(t)\rangle = \beta^2 \langle q_j q_k q_i(t)\rangle^{(0)} \tag{176}$$

which constitutes a triple relationship among the second-order response, the first-order noise, and the equilibrium third moment for a step-driven process. It is apparent that further differentiation of Eqs. (36) and (171) would yield a whole hierarchy of analogous higher order thermodynamic relationships.

Although they apply literally only to step-driven process, Eqs. (172) and (176) exhibit most of the essential elements of the more general theory. Therefore, the results presented above characterize the general structure of irreversible thermodynamics.

Finally, we compare our results for a step-driven process with the results of time-independent equilibrium fluctuation theory. Letting $t=0$, Eqs. (172) and (176) reduce to

$$\frac{\partial}{\partial F_j}\langle q_i\rangle^{(0)} = -\beta \langle q_i q_j\rangle^{(0)}, \tag{177}$$

$$\frac{\partial^2}{\partial F_j \partial F_k}\langle q_i\rangle^{(0)} = \beta^2 \langle q_i q_j q_k\rangle^{(0)} = -\beta \frac{\partial}{\partial F_k}\langle q_i q_j\rangle^{(0)}. \tag{178}$$

Equations (177) and (178) are precisely those which can be derived for a generalized canonical ensemble using standard equilibrium fluctuation theory.[16]

15. THE PATH DISTRIBUTION FUNCTION

Recently one of us has discussed the first-order term in the nonequilibrium path distribution function $W_1(q,t)$[8]. This function specifies the probability that the macroscopic variable corresponding to the operator Q has the value q in the driven ensemble at the time t. In this section we review the theory of the path distribution function and its application to the first-order problem discussed in Secs. 5 through 7. We also discuss the path distribution function for a step-driven process.

In order to keep the notation simple, we restrict ourselves initially to a one-dimensional process. The distribution function $W_1(q,t)$ can be expressed in terms of its characteristic function $K_1(\nu,t)$.

$$W_1(q,t) = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\nu e^{i\nu q} K_1(\nu,t) \tag{179}$$

whence $K_1(\nu,t)$ is given by

$$K_1(\nu,t) = \frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} dq e^{-i\nu q} W_1(q,t)$$

$$= \frac{1}{(2\pi)^{\frac{1}{2}}}\langle e^{-i\nu q(t)}\rangle = \frac{1}{(2\pi)^{\frac{1}{2}}}\operatorname{Tr}\rho^{(0)} e^{-i\nu Q(t)}, \tag{180}$$

where $e^{-i\nu Q(t)} = U^\dagger(t) e^{-i\nu Q} U(t)$. Then

$$W_1(q,t) = \operatorname{Tr}\rho^{(0)}\delta(q-Q(t)) = \langle \delta(q-Q(t))\rangle, \tag{181}$$

where $\delta(q-Q(t))$ is the driven δ-function operator $U^\dagger(t)\delta(q-Q)U(t)$, which selects from $\rho^{(0)}$ the appropriate contributions to $W_1(q,t)$.

Since $W_1(q,t)$ is just the expectation of value of $\delta(q-Q)$ in the driven system at time t, the theory developed previously for the driven response $\langle Q(t)\rangle$ can be applied directly to the path distribution function. Thus, for example, the first-order term $W_1^{(1)}(q,t)$ is obtained in symmetrized form from Eq. (88) for $\langle Q_i(t)\rangle^{(1)}$ by simply replacing Q_i by $\delta(q-Q)$.

$$W_1^{(1)}(q,t) = -\int_{-\infty}^{t} dt_1 F(t_1)\int_{-\infty}^{\infty} dt_1' \Gamma(t_1 - t_1')$$
$$\times \langle \tfrac{1}{2}[\dot{Q}^{(0)}(t_1'-t), \delta(q-Q)]_+\rangle^{(0)}, \tag{182}$$

the t dependence in the integrand has been transferred to $\dot{Q}$ by performing a unitary transformation with $\exp\{\pm i[H^{(0)}t/\hbar]$.

The quantity $\langle \frac{1}{2}[\dot{Q}^{(0)}(t_1'-t), \delta(q-Q)]_+\rangle^{(0)}$ is interpreted in the following way. Since the classical analog of the operator $\delta(q-Q)$ is simply the δ function $\delta(q-q')$, we can calculate the equilibrium correlation moment of the variables corresponding to the operators $\dot{Q}^{(0)}(t_1'-t)$ and $\delta(q-Q)$ according to

$$\langle \tfrac{1}{2}[\dot{Q}^{(0)}(t_1'-t), \delta(q-Q)]_+\rangle^{(0)}$$
$$= \int_{-\infty}^{\infty} dq' \delta(q-q') W_1^{(0)}(q') \langle \dot{Q}^{(0)}(t_1'-t)\rangle_{q'}^{(0)} \tag{183}$$

where $W_1^{(0)}(q)$ is the equilibrium probability distribu-

[16] See for example R. F. Greene and H. B. Callen, Phys. Rev. 83, 1231 (1951).

tion, and $\langle \dot{Q}^{(0)}(t_1'-t)\rangle_q{}^{(0)}$ denotes the equilibrium expectation value of the variable corresponding to the operator $\dot{Q}$ at time $(t'-t)$ conditional on the variable corresponding to Q having the value q at time zero. The q' integration can be performed immediately to yield

$$\langle \tfrac{1}{2}[\dot{Q}^{(0)}(t_1'-t),\delta(q-Q)]_+\rangle^{(0)} = W_1{}^{(0)}(q)\langle \dot{Q}^{(0)}(t_1'-t)\rangle_q{}^{(0)}. \quad (184)$$

Substituting the result (184) back into Eq. (182) we obtain

$$W_1{}^{(1)}(q,t) = -W_1{}^{(0)}(q)\int_{-\infty}^{t} dt_1 F(t_1) \times \int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1')\langle \dot{Q}^{(0)}(t_1'-t)\rangle_q{}^{(0)}. \quad (185)$$

The corresponding first-order term $W_1{}^{(1)}(q_1,\cdots,q_n;t)$ in the path distribution function for an n-dimensional process can be developed in a completely analogous way. In place of the single operator $\delta(q-Q)$, we introduce a symmetrized form of the product $\delta(q_1-Q_1)\cdots\delta(q_n-Q_n)$ of δ-function operators. The result is

$$W_1{}^{(1)}(q_1,\cdots,q_n;t) = -W_1{}^{(0)}(q_1,\cdots,q_n)\sum_{j=1}^{n}\int_{-\infty}^{t} dt_1 F_j(t_1) \times \int_{-\infty}^{\infty} dt_1'\Gamma(t_1-t_1')\langle \dot{Q}_j{}^{(0)}(t_1'-t)\rangle_{q_1\cdots q_n}{}^{(0)}. \quad (186)$$

$W_1{}^{(0)}(q_1,\cdots,q_n)$ is the simultaneous equilibrium probability distribution for the variables $q_1,\cdots,q_n$, while $\langle \dot{Q}_j{}^{(0)}(t_1'-t)\rangle^{(0)}{}_{q_1\cdots q_n}$ denotes the equilibrium expectation value of the variable corresponding to $\dot{Q}_j$ at time $(t_1'-t)$ conditional on the variables corresponding to $Q_i,\cdots,Q_n$ having the values $q_1,\cdots,q_n$ at time zero. In the classical limit, Eq. (186) reduces to

$$W_1{}^{(1)}(q_1,\cdots,q_n;t) \underset{\beta\to 0}{\longrightarrow} -\beta W_1{}^{(0)}(q_1,\cdots,q_n) \times \sum_{j=1}^{n}\int_{-\infty}^{t} dt_1 F_j(t_1)\langle \dot{q}_j(t_1-t)\rangle_{q_1\cdots q_n}{}^{(0)}. \quad (187)$$

Equation (186) constitutes a generalized statement of the fluctuation-dissipation theorem, expressing $W_1{}^{(1)}(q_1,\cdots,q_n;t)$ in terms of the equilibrium probability distribution $W_1{}^{(0)}(q_1,\cdots,q_n)$ and the equilibrium conditional expectation value $\langle \dot{Q}_j{}^{(0)}(t_1'-t)\rangle_{q_1\cdots q_n}{}^{(0)}$. Since all of the previous theorems regarding the first-order problem can be derived from Eq. (186), this form can be considered the fundamental relationship for the linear theory of irreversibility.

We now consider the full path distribution function $W_1(q_1,\cdots,q_n;t)$ for a classical step-driven process. The step-driven response is written in terms of $W_1(q_1,\cdots,q_n;t)$ as

$$\langle q_i(t)\rangle = \int_{-\infty}^{\infty} dq_1\cdots\int_{-\infty}^{\infty} dq_n q_i W_1(q_1,\cdots,q_n;t). \quad (188)$$

According to Eq. (36), however, $\langle q_i(t)\rangle$ can also be written

$$\langle q_i(t)\rangle = \int_{-\infty}^{\infty} dq_1\cdots\int_{-\infty}^{\infty} dq_n q_i W_1{}^{(0)}(q_1,\cdots,q_n) \times\langle \exp[-\beta\sum_j F_j q_j(-t)\rangle_{q_1\cdots q_n}{}^{(0)} / \langle \exp(-\beta\sum_j F_j q_j)\rangle^{(0)}. \quad (189)$$

The t dependence of the time-stationary quantity $\langle \exp(-\beta\sum_j F_j q_j) q_i(t)\rangle^{(0)}$ has been translated into the exponential $\exp(-\beta\sum_j F_j q_j)$.

$$\langle \exp[-\beta\textstyle\sum_j F_j q_j(-t)]\rangle_{q_1\cdots q_n}{}^{(0)}$$

denotes the equilibrium expectation value of

$$\exp(-\beta\textstyle\sum_j F_j q_j)$$

at time $-t$ conditional on all variables having the values $q_1,\cdots,q_n$ at time zero.

Since Eqs. (188) and (189) must be identical, it follows that the step-driven path distribution function $W_1(q_1,\cdots,q_n;t)$ is given, in the classical limit, by

$$W_1(q_1,\cdots,q_n;t) = W_1{}^{(0)}(q_1,\cdots,q_n)\langle \exp[-\beta\sum_j F_j q_j(-t)]\rangle_{q_1\cdots q_n}{}^{(0)} / \langle \exp-\beta\sum_j F_j q_j)\rangle^{(0)}. \quad (190)$$

Equation (190) expresses the path distribution function, characterizing the time evolution of a step-driven ensemble, in terms of the equilibrium probability distribution $W_1{}^{(0)}(q_1,\cdots,q_n)$, together with the conditional expectation value $\langle \exp[-\beta\sum_j F_j q_j(-t)\rangle_{q_1\cdots q_n}{}^{(0)}$.

The significance of this result for the path distribution function can be made more apparent by rewriting Eq. (36) for $\langle q_i(t)\rangle$ in the form

$$\langle q_i(t)\rangle = \int_{-\infty}^{\infty} dq_1\cdots\int_{-\infty}^{\infty} dq_n W_1{}^{(0)}(q_1,\cdots,q_n) \times\exp(-\beta\sum_j F_j q_j)\langle q_i(t)\rangle_{q_1\cdots q_n}{}^{(0)} / \langle \exp(-\beta\sum_j F_j q_j)\rangle^{(0)}. \quad (191)$$

However, letting $t=0$ in Eq. (189), we find that the initial perturbed equilibrium probability distribution

$W_1(q_1,\cdots,q_n;0)$ is given by

$$W_1(q_1,\cdots q_n;0) = W_1^{(0)}(q_1,\cdots,q_n)\exp(-\beta\sum_j F_jq_j)/ \times\langle\exp(-\beta\sum_j F_jq_j)\rangle^{(0)}. \quad (192)$$

Inserting this result in Eq. (191), we obtain

$$\langle q_i(t)\rangle = \int_{-\infty}^{\infty} dq_1\cdots\int_{-\infty}^{\infty} dq_n W_1(q_1,\cdots,q_n;0) \times\langle q_i(t)\rangle_{q_1\cdots q_n}{}^{(0)}. \quad (193)$$

Equation (193) shows explicitly how the step-driven response $\langle q_i(t)\rangle$ is built up from the regression of the equilibrium fluctuations, characterized by the equilibrium conditional expectation value $\langle q_i(t)\rangle_{q_1\cdots q_n}{}^{(0)}$, and weighted according to the initial perturbed distribution $W_1(q_1,\cdots,q_n;0)$. Although this result is precisely that which we might intuitively expect, it has often been pointed out in the literature[2,6] that there is no clear *a priori* justification for identifying the behavior of a system undergoing an irreversible process with the spontaneous equilibrium fluctuations in this way. The equilibrium fluctuations are microscopic in nature and generally on an extremely small scale, whereas the macroscopic response functions measured in the laboratory are normally orders of magnitude larger. Nevertheless, the proof of the assumption that macroscopic processes follow the same laws of regression as the equilibrium fluctuations is provided by Eq. (193).

16. THE JOINT PATH DISTRIBUTION FUNCTION

Just as a more detailed description of the equilibrium behavior can be obtained by introducing joint probability distributions containing two or more times, it is possible to describe in greater detail the evolution of a driven ensemble by introducing joint path distribution functions. In this final section we extend the theory of the previous section to include the joint path distribution $W_2(q,t;q',t')$, which specifies the probability that the variable corresponding to the operator Q has the value q at time t *and* the value q' at time t' in a driven ensemble. We consider explicitly the case of a single variable, although the extension of the theory to multidimensional processes is quite straightforward.

$W_2(q,t;q',t')$ can be expressed in terms of its characteristic function $K_2(\nu,t;\nu',t')$.

$$W_2(q,t;q',t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\nu\int_{-\infty}^{\infty} d\nu' e^{i\nu q}e^{i\nu' q'}K_2(\nu,t;\nu',t') \quad (194)$$

where $K_2(\nu,t;\nu',t')$ is given by

$$K_2(\nu,t;\nu',t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} dq\int_{-\infty}^{\infty} dq' e^{-i\nu q}e^{-i\nu' q'}W_2(q,t;q',t') = \frac{1}{2\pi}\langle e^{-i\nu q(t)}e^{-i\nu' q(t')}\rangle. \quad (195)$$

According to the discussion of Sec. 3, the quantum-mechanical form of the driven second moment $K_2(\nu,t;\nu',t')$ is

$$K_2(\nu,t;\nu',t') = \frac{1}{2\pi}\langle\tfrac{1}{2}[e^{-i\nu Q(t)},e^{-i\nu' Q(t')}]_+\rangle^{(0)} \quad (196)$$

so that Eq. (194) for $W_2(q,t;q',t')$ becomes

$$W_2(q,t;q',t') = \frac{1}{(2\pi)^2}\int_{-\infty}^{\infty} d\nu\int_{-\infty}^{\infty} d\nu'\langle\tfrac{1}{2}[e^{i\nu[q-Q(t)]},e^{i\nu'[q'-Q(t')]}]_+\rangle^{(0)} = \langle\tfrac{1}{2}[\delta(q-Q(t)),\delta(q'-Q(t'))]_+\rangle^{(0)}. \quad (197)$$

Equation (197) states that $W_2(q,t;q',t')$ is just the driven correlation moment between the δ-function operators $\delta(q-Q(t))$ and $\delta(q'-Q(t'))$. Therefore, the treatment of driven second moments developed throughout the preceding sections of this paper is immediately applicable to the joint path distribution function.

We limit ourselves here to a discussion of the joint path distribution function for a classical step-driven process. The driven second moment $\langle q(t)q(t')\rangle$ can be written in terms of $W_2(q,t;q',t')$ as

$$\langle q(t)q(t')\rangle = \int_{-\infty}^{\infty} dq\int_{-\infty}^{\infty} dq' qq' W_2(q,t;q',t'). \quad (198)$$

On the other hand, according to Eq. (171), $\langle q(t)q(t')\rangle$ can be computed according to

$$\langle q(t)q(t')\rangle = \int_{-\infty}^{\infty} dq\int_{-\infty}^{\infty} dq' qq' W_2^{(0)}(q;q',t-t') \times\frac{\langle e^{-\beta Fq(-t')}\rangle_{q,q'(t-t')}{}^{(0)}}{\langle e^{-\beta Fq}\rangle^{(0)}} \quad (199)$$

where $W_2^{(0)}(q;q',t-t')$ is the (time-stationary) equilibrium joint probability distribution and $\langle e^{-\beta Fq(-t')}\rangle_{q,q'(t-t')}{}^{(0)}$ denotes the equilibrium expectation value of $e^{-\beta Fq}$ at time $-t'$ conditional on q at time zero and q' at time $(t-t')$.

From Eqs. (198) and (199) it follows that the step-driven joint path distribution function is given, in the classical limit, by

$$W_2(q,t;q',t')=W_2^{(0)}(q;q',t-t')\times\frac{\langle e^{-\beta Fq(-t')}\rangle_{q,q'(t-t')}{}^{(0)}}{\langle e^{-\beta Fq}\rangle^{(0)}}. \quad (200)$$

Thus, $W_2(q,t;q',t')$ is related in a particularly simple way to the equilibrium joint probability $W_2^{(0)}(q;q',t-t')$ and the equilibrium conditional expectation value $\langle e^{-\beta Fq(-t')}\rangle_{q,q'(t-t')}{}^{(0)}$.

Finally, we rewrite Eq. (171) for $\langle q(t)q(t')\rangle$ so as to further emphasize the relationship of this quantity to the regression of equilibrium fluctuations.

$$\langle q(t)q(t')\rangle=\int_{-\infty}^{\infty}dqW_1^{(0)}(q)e^{-\beta Fq}\frac{\langle q(t)q(t')\rangle_q{}^{(0)}}{\langle e^{-\beta Fq}\rangle^{(0)}}. \quad (201)$$

$\langle q(t)q(t')\rangle_q{}^{(0)}$ denotes the second equilibrium correlation moment between $q(t)$ and $q(t')$, conditional on the value q at time zero. However, according to Eq. (192) $W_1^{(0)}(q)e^{-\beta Fq}/\langle e^{-\beta Fq}\rangle^{(0)}$ is just the initial ($t=0$) perturbed equilibrium distribution function $W_1(q,0)$. Hence, Eq. (200) becomes

$$\langle q(t)q(t')\rangle=\int_{-\infty}^{\infty}dqW_1(q,0)\langle q(t)q(t')\rangle_q{}^{(0)}. \quad (202)$$

This result shows explicitly how the step-driven second moment $\langle q(t)q(t')\rangle$ is built up from the regression of the equilibrium fluctuations, characterized by the conditional equilibrium second moment $\langle q(t)q(t')\rangle_q{}^{(0)}$ and weighted according to the initial perturbed distribution $W_1(q,0)$.

APPENDIX A

In this appendix we compare a system driven from $t\to-\infty$ by the step-function forces defined in Sec. 4 to the subsequent motion of a system characterized at $t=0$ by the generalized canonical density operator $\rho(0)$ of Eq. (25).

Consider the first-order term $\langle Q_i(t)\rangle^{(1)}$ in the response during a step-driven process, as given by Eq. (23). The equilibrium expectation value appearing in this expression can be written

$$\begin{aligned}\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)} &=\langle Q_j^{(0)}(t_1)Q_i^{(0)}(t) - Q_i^{(0)}(t)\exp[\pm\beta H^{(0)}]Q_j^{(0)}(t_1)\rangle^{(0)}\\ &=\langle Q_j^{(0)}(t_1)Q_i^{(0)}(t)-\exp[\beta H^{(0)}]Q_j^{(0)}(t_1)\times\exp[-\beta H^{(0)}]Q_i^{(0)}(t)\rangle^{(0)} \quad (A\text{-}1)\end{aligned}$$

where we have inserted $\exp[\pm\beta H^{(0)}]$ in the second term as indicated and permuted the operators cyclicly.

This form can be further rewritten as follows.

$$\begin{aligned}\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)} &=-\int_0^\beta d\lambda_1\frac{\partial}{\partial\lambda_1}\langle\exp[\lambda_1 H^{(0)}]Q_j^{(0)}(t_1)\times\exp[-\lambda H^{(0)}]Q_i^{(0)}(t)\rangle^{(0)}\\ &=-\int_0^\beta d\lambda_1\langle[H^{(0)},Q_j^{(0)}(t_1-i\hbar\lambda_1)]_-Q_i^{(0)}(t)\rangle^{(0)}. \quad (A\text{-}2)\end{aligned}$$

Noting that $[H^{(0)},Q_j^{(0)}(t_1-i\hbar\lambda_1)]=-i\hbar\dot{Q}_j^{(0)}(t_1-i\hbar\lambda_1)$, we have

$$\langle[Q_j^{(0)}(t_1),Q_i^{(0)}(t)]_-\rangle^{(0)}=i\hbar\int^\beta d\lambda_1\langle\dot{Q}_j^{(0)}(t_1-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}. \quad (A\text{-}3)$$

Inserting the result (A-3) into Eq. (23) and performing the time integration, we obtain

$$\langle Q_i(t)\rangle^{(1)}=-\sum_j F_j\int_0^\beta d\lambda_1[\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}-\lim_{t_1\to-\infty}\langle Q_j^{(0)}(t_1-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}]. \quad (A\text{-}4)$$

The contribution to (A-4) from the $t_1\to-\infty$ limit is evaluated by taking

$$\lim_{t_1\to-\infty}\int_0^\beta d\lambda_1\langle Q_j^{(0)}(t_1-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}=\lim_{T\to-\infty}\frac{1}{T}\int_0^\beta d\lambda_1\int_0^T dt_1\langle Q_j^{(0)}(t_1-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}. \quad (A\text{-}5)$$

Because of the factor $1/T$, the oscillatory part of the integrand gives no contribution, and we are left with

$$\lim_{t_1\to-\infty}\int_0^\beta d\lambda_1\langle Q_j^{(0)}(t_1-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}=\int_0^\beta d\lambda_1\langle\tilde{Q}_i\tilde{Q}_j\rangle^{(0)}=\beta\langle\tilde{Q}_i\tilde{Q}_j\rangle^{(0)} \quad (A\text{-}6)$$

where $\tilde{Q}_1$ denotes the diagonal portion of the operator Q_i with respect to the unperturbed Hamiltonian $H^{(0)}$.

Using the result (A-6), Eq. (A-4) for $\langle Q_i(t)\rangle^{(1)}$ becomes

$$\langle Q_i(t)\rangle^{(1)}=-\sum_j F_j\left[\int_0^\beta d\lambda_1\langle Q_j^{(0)}(-i\hbar\lambda_1)Q_i^{(0)}(t)\rangle^{(0)}-\beta\langle\tilde{Q}_i\tilde{Q}_j\rangle^{(0)}\right]. \quad (A\text{-}7)$$

The paradoxical contrast between Eq. (A-7) and Eq. (32) for $\langle Q_i(t)\rangle^{(1)}$ has been discussed by R. Kubo,[9] who suggests that the former equation refers to an adiabatic system, whereas the latter refers to an isothermal system, so that the two need not be equal.

However, the same difficulty is found to arise even in an equilibrium isothermal system. Thus, in the limit $t\rightarrow\infty$, the equilibrium correlation moment

$$\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}$$

becomes

$$\lim_{t\rightarrow\infty}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}=\langle\tilde{Q}_i\tilde{Q}_j\rangle^{(0)} \qquad \text{(A-8)}$$

where the limit is evaluated as in Eq. (A-6). In order for the ensemble to be ergodic, however, in the sense that as $t\rightarrow\infty$ the quantities involved become completely uncorrelated, we require

$$\lim_{t\rightarrow\infty}\langle\tfrac{1}{2}[Q_i,Q_j^{(0)}(t)]_+\rangle^{(0)}=\langle Q_i\rangle^{(0)}\langle Q_j\rangle^{(0)}. \qquad \text{(A-9)}$$

We believe that the resolution of this problem lies in the following interpretation. Throughout the discussion we consider an ensemble in continual interaction with a temperature reservoir. This should be contrasted with the interpretation adopted by Kubo, which is that the interaction with the temperature reservoir is removed at the moment of imposition of the applied forces, the ensemble thereafter being adiabatic. In our interpretation the Hamiltonian $H^{(0)}$ therefore contains a term corresponding to the interaction with a temperature reservoir, which we have not indicated explicitly for reasons to be explained momentarily. The additional interaction term induces incoherent transitions among the states of the system such that the ensemble "forgets" the details of its previous behavior after a sufficiently long time. This insures that the ensemble satisfies the ergodic requirement states in Eq. (A-9).

The justification for not indicating the interaction term explicitly in calculating the driven response is as follows. It is always possible to choose the term of interaction with the temperature reservoir to be so small that, for times comparable to those in which we are interested, the disordering effects arising from this source are negligible. Since Eq. (32) gives the first-order response $\langle Q_i(t)\rangle^{(1)}$ corresponding to an ensemble chosen so as to be in (generalized) canonical equilibrium up to $t=0$, it must therefore yield the appropriate evolution of $\langle Q_i(t)\rangle^{(1)}$ for any finite time $t>0$.

However, in the limit $t\rightarrow\infty$, the effects of the continued temperature interaction manifest themselves, regardless of the strength of the interaction. In this limit Eq. (32) reduces to

$$\langle Q_i(t)\rangle^{(1)}\underset{t\rightarrow\infty}{\longrightarrow}-\sum_j F_j[\beta\langle\tilde{Q}_i\tilde{Q}_j\rangle^{(0)}-\beta\langle Q_i\rangle^{(0)}\langle Q_j\rangle^{(0)}]. \qquad \text{(A-10)}$$

Here it is necessary to take explicit account of the interaction with the temperature reservoir. This can be accomplished, according to a comparison of Eqs. (A-8) and (A-9), by replacing the quantity $\tilde{Q}_i$ by the average value $\langle Q_i\rangle^{(0)}$. The foregoing arguments apply as well to the time evolution of the full step-driven response $\langle Q_i(t)\rangle$ given in Eq. (26), in the expansion of which Eq. (32) is the first-order term.

In order to make Eq. (A-7) consistent with our interpretation, we recall that the quantity $\tilde{Q}_i$ appearing in it arose from the evaluation of a $t\rightarrow\infty$ limit. Again we take explicit account of the temperature interaction in this limit by replacing $\tilde{Q}_i$ by $\langle Q_i\rangle^{(0)}$. Thus, Eq. (A-7) becomes identical to Eq. (32). If we evaluate Eq. (24), for $\langle Q_i(t)\rangle^{(2)}$ and the corresponding higher-order terms in the response $\langle Q_i(t)\rangle$ during a step-driven process, replacing quantities of the type $\tilde{Q}_i$ by $\langle Q_i\rangle^{(0)}$ whenever they appear, we obtain expressions identical to Eqs. (33), (34), etc. The technique for accomplishing this is essentially an iteration of that employed in putting Eq. (23) into the form (A-7).

APPENDIX B

The causal nature of a linear process finds expression in the well-known Kramers-Krönig dispersion formulas relating the real and imaginary parts of the complex admittance matrix elements.

We first indicate the proof of these relations. Consider the Fourier transform of Eq. (63) for $Y_{ij}(\omega)$.

$$\int_{-\infty}^{\infty}d\omega e^{i\omega t}\frac{Y_{ij}(\omega)}{i\omega}=\int_{-\infty}^{\infty}d\omega\int_0^{\infty}dt' e^{i\omega(t-t')}\phi_{ij}^{(1)}(t')$$
$$=2\pi\int_0^{\infty}dt'\delta(t-t')\phi_{ij}^{(1)}(t'). \qquad \text{(B-1)}$$

Therefore,

$$\int_{-\infty}^{\infty}d\omega e^{i\omega t}\frac{Y_{ij}(\omega)}{i\omega}=\begin{cases}2\pi\phi_{ij}^{(1)}(t) & \text{for } t>0\\ 0 & \text{for } t<0\end{cases} \qquad \text{(B-2)}$$

whence it follows that $Y_{ij}(\omega)/i\omega$ can have poles only in the upper half of the complex ω plane.

For a function $Y_{ij}(\omega)/i\omega$ which is everywhere analytic in the lower half of the ω plane, Cauchy's integral theorem states that

$$\frac{Y_{ij}(\omega)}{i\omega}=\frac{P}{i\pi}\oint d\omega'\frac{Y_{ij}(\omega')}{i\omega'(\omega'-\omega)}$$
$$=-\frac{P}{i\pi}\int_{-\infty}^{\infty}d\omega'\frac{Y_{ij}(\omega')}{i\omega'(\omega'-\omega)} \qquad \text{(B-3)}$$

where the complex integration is taken around the contour shown in Fig. 5, and P denotes a Cauchy principal value. Decomposing $Y_{ij}(\omega)$ into its real and imaginary parts $Y_{ij}(\omega)=\text{Re }Y_{ij}(\omega)+i\text{ Im }Y_{ij}(\omega)$ and equating the real and imaginary parts of Eq. (B-3), we

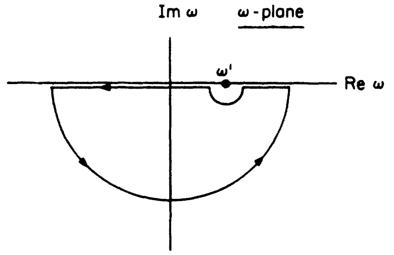

FIG. 5.

obtain

$$\frac{\operatorname{Re} Y_{ij}(\omega)}{\omega}=-\frac{P}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\operatorname{Im} Y_{ij}(\omega')}{\omega'(\omega'-\omega)}, \quad \text{(B-4)}$$

$$\frac{\operatorname{Im} Y_{ij}(\omega)}{\omega}=\frac{P}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\operatorname{Re} Y_{ij}(\omega')}{\omega'(\omega'-\omega)}. \quad \text{(B-5)}$$

Equations (B-4) and (B-5) are the Kramers-Krönig dispersion relations.

We use Eq. (B-5), together with the results of equilibrium fluctuation theory, to derive the $t=0$ form of the fluctuation-dissipation theorem, Eq. (73). Letting $\omega=0$, the quantity $[\operatorname{Im} Y_{ij}(\omega)/\omega]$ becomes simply the capacitance $[\partial\langle q_j\rangle^{(0)}/\partial F_i]$, so that Eq. (B-5) assumes the form

$$\frac{\partial\langle q_j\rangle^{(0)}}{\partial F_i}=\frac{P}{\pi}\int_{-\infty}^{\infty} d\omega' \frac{\operatorname{Re} Y_{ij}(\omega')}{\omega'^2}. \quad \text{(B-6)}$$

However, for a generalized canonical ensemble in contact with a series of reservoirs with constant intensive parameters $\cdots, F_i, F_j, \cdots$, the equilibrium second moment $\langle q_i q_j\rangle^{(0)}$ is given by[16]

$$\langle q_i q_j\rangle^{(0)}=-\frac{1}{\beta}\frac{\partial\langle q_j\rangle^{(0)}}{\partial F_i}. \quad \text{(B-7)}$$

Substitution of Eq. (B-7) into Eq. (B-6) yields the result

$$\langle q_i q_j\rangle^{(0)}=-\frac{P}{\pi\beta}\int_{-\infty}^{\infty} d\omega \frac{\operatorname{Re} Y_{ij}(\omega)}{\omega^2} \quad \text{(B-8)}$$

which is identical to Eq. (73) with t set$=0$.

APPENDIX C

In this Appendix, following Kubo,[9] we evaluate the universal function $\Gamma(t)$, defined in Eq. (83). For $t>0$, this can be calculated by performing a contour integration around the upper half of the complex ω plane, while for $t<0$, the integration is taken around the lower half-plane. We consider explicitly the case $t>0$, since the $t<0$ calculation proceeds in an identical way.

Letting $\alpha=\hbar\beta\omega$, Eq. (83) can be rewritten as a contour integral in the complex α plane.

$$\Gamma(t)=\frac{1}{\pi\hbar}\oint d\alpha \exp\left(i\frac{\alpha t}{\hbar\beta}\right)\frac{1}{\alpha}\left(\frac{1-e^{-\alpha}}{1+e^{-\alpha}}\right). \quad \text{(C-1)}$$

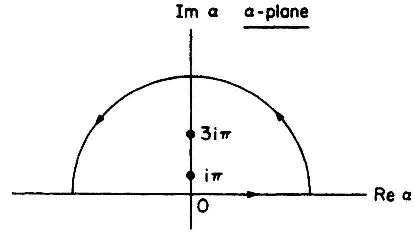

FIG. 6.

The integral is to be taken along the contour shown in Fig. 6. The integrand has simple poles at $\alpha_l=(2l+1)i\pi$, $l=0, \pm 1, \cdots$. The residue of the integrand at the pole is obtained by letting $\alpha=\alpha_l+\Delta\alpha$, multiplying the integrand by $\Delta\alpha$, and taking the limit as $\Delta\alpha\rightarrow 0$. Thus

residue at α_l

$$=\lim_{\Delta\alpha\rightarrow 0}\frac{\Delta\alpha}{\pi\hbar}\exp\left[i\frac{(\alpha_l+\Delta\alpha)}{\hbar\beta}t\right]\frac{1}{(\alpha_l+\Delta\alpha)}\left[\frac{1-e^{-(\alpha_l+\Delta\alpha)}}{1+e^{-(\alpha_l+\Delta\alpha)}}\right]$$

$$=\frac{2}{\pi\hbar}\frac{\exp[-(2l+1)\pi t/\hbar\beta]}{(2l+1)\pi i}\lim_{\Delta\alpha\rightarrow 0}\frac{\Delta\alpha}{(1-e^{-\Delta\alpha})}$$

$$=\frac{2\exp[-(2l+1)\pi t/\hbar\beta]}{\pi^2\hbar(2l+1)i}. \quad \text{(C-2)}$$

Equation (C-1) ls now evaluated by taking

$$\Gamma(t)=2\pi i\sum_{l=0}^{\infty}(\text{residue at } \alpha_l)$$

$$=\frac{4}{\pi\hbar}\sum_{l=0}^{\infty}\frac{\exp[-(2l+1)\pi t/\hbar\beta]}{(2l+1)}. \quad \text{(C-3)}$$

It is convenient to take the time derivative of Eq. (C-3) before performing the summation.

$$\frac{d\Gamma(t)}{dt}=-\frac{4}{\hbar^2\beta}\sum_{l=0}^{\infty}\exp[-(2l+1)\pi t/\hbar\beta]$$

$$=-\frac{4}{\hbar^2\beta}\frac{\exp[-(\pi t/\hbar\beta)]}{1-\exp(-2\pi t/\hbar\beta)}=-\frac{2}{\hbar^2\beta}\operatorname{csch}\frac{\pi t}{\hbar\beta}. \quad \text{(C-4)}$$

In performing the summation in Eq. (C-4) we have made use of the expansion $\sum_l x^l=[1/(1-x)]$. We now integrate Eq. (C-4) with respect to t, which yields finally the desired result,

$$\Gamma(t)=\frac{2}{\pi\hbar}\ln\coth\frac{\pi t}{2\hbar\beta}. \quad \text{(C-5)}$$

The corresponding result for $t<0$ is identical to Eq. (C-5), except that t is replaced by $-t$. Thus, for all t, we can write that

$$\Gamma(t)=\frac{2}{\pi\hbar}\ln\coth\frac{\pi|t|}{2\hbar\beta}. \quad \text{(C-6)}$$