On a Theorem of Irreversible Thermodynamics*

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A relation is obtained between the parameter describing the irreversible response of a driven dissipative system and the spontaneous fluctuations of the thermodynamic extensive parameters of the system in equilibrium. The development given in this paper extends the theorem, previously proven in the statistical mechanical domain, to the macroscopic thermodynamic domain.

1. INTRODUCTION

THIS paper is one of a series of contributions to the development of a theory of "irreversible thermodynamics"—that is, to the extension of the methods of thermodynamics to the treatment of real irreversible processes. We shall show that the mean square deviation of the spontaneously fluctuating extensive parameters of a thermodynamic system in equilibrium is related to the dissipative part of the admittance function which characterizes the irreversible response of the system to applied forces. If $\langle\xi^2\rangle$ denotes the mean square fluctuation in the frequency interval determined by the range of integration, we shall show that

$$\langle\xi^2\rangle=\frac{-2k}{\pi}\int d\omega\sigma_s(\omega)\omega^{-2} \tag{1.1}$$

or

$$\langle\xi^2\rangle=\frac{2kT}{\pi}\int d\omega\sigma_U(\omega)\omega^{-2}. \tag{1.2}$$

The first of these equations applies to a system in which all extensive parameters other than that which fluctuates are held constant, whereas the second equation applies to a system with similar constraints except that the constraint on the energy is replaced by the condition of adiabatic insulation. The quantities $\sigma_s(\omega)$ and $\sigma_U(\omega)$ are conductances defined appropriately to these respective constraints. These equations may be re-expressed, although somewhat less directly, in terms of equivalent fluctuating forces and then appear as generalizations of the Nyquist electrical noise formula.[1]

The modern theory of irreversible thermodynamics was first projected in 1931 by Onsager[2] with the formulation of a general relation of reciprocity in the mutual interference of two simultaneous irreversible processes. Applications of this one basic theorem constitute the totality of the existing theory of irreversible thermodynamics.[3]

There are two possible methods of approach to the theory of irreversible thermodynamics, which might be characterized as the statistical approach and the thermodynamic approach. The statistical approach consists of generalizing the methods of statistical mechanics, and a theorem proved in this framework must then, of course, be projected into the macroscopic thermodynamic domain by a reasoning similar to that which projects the statistical mechanical H theorem into the macroscopic second law of thermodynamics. The alternative, or thermodynamic, approach consists in generalizing the methods of thermodynamics itself, which is already on a macroscopic level. Whereas the results of the thermodynamic approach are thus in more immediate contact with macroscopic irreversibility than are the results of the statistical approach, the postulates of the latter are closer to fundamental theory. Each approach clearly has its advantages and each may be independently prosecuted. The Onsager reciprocity theorem, originally obtained by a thermodynamic approach, has also been derived by the statistical approach.[4]

The touchstone of the thermodynamic approach to irreversibility theory lies in the intimate connection between irreversible processes and the regression of spontaneous fluctuations in equilibrium systems. This connection has occasionally been criticized because conventional thermodynamic fluctuation theory is an approximate theory valid only for small fluctuations, whereas real irreversible processes may involve appreciable deviations from equilibrium.[5] However, in a previous paper[6] of this series we have reformulated thermodynamic fluctuation theory on an exact basis which is valid for fluctuations of arbitrary size. The thermodynamic approach, based on the analysis of the regression of spontaneous fluctuations, will be employed in this paper.

In addition to Onsager's reciprocity theorem a new theorem has recently been established.[7] This relates the dissipation parameter (the "resistance") to the spectral density of the equilibrium fluctuations and is the

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[1] H. Nyquist, Phys. Rev. **32**, 110 (1928).
[2] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931); see also H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945).
[3] See S. R. DeGroot, *Thermodynamics of Irreversible Processes* (North-Holland Publishing Company, Amsterdam, 1951).
[4] H. B. Callen, thesis, Department of Physics, Massachusetts Institute of Technology, 1948.
[5] The extent of the deviation from equilibrium which is compatible with the validity of the Onsager reciprocity theorem is established by the statistical approach (reference 4) and has also been considered by I. Priogogine (see bibliography in reference 3).
[6] R. F. Greene and H. B. Callen, Phys. Rev. **83**, 1231 (1951).
[7] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).

generalized analog of the Nyquist electrical noise formula. The statistical approach was employed in the derivation of this theorem, and the final projection of the theorem into the macroscopic domain was omitted. Thus, although a number of significant implications can be drawn from the theorem, nevertheless it remains a statistical mechanical rather than a thermodynamic theorem. It is, in fact, difficult to see from the statistical derivation what the macroscopic operational meaning of certain quantities appearing in the formulas would be. It is, therefore, necessary either to close the hiatus between the statistical theorem and the macroscopic domain or to re-establish the theorem entirely within the thermodynamic domain. In this paper we shall establish the theorem by a totally thermodynamic approach.

An extension of these results to systems having more than one fluctuating parameter will be shown in a subsequent paper to yield a generalization of Onsager's reciprocal relations.[8]

2. THE METHOD OF APPROACH

The theorem which we wish to establish is a relation between the generalized admittance (or impedance) of a dissipative system and the spectral density of the spontaneous fluctuations exhibited by the system in equilibrium. The proof employs certain theorems relating to random variables, as summarized in Appendix A. In particular the Wiener-Khinchin formula (A.18) relates the spectral density $G(\omega)$ to the autocorrelation function $\langle\xi(t)\xi(t+\tau)\rangle$,

$$G(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\tau\langle\xi(t)\xi(t+\tau)\rangle e^{-i\omega\tau}. \tag{2.1}$$

The autocorrelation function, in turn, is given by (see Eq. (A.6))

$$\langle\xi(t)\xi(t+\tau)\rangle=\int d\xi' W_1(\xi')\xi'\langle\tau, \xi'|\xi\rangle, \tag{2.2}$$

where $W_1(\xi')d\xi'$ is the probability of finding ξ in the range $\xi'<\xi<\xi'+d\xi'$ and where $\langle\tau, \xi'|\xi\rangle$ is the expectation value of ξ at a given time if it is known that ξ had the value ξ' at τ seconds earlier. Thus the theory of random variables permits us to compute the spectral density of the equilibrium fluctuations if we know the two quantities $W_1(\xi)$ and $\langle\tau, \xi'|\xi\rangle$. The function $W_1(\xi)$ is, however, simply the distribution function of conventional thermodynamic fluctuation theory. The method of computing the conditional average $\langle\tau, \xi'|\xi\rangle$ is the essential element of the proof. The average shape of a spontaneous fluctuation pulse is identical with the observed shape of a macroscopic irreversible decay toward equilibrium and is, therefore, describable in terms of the macroscopic admittance function. The conditional average $\langle\tau, \xi'|\xi\rangle$ can, therefore, be computed in terms of the admittance function, and Eqs. (2.1) and (2.2) then yield the desired relation between the spectral density $G(\omega)$ and the admittance function.

Spontaneous fluctuations under various types of constraint are of interest. A system may be placed under constraints microcanonical with respect to all but that particular extensive parameter in the fluctuation of which we are interested. Alternatively, the microcanonical constraint on the energy may be replaced by thermal isolation (all extensive parameters other than the energy and the parameter whose fluctuation we are interested in remain microcanonically constrained). Finally, the constraints may be such that more than one parameter is permitted to fluctuate. We shall confine ourselves in this paper to consideration of the first two of the above mentioned types of constraints, postponing treatment of several simultaneously fluctuating parameters to a later paper. The microcanonical constraints will be considered first, and only minor alterations in this development (considered in Sec. VI) will be required to adapt the results to the fluctuations under thermal isolation.

3. THE ADMITTANCE OF THERMODYNAMIC SYSTEMS

In this section we shall formulate a thermodynamic definition of the admittance which characterizes the response of thermodynamic systems to applied "forces." Certain analytic characteristics of the admittance will be dictated by thermodynamic considerations.

It is intuitively clear that a thermodynamic system can be subjected to periodic generalized forces, evoking periodic changes in the thermodynamic parameters. Thus, a gas enclosed in a cylinder with a movable piston can be subjected to a periodic external pressure evoking periodic changes in the volume. Similarly, a periodic ambient temperature will evoke periodic changes in the internal energy. For very low frequencies the system will respond quasi-statically to the applied force, but at higher frequencies the system responds in an essentially irreversible way. The fact that the conventional intensive parameters (temperature, pressure, etc.) have no strict meaning in a nonequilibrium system constitutes the chief difficulty in the formulation of a quantitative thermodynamic definition of the forces and hence also of the admittance.

We shall find it convenient to frame our thermodynamic analysis in the "entropy language," in which the entropy S is taken as a function of the internal energy X_0 and of the equilibrium values of the various other extensive parameters of the system $X_1, X_2\cdots$ (volume, mole numbers, etc.),

$$S=S(X_0, X_1, X_2, \cdots). \tag{3.1}$$

The intensive parameters in this formulation are

$$F_K\equiv\partial S/\partial X_K, \tag{3.2}$$

[8] A preliminary expression of these results appears in R. F. Greene, thesis (University of Pennsylvania, September, 1951) (unpublished).

so that $F_0=1/T$, and various other intensive parameters are P/T, $-\mu/T$, etc. Except for F_0, the intensive parameters in the entropy language are simply $-1/T$ times the intensive parameters in the more common "energy language." The instantaneous values of the extensive parameters will be denoted by x_j, as distinguished from the equilibrium values denoted by X_j. The deviation of x_j from its equilibrium value will be denoted by ξ_j,

$$\xi_j \equiv x_j - X_j. \tag{3.3}$$

The boundary conditions on an equilibrium system are generally idealized as being of either of two limiting types. That is, the extensive parameters may be rigidly constrained (as is the volume of a system enclosed in a rigid box) or they may be completely unconstrained (as is the volume of a system enclosed within a cylinder fitted with a freely movable piston). In order that the latter type of system may be in equilibrium it must be in interaction with another system, and the condition of equilibrium is the equality of the appropriate intensive parameters. Thus, a system enclosed in a cylinder with a movable diathermal piston will be in equilibrium if the outside of the piston is in contact with another system and if the two systems have equal values of the intensive parameters $1/T$ and P/T. A system may be said to be "microcanonical" with respect to those of its extensive parameters which are rigidly constrained and to be "canonical" with respect to those of its extensive parameters which are not constrained. The external system, with which the system of interest is in contact, will here be referred to as the "driving reservoir"; the rationale of this nomenclature will become evident immediately.

Let us suppose that the various extensive parameters of the driving reservoir are now varied in such a way that the intensive parameters of the driving reservoir vary sinusoidally with angular frequency ω. The system of interest is, in turn, acted upon by these *generalized forces* and will respond with a suitable time variation of its extensive parameters. *The generalized force is defined as the intensive parameter of the driving reservoir.* For the purpose of this definition we require two distinct characteristics of the driving reservoir. Firstly, the driving reservoir must have characteristic relaxation times small compared with $1/\omega$, so that it is always in quasi-static equilibrium and hence may be assigned instantaneous intensive thermodynamic parameters. Secondly, the size of the driving reservoir must be large in comparison with that of the system of interest, so that the induced changes in extensive parameters of the system do not react to change the instantaneous values of the intensive parameters of the driving reservoir.

Consider a system canonical with respect to a particular extensive parameter x (where for convenience we omit the subscript j) and microcanonical with respect to all other extensive parameters. Let the corresponding intensive parameter of the driving reservoir be $f(t)$ and write

$$f(t)=F+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega\beta(\omega)e^{i\omega t}. \tag{3.4}$$

This time-dependent applied force will induce a time-dependent response $x(t)$, which may be written in the form

$$x(t)=X+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty} d\omega\alpha(\omega)e^{i\omega t}, \tag{3.5}$$

where X is the equilibrium value of x associated with the value F of f. The amplitude of the response $\alpha(\omega)$ will be proportional to the amplitude of the applied force $\beta(\omega)$ for sufficiently small amplitudes. This linearity-in-the-small may be characterized by an impedance or an admittance function.

$$Y(\omega)=i\omega\alpha(\omega)/\beta(\omega). \tag{3.6}$$

An important analytic requirement on the admittance function follows from the fact that a constant impressed force induces a finite and definite value of the extensive parameter x. To formulate this requirement in terms of the properties of the admittance function, consider an impressed force of the constant magnitude

$$f(t)=F+\Delta F, \quad \text{or} \quad \delta f(t)=\Delta F, \tag{3.7}$$

which may be written in the form

$$\delta f(t)=\Delta F\int_{-\infty}^{\infty} d\omega\delta(\omega)e^{i\omega t}, \tag{3.8}$$

where $\delta(\omega)$ is the Dirac delta-function. The response follows from the definition (3.6) of the admittance function

$$\xi(t)=\Delta F\int_{-\infty}^{\infty} d\omega\delta(\omega)Y(\omega)e^{i\omega t}/i\omega, \tag{3.9}$$

and we now inquire as to what properties $Y(\omega)$ must have in order that $\xi(t)$ shall be a finite constant ΔX. Expanding $Y(\omega)$ in a Laurent series in the vicinity of $\omega=0$

$$Y(\omega)=\sum_{-\infty}^{\infty} y_n\omega^n, \tag{3.10}$$

and inserting this expansion into (3.9) we immediately see that all y_n with $n\leqslant 0$ must vanish if $\delta x(t)$ is to be bounded. Thus, we find

$$Y(\omega)=\omega y_1+O(\omega^2), \tag{3.11}$$

where $0(\omega^2)$ denotes a function of the order of ω^2. This gives, in turn, from (3.11) and (3.9)

$$\Delta X=\Delta F y_1/i, \tag{3.12}$$

or

$$y_1=i\partial X/\partial F, \tag{3.13}$$

where the partial derivative is a thermodynamic derivative implying constant values of all other extensive parameters. We thus finally conclude that the admittance function is of the form

$$Y(\omega)=i\omega\partial X/\partial F+O(\omega^2). \qquad (3.14)$$

The causal relationship between the applied force and the induced response has its analytic statement in the further requirement that the impedance function $Y(\omega)$ may have poles only in the upper half of the complex ω-plane. For then Jordan's Lemma[9] indicates that

$$\int_{-\infty}^{\infty} d\omega Y(\omega)e^{i\omega(t-\theta)}/i\omega=0 \text{ for } t<\theta, \qquad (3.15)$$

so that

$$\xi(t)=x(t)-X$$

$$=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\theta\delta f(\theta)Y(\omega)e^{i\omega(t-\theta)}/i\omega \qquad (3.16)$$

receives no contribution from $\delta f(\theta)\equiv f(\theta)-F$ except for times θ which precede t; that is, the response of the system is independent of the future behavior of the force.

It should be kept in mind that the admittance function describes the response to small changes in the force in the vicinity of some equilibrium value F. The admittance function is, therefore, a function of the equilibrium value F and is consequently a state function of the system. This is reflected in the relation between $Y(\omega)$ and $\partial X/\partial F$, the latter derivative being a conventional state function of the system.

4. THE CONDITIONAL EXPECTATION VALUE $\langle\tau, \xi'|\xi\rangle$

Having now formulated a thermodynamically acceptable definition of the admittance function, we proceed with the analysis as outlined in Sec. 2. In particular we are interested in computing the conditional expectation value $\langle\tau, \xi'|\xi\rangle$. That is, we seek the expectation value of ξ at time $t+\tau$ conditional on ξ having had the value ξ' at time t. This problem may be indicated schematically as follows: Let Fig. 1 represent a record of the spontaneous fluctuations of ξ as a function of time in an equilibrium system. On such a record we may locate all of the times at which ξ assumes the value ξ'. From each such value we then translate a distance τ to the right and read a new value of ξ. The average of all of these displaced values of ξ is $\langle\tau, \xi'|\xi\rangle$.

Consider now the collection of all the states represented in Fig. 1 by the condition $\xi=\xi'$. In this collection of macroscopic states every microstate consistent with the condition $\xi=\xi'$ is equally represented. This fact follows directly from the theory of thermodynamic fluctuations.[6] *Thus, the ensemble of microstates associated with the fluctuations to the value ξ' is precisely the conventional microcanonical ensemble associated with the extensive parameter $X+\xi'$.*

[9] E. Whittaker and G. Watson, *A Course of Modern Analysis* (Cambridge University Press, London, England, 1927).

To illustrate the above statement we may consider that the parameter x denotes the energy. The probability of an energy eigenstate with energy $X_0+\xi_0'$ is proportional to $\exp[-(X_0+\xi_0')/kT]$ and is, therefore, the same for every microstate of energy $X_0+\xi_0'$. Thus the collection of microstates associated with spontaneous fluctuations to the energy $X_0+\xi_0'$ is composed of all energy eigenstates with eigenvalues $X_0+\xi_0'$, each with equal probability. This is just the microcanonical ensemble associated with a system with total internal energy equal to $X_0+\xi_0'$.

The problem of obtaining $\langle\tau, \xi'|\xi\rangle$ may now be reformulated. If a microcanonical ensemble corresponding to $X+\xi'$ is established at time t, the ensemble average of ξ at time $t+\tau$ will be $\langle\tau, \xi'|\xi\rangle$. This suggests a direct macroscopic method of observing $\langle\tau, \xi'|\xi\rangle$. One merely imposes microcanonical constraints on the system, forcing it to have $x=X+\xi'$, and allows the system to come to equilibrium. The macroscopic system then represents the microcanonical ensemble of interest.

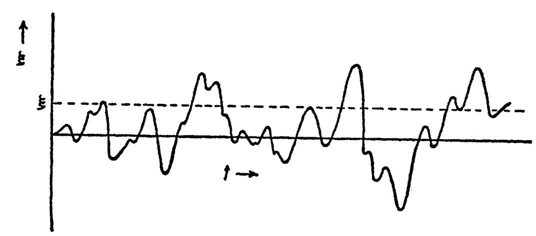

FIG. 1. The spontaneous fluctuations in an equilibrium system.

At time $t=0$ the microcanonical constraint is lifted, and the external force F is applied. The system then decays toward the value $x=X$. The macroscopically observed value of ξ at time $t=\tau$ is $\langle\tau, \xi'|\xi\rangle$. *Thus, by a consideration of the associated statistical ensembles we are led to a connection between spontaneous fluctuations and macroscopic irreversible processes.*

We can now identify the average regression of a spontaneous fluctuation with the decay function which describes the macroscopic behavior of a system after a microcanonical constraint has been lifted. Now there is a simple way to get this macroscopic decay function. Rather than impose a constraint which is to be lifted at $t=0$, we may impose an appropriately chosen force which is again to be lifted at $t=0$. This force, of course, is chosen so as to induce the same initial macroscopic state of the system as would the constraint which it replaces.[10] That is, we shall consider that until $t=0$ the system is in equilibrium with an applied force $F+\delta F$ of such a magnitude as to produce a value $X+\xi'$

[10] From the microscopic point of view we have merely replaced the initial microcanonical ensemble by a canonical ensemble—a change which, as we know, does not influence the macroscopic thermodynamics of the system.

of x. At time $t=0$ the applied force is suddenly changed to F, and the macroscopically observed value of ξ at $t=\tau$ is again $\langle\tau, \xi'|\xi\rangle$. The problem is now in a form suitable for analysis in terms of the impedance function. The applied force is

$$\delta f=\begin{cases}\delta F=(\partial F/\partial X)\xi', & t<0\\ 0, & t>0\end{cases} \tag{4.1}$$

or

$$\delta f=\frac{1}{(2\pi)^{\frac{1}{2}}}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega\left[\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\delta(\omega)+\frac{i}{(2\pi)^{\frac{1}{2}}\omega}\right]e^{i\omega t}, \tag{4.2}$$

where the improper integral is to be interpreted in terms of a Cauchy principal value. The response to this applied force is

$$\xi(t)=\frac{1}{(2\pi)^{\frac{1}{2}}}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega\frac{Y(\omega)}{i\omega}\left[\left(\frac{\pi}{2}\right)^{\frac{1}{2}}\delta(\omega)+\frac{i}{(2\pi)^{\frac{1}{2}}\omega}\right]e^{i\omega t}, \tag{4.3}$$

or using Eq. (3.14),

$$\xi(t)=\tfrac{1}{2}\xi'+\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega Y(\omega)\omega^{-2}e^{i\omega t}. \tag{4.4}$$

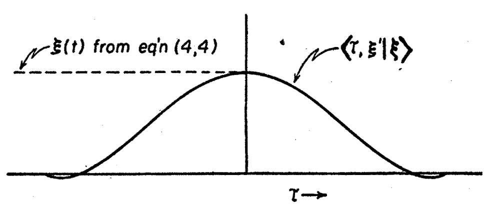

FIG. 2. The conditional expectation value $\langle\tau, \xi'|\xi\rangle$.

This equation gives a response such as is indicated schematically in Fig. 2. A moment's reflection makes it clear that $\xi(\tau)$ will be equal to $\langle\tau, \xi'|\xi\rangle$ only if τ is positive. The value of $\langle\tau, \xi'|\xi\rangle$ for negative values of τ may be immediately obtained, however, by invoking the principle of microscopic reversibility.[2] That is, we need merely realize that $\langle\tau, \xi'|\xi\rangle$ must be an even function of τ, because the spontaneous fluctuations of Fig. 1 are, on the average, symmetric.[11] Thus $\langle\tau, \xi'|\xi\rangle$ is given by the solid curve in Fig. 2, or

$$\langle\tau, \xi'|\xi\rangle=\tfrac{1}{2}\xi'+\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega Y(\omega)\omega^{-2}e^{i\omega\tau}, \quad \tau>0$$

and (4.5)

$$\langle\tau, \xi'|\xi\rangle=\tfrac{1}{2}\xi'+\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega Y(\omega)\omega^{-2}e^{-i\omega\tau}, \quad \tau<0.$$

Now Fig. 2 shows that $\langle\tau, \xi'|\xi\rangle$ can be written as

$$\langle\tau, \xi'|\xi\rangle=\xi(\tau)+\xi(-\tau)-\xi', \tag{4.6}$$

so that, for all τ we obtain

$$\langle\tau, \xi'|\xi\rangle=\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega Y(\omega)\omega^{-2}(e^{i\omega t}+e^{-i\omega\tau}), \tag{4.7}$$

or

$$\langle\tau, \xi'|\xi\rangle=\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega[Y(\omega)+Y^*(\omega)]\omega^{-2}e^{i\omega\tau}. \tag{4.8}$$

5. THE SPECTRAL DENSITY

The essential part of our analysis has been carried out with the calculation in the previous section of the conditional average $\langle\tau, \xi'|\xi\rangle$. It now remains merely to substitute this quantity into Eqs. (2.2) and (2.1) to obtain the spectral density of the spontaneous fluctuations of ξ. From (2.2) and (4.8) we compute the autocorrelation function

$$\langle\xi(t)\xi(t+\tau)\rangle=\int d\xi' W_1(\xi')\xi' \times\left[\frac{1}{2\pi}\frac{\partial F}{\partial X}\xi'\int_{-\infty}^{\infty}d\omega[Y(\omega)+Y^*(\omega)]\omega^{-2}e^{i\omega\tau}\right], \tag{5.1}$$

or

$$\langle\xi(t)\xi(t+\tau)\rangle=\frac{1}{2\pi}\frac{\partial F}{\partial X}\langle\xi^2\rangle\int_{-\infty}^{\infty}d\omega[Y(\omega)+Y^*(\omega)]\omega^{-2}e^{i\omega\tau}. \tag{5.2}$$

Now, from Eq. (2.1) or more directly from Eq. (A.15), we find

$$G(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\frac{\partial F}{\partial X}\langle\xi^2\rangle[Y(\omega)+Y^*(\omega)]\omega^{-2}. \tag{5.3}$$

The theory of thermodynamic fluctuations predicts precisely the mean square fluctuation $\langle\xi^2\rangle$. For a system canonical only with respect to a single extensive parameter x, the mean square fluctuation is simply[6]

$$\langle\xi^2\rangle=-k\partial X/\partial F, \tag{5.4}$$

where the partial differentiation connotes constant values of all the other extensive parameters.

The spectral density of the spontaneous fluctuations now becomes

$$G(\omega)=-(2/\pi)^{\frac{1}{2}}k\sigma_s(\omega)/\omega^2, \tag{5.5}$$

where the conductance,

$$\sigma_s(\omega)\equiv\tfrac{1}{2}[Y(\omega)+Y^*(\omega)], \tag{5.6}$$

is the real, or dissipative, part of the admittance. The mean square fluctuations may be written in terms of the spectral density by (A.17);

$$\langle\xi^2\rangle=-\frac{2k}{\pi}\int_{-\infty}^{\infty}d\omega\sigma_s(\omega)/\omega^2 \tag{5.7}$$

[11] We here implicitly ignore magnetic or Coriolis fields. If these are present $\langle\tau, \xi'|\xi\rangle$ is symmetric only with respect to a simultaneous inversion of the time and the magnetic (or Coriolis) field.

which is our essential result for a system with microcanonical constraints.

It is sometimes convenient to describe the spontaneous fluctuations in the extensive parameters in terms of a hypothetical generalized force $\mathfrak{F}$. This equivalent force is taken as that which, if it were to act on the system, would induce the observed spontaneous behavior of the extensive parameter. This hypothetical force and the fluctuating extensive parameter are thus related by the admittance function as in Eqs. (3.4) to (3.6), and the spectral density of the force is, therefore, given by [see Eq. (A.16)]

(Spectral density of "force")

$$=\frac{\omega^2}{Y(\omega)Y^*(\omega)}G(\omega) \tag{5.8}$$

$$=-\frac{k}{(2\pi)^{\frac{1}{2}}}[Y^{-1}(\omega)+Y^{*-1}(\omega)] \tag{5.9}$$

$$=-(2/\pi)^{\frac{1}{2}}kR_s(\omega), \tag{5.10}$$

where $R_s(\omega)$, the resistance, is the real part of the impedance $Y^{-1}(\omega)$. The mean square of the effective force is

$$\langle\delta\mathfrak{F}^2\rangle=-(2/\pi)k\int R_s(\omega)d\omega. \tag{5.11}$$

6. FLUCTUATIONS UNDER AN ADIABATIC CONSTRAINT

We have now obtained a theorem relating admittance function and spontaneous fluctuations, each measured under conditions in which all but a single extensive parameter of the system is held constant. Our theorem would apply to energy fluctuations if volume and mole number were to be held constant or to volume fluctuations if energy and mole number were to be kept constant. Unfortunately these are not always operationally convenient requirements. In particular, in studying spontaneous volume fluctuations we may easily keep the mole number constant, but we would find it extremely impractical to attempt to keep the internal energy constant. A more practical arrangement would be to study the spontaneous volume fluctuations of an adiabatically insulated system, of constant mole number. We thus seek to adapt our theorem to the replacement of the condition $X_0=$constant by the condition of adiabatic insulation when treating the spontaneous fluctuations of any parameter x_K, $K\neq 0$.

Consider an adiabatically insulated system—that is, a system enclosed by a wall which is impervious to the flow of heat. For such a system the energy x_0 and the other extensive parameters x_1, x_2, $\cdots$ are not independent. In fact, if x_K is the fluctuating parameter (all x_j, $j\neq 0$ or K, being held constant), then the work done by the reservoir on the system is simply

$$\delta x_0=P_K\delta x_K, \tag{6.1}$$

where

$$P_K\equiv\left.\frac{\partial X_0}{\partial X_K}\right)_{S,X_j\cdots}$$

is the intensive parameter in the energy language of the driving reservoir. Then we can see that the first-order differential change in the entropy of the system vanishes

$$\delta s=(1/T)\delta x_0-(P_K/T)\delta x_K$$
$$=(P_K/T)\delta x_K-(P_K/T)\delta x_K=0. \tag{6.2}$$

Thus, we see that the adiabatic constraint is equivalent, although only to first order in differentials, to the condition of constant entropy. Therefore, the appropriate set of independent variables for the analysis of fluctuations under an adiabatic constraint is S, X_1, X_2, $\cdots$. This is just the set of independent parameters which defines the energy language in which the fundamental relation is

$$X_0=X_0(S, X_1, X_2, \cdots). \tag{6.3}$$

This is to be contrasted with the use of the set of independent parameters X_0, X_1, X_2, $\cdots$ which was appropriate for the analysis of fluctuations under microcanonical constraints, and which defines the entropy language.

In adapting the analysis of the microcanonical case to fluctuations under an adiabatic constraint, the generalized force F is to now be replaced by P (where for convenience we omit the subscript K). Thus we replace (3.4) by

$$p(t)=P+\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega\beta(\omega)e^{i\omega t}, \tag{6.4}$$

and $Y(\omega)$, as defined in (3.6), now has the dimensions of X/P rather than of X/F. The Laurent expansion of the energy language admittance function in analogy with (3.14) is

$$Y(\omega)=i\omega\partial X/\partial P)_S+O(\omega^2). \tag{6.5}$$

Similarly, appropriately replacing (4.1) and succeeding equations we find in analogy with (5.3)

$$G(\omega)=(2\pi)^{-\frac{1}{2}}\partial P/\partial X)_S\langle\xi^2\rangle[Y(\omega)+Y^*(\omega)]\omega^{-2}, \tag{6.6}$$

or

$$G(\omega)=(2/\pi)^{\frac{1}{2}}\partial P/\partial X)_S\langle\xi^2\rangle\sigma_U(\omega)\omega^{-2}, \tag{6.7}$$

where

$$\sigma_U(\omega)=\tfrac{1}{2}[Y(\omega)+Y^*(\omega)]. \tag{6.8}$$

The conductance $\sigma_U(\omega)$ carries the subscript U to explicitly indicate the fact that it is the real part of an energy language admittance.

In order to complete the analysis it remains only to evaluate the mean square fluctuation $\langle\xi^2\rangle$ under an adiabatic constraint. This result is shown in Appendix B to be

$$\langle\xi^2\rangle=+kT\partial X/\partial P)_S. \tag{6.9}$$

Then we obtain the final result

$$\langle\xi^2\rangle=\frac{2kT}{\pi}\int_0^\infty d\omega\sigma_U(\omega)\omega^{-2}. \tag{6.10}$$

This result may also be expressed in terms of the mean square fluctuation of an equivalent generalized force, [see Eq. (5.11)],

$$\langle\delta\mathcal{P}^2\rangle=\frac{2kT}{\pi}\int_0^\infty d\omega R_U(\omega), \tag{6.11}$$

where $R_U(\omega)$ is the real part of the energy language impedance function.

7. CONCLUSION

We have now obtained the explicit relation between the spontaneous fluctuations in an equilibrium system and the function characterizing the irreversible response of the system to applied forces. The results have been obtained for two types of constraints which allow the independent fluctuation of but a single extensive parameter. The theorems are the generalization of the Nyquist electrical noise formula and are the thermodynamic statement of an analogous statistical theorem previously proven.[7] Applications of the relations have been indicated in the paper on the statistical theorem.

In a succeeding paper the analysis will be extended to systems in which more than one extensive parameter is capable of independent fluctuation. It will then be shown that the extended theorem includes[8] a generalized form of the Onsager reciprocy theorem.

APPENDIX A: RANDOM VARIABLES AND THE WIENER-KHINCHIN FORMULA

We here review certain pertinent aspects of the theory of stationary random variables.[12] At a given time we can consider the past behavior of a random variable ξ to be described by a definite mathematical function $\xi(t)$. The future behavior of a stationary random variable is, however, only defined by a set of probability functions

$$W_1(\xi'),\ W_2(\xi';\xi'',\tau),\ W_3(\xi';\xi'',\tau;\xi''',\tau''')\cdots$$

such that $W_1(\xi')d\xi'$ is the probability of ξ being in the range $\xi'<\xi<\xi'+d\xi'$ at any given future time; and $w_2(\xi';\xi'',\tau)d\xi'd\xi''$ is the joint probability of ξ being in the range $\xi'<\xi<\xi'+d\xi'$ at any given future time, and of also being in the range $\xi''<\xi<\xi''+d\xi''$ at τ seconds later.

A conditional probability function may be conveniently defined by the relation

$$P_2(\xi'|\xi'',\tau)=W_2(\xi';\xi'',\tau)/W_1(\xi'), \tag{A.1}$$

and $P_2(\xi'|\xi'',\tau)d\xi''$ gives the probability that a measurement, made τ seconds after a previous measurement which gave $\xi=\xi'$, will give a value of ξ in the range $\xi''<\xi<\xi''+d\xi''$.

In terms of these probability functions we may compute any desired average values. Thus, the expectation value of ξ is

$$\langle\xi\rangle=\int\xi'W_1(\xi')d\xi', \tag{A.2}$$

and

$$\langle\xi^2\rangle=\int(\xi')^2W_1(\xi')d\xi'. \tag{A.3}$$

The autocorrelation function is defined as the expectation value of the product $\xi(t)\xi(t+\tau)$ (which, for a stationary variable, is independent of t). Then

$$\langle\xi(t)\xi(t+\tau)\rangle=\int d\xi'\int d\xi''\xi'\xi''W_2(\xi';\xi'',\tau), \tag{A.4}$$

or

$$\langle\xi(t)\xi(t+\tau)\rangle=\int d\xi'\xi'W_1(\xi')\int d\xi''\xi''P_2(\xi'|\xi'',\tau). \tag{A.5}$$

This equation can be written in the useful form

$$\langle\xi(t)\xi(t+\tau)\rangle=\int d\xi'W_1(\xi')\xi'\langle\tau,\xi'|\xi\rangle, \tag{A.6}$$

where

$$\langle\tau,\xi'|\xi\rangle\equiv\int d\xi''P_2(\xi'|\xi'',\tau)\xi''. \tag{A.7}$$

This latter quantity $\langle\tau,\xi'|\xi\rangle$ has the significance of the expectation value of ξ at a given time if it is known that ξ had the value ξ' at τ seconds previous.

For a stationary random variable the probability functions defining its future behavior may be determined by observations on its past behavior. Similarly various average values may be computed by direct reference to the known function $\xi(t)(t<0)$. In particular the autocorrelation function is given by

$$\langle\xi(t)\xi(t+\tau)\rangle=\lim_{T\to\infty}\frac{1}{T}\int_{-T}^0 dt\xi(t)\xi(t+\tau). \tag{A.8}$$

It is convenient to analyze the past behavior of the variable in terms of the Fourier transform of $\xi(t)$ rather than in terms of $\xi(t)$ itself. A minor complication arises, however, because $\xi(t)$ is not integrable square in the infinite range of t. This difficulty may be overcome by defining a "cut-off function" $\xi_T(t)$ such that

$$\xi_T(t)\equiv\begin{cases}\xi(t), & -T<t<0\\ 0 & \text{otherwise.}\end{cases} \tag{A.9}$$

Then

$$\xi_T(t)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^\infty d\omega\beta_T(\omega)e^{i\omega t}, \tag{A.10}$$

[12] See M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. 17, 323 (1945); and N. Wiener, Acta Math. 55, 117 (1930).

and inversely

$$\beta_T(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}dt\xi_T(t)e^{-i\omega t}=\beta_T^*(-\omega). \quad \text{(A.11)}$$

The autocorrelation function becomes

$$\langle\xi_T(t)\xi_T(t+\tau)\rangle=\frac{1}{2\pi T}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega' \times\beta_T(\omega)\beta_T(\omega')e^{i(\omega+\omega')t}e^{i\omega\tau}. \quad \text{(A.12)}$$

But

$$\int_{-\infty}^{\infty}dte^{i(\omega+\omega')t}=2\pi\delta(\omega+\omega'), \quad \text{(A.13)}$$

whence

$$\langle\xi_T(t)\xi_T(t+\tau)\rangle=\frac{1}{T}\int_{-\infty}^{\infty}d\omega|\beta_T(\omega)|^2e^{i\omega\tau}, \quad \text{(A.14)}$$

or

$$\langle\xi(t)\xi(t+\tau)\rangle=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega G(\omega)e^{i\omega\tau}, \quad \text{(A.15)}$$

where

$$G(\omega)=(2\pi)^{\frac{1}{2}}\lim_{T\to\infty}\frac{1}{T}|\beta_T(\omega)|^2. \quad \text{(A.16)}$$

If we take the particular value $t=0$, Eq. (A.15) becomes

$$\langle\xi^2(t)\rangle=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}d\omega G(\omega)=\left(\frac{2}{\pi}\right)^{\frac{1}{2}}\int_0^{\infty}d\omega G(\omega), \quad \text{(A.17)}$$

so that $G(\omega)$ is identified as the spectral density. Equation (A.15) is the statement of the Wiener-Khinchin relation, to the effect that the autocorrelation function and the spectral density are mutual Fourier transforms. We use this theorem in its inverted form

$$G(\omega)=\frac{1}{(2\pi)^{\frac{1}{2}}}\int_{-\infty}^{\infty}dt\langle\xi(t)\xi(t+\tau)\rangle e^{-i\omega\tau}. \quad \text{(A.18)}$$

APPENDIX B: FLUCTUATIONS UNDER AN ADIABATIC CONSTRAINT

The theory of thermodynamic fluctuations has not been extended to the treatment of fluctuations under an adiabatic constraint. We recall that for a system canonical with respect to both the energy X_0 and some other particular extensive parameter X the probability of a fluctuation to instantaneous values x_0, x is[5]

$$W=\Omega_0\exp\left\{-\frac{1}{k}\left[S-s-\frac{1}{T}(X_0-x_0)-\frac{P}{T}(X-x)\right]\right\}. \quad \text{(B.1)}$$

From this ensemble, however, only that subset of states consistent with the condition

$$P(x-X)=x_0-X_0 \quad \text{(B.2)}$$

is accessible to a system under an adiabatic constraint. Thus, for such a system the probability of fluctuation to the state x is [inserting (B.2) in (B.1)]

$$W=\Omega_0e^{-[S-s]/k}, \quad \text{(B.3)}$$

where by virtue of (B.2) s is now to be considered a function of x only. Then we can write

$$\langle\xi^2\rangle=\int dx(x-X)^2W \quad \text{(B.4)}$$

$$=\Omega_0\int dxe^{-(S-s)/k}(x-X)^2. \quad \text{(B.5)}$$

This integral may be evaluated by making a series expansion in the exponential and discarding higher order terms

$$s=S+\frac{\partial S}{\partial X_0}\delta x_0+\frac{\partial S}{\partial X}\delta x +\frac{1}{2}\left[\frac{\partial^2S}{\partial X^2}\delta x^2+2\frac{\partial^2S}{\partial X\partial X_0}\delta x\delta x_0+\frac{\partial^2S}{\partial X_0{}^2}\delta x_0{}^2\right], \quad \text{(B.6)}$$

whence using (B.2) to eliminate the first-order terms

$$(s-S)=\frac{1}{2}\left[\frac{\partial^2S}{\partial X^2}\delta x^2+2\frac{\partial^2S}{\partial X\partial X_0}\delta x\delta x_0+\frac{\partial^2S}{\partial X_0{}^2}\delta x_0{}^2\right],$$

$$(s-S)=\frac{1}{2}\left[-\frac{\partial}{\partial X}\left(\frac{P}{T}\right)+2P\frac{\partial}{\partial X_0}\left(\frac{P}{T}\right) +P^2\frac{\partial}{\partial X_0}\left(\frac{1}{T}\right)\right](\delta x)^2,$$

$$(s-S)=\frac{1}{2}\left[-\frac{\partial}{\partial X}\left(\frac{P}{T}\right)_s-P\frac{\partial}{\partial X_0}\left(\frac{P}{T}\right) +\frac{\partial}{\partial X_0}\left(\frac{1}{T}\right)P^2\right](\delta x)^2, \quad \text{(B.7)}$$

where the subscript s indicates that s is held constant in the differentiation rather than X_0 as would be implied by the derivative with no explicit subscript. Then by the identity

$$\frac{\partial}{\partial X_0}\left(\frac{P}{T}\right)=-\frac{\partial}{\partial X_0}\frac{\partial S}{\partial X}=\frac{-\partial}{\partial X}\frac{\partial S}{\partial X_0}=-\frac{\partial}{\partial X}\left(\frac{1}{T}\right), \quad \text{(B.8)}$$

we find

$$(s-S)=\frac{1}{2}\Big[-\frac{\partial}{\partial X}\Big(\frac{P}{T}\Big)_s+P\frac{\partial}{\partial X}\Big(\frac{1}{T}\Big)$$

$$+P^2\frac{\partial}{\partial X_0}\Big(\frac{1}{T}\Big)\Big](\delta x)^2$$

$$=\frac{1}{2}\Big[-\frac{\partial}{\partial X}\Big(\frac{P}{T}\Big)_s+P\frac{\partial}{\partial X}\Big(\frac{1}{T}\Big)_s\Big](\delta x)^2$$

$$=-\frac{1}{T}\frac{\partial P}{\partial X_0}\Big)_s(\delta x)^2. \qquad \text{(B.9)}$$

Thus

$$W=\Omega_0\exp\Big\{\frac{1}{2k}\Big[-\frac{1}{T}\frac{\partial P}{\partial X}\Big)_s\Big](\delta x)^2\Big\}, \qquad \text{(B.10)}$$

whence

$$\langle\xi^2\rangle=\frac{\int dx(\delta x)^2\exp\Big\{\frac{1}{2k}\Big[-\frac{1}{T}\frac{\partial P}{\partial X}\Big)_s\Big](\delta x)^2\Big\}}{\int dx\exp\Big\{\frac{1}{2k}\Big[-\frac{1}{T}\frac{\partial P}{\partial X}\Big)_s\Big](\delta x)^2\Big\}}. \qquad \text{(B.11)}$$

$$=2kT\frac{\partial X}{\partial P}\Big)_s\int d\theta\theta^2e^{-\theta^2}\Big/\int d\theta e^{-\theta^2}.$$

$$\langle\xi^2\rangle=kT\partial X/\partial P)_s. \qquad \text{(B.12)}$$

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Second-Order Acoustic Fields: Relations Between Density and Pressure*

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In acoustics the relations between the excess pressure and the excess density neglect effects of the fluid flow. The object of this paper is to derive a general relation between the pressure and density which includes streaming. This is done for a nonabsorbing ideal fluid from general thermodynamic arguments. The results justified the static derivations (neglecting flow terms) which are used for more complex media.

I. INTRODUCTION

IN acoustics, one assumes (for a nonabsorbing medium) that the relation between the excess pressure p_e and the excess density ρ_e is of the form

$$p_e=F(\rho_e), \qquad (1)$$

where F is some function. For second-order fields the pressure and density are expanded into first- and second-order terms, i.e., $p_e=p_1+p_2$ and $\rho_e=\rho_1+\rho_2$ (p_1 and ρ_1 are solutions of the wave equation[1]). Equation (1) can be expanded in the form

$$p_1+p_2=c_0^2(\rho_1+\rho_2)+\tfrac{1}{2}(c_\rho^2+c_0^2c_p^2)\rho_1^2, \qquad (2)$$

where

$c_0^2=(\partial F/\partial\rho)_s$, evaluated at equilibrium values of the pressure, p_0, and density, ρ_0;

$c_p^2=(\partial c_0^2/\partial p)_\rho$, evaluated at p_0 and ρ_0;

$c_\rho^2=(\partial c_0^2/\partial\rho)_p$, evaluated at p_0 and ρ_0;

and s is the entropy. Using directional derivatives we can see that the term in (2) which multiplies ρ_1^2 is $(\partial^2F/\partial\rho^2)_s$.

The above argument takes no account of the fluid flow. In this paper a relation is derived between p_e and ρ_e which takes the flow into account. The derivation is based on Eckart's irreversible thermodynamics.[2] From this new equation a relation corresponding to (2) will be obtained.

II. EXACT PRESSURE DENSITY RELATION

We shall be interested only in a simple fluid where ϵ is a function of p and ρ alone. Since the time does not enter explicitly into ϵ, thermal or structural relaxation is thus eliminated.[3] Because of the simplicity of the case considered, standard equilibrium thermodynamic equations can be used.

Eckart has considered the energy relations in a moving medium composed of a simple fluid. An equation relating the energy, pressure, density, and particle velocity[4] is

$$\rho D\epsilon/Dt+p\nabla\cdot\mathbf{u}=0, \qquad (3)$$

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[1] C. Eckart, Phys. Rev. 73, 68 (1948).

[2] C. Eckart, Phys. Rev. 58, 267 (1940).

[3] L. I. Mandelstam and M. A. Leontovich, J. Exp. Theoret. Phys. 7, 438 (1937), have treated relaxation of fluids by considering the Helmholtz free energy to be given by the usual thermodynamic variables and an additional one which can be associated with time. It would seem that the assumption $\epsilon(\rho, p)$ elimates thermal and structural relaxation.

[4] Equation (3) follows from the first equation after Eq. (9) of Eckart's paper (see reference 2). The entropy change is set equal to zero.