Statistical Mechanics of Open Systems*

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We have generalized Kubo's treatment of isolated nonequilibrium systems to open systems in contact with thermal reservoirs. When the system is in contact with one reservoir and is subject to a weak external field, the deviation of the average of any quantity from its equilibrium value is related to a time-correlation function which incorporates the effect of the reservoir. A corollary is an isothermal fluctuation-dissipation theorem, which gives an explicit expression in terms of a time-correlation function for the rate at which energy flows from the driving field into the reservoir via the system. As an application, we compute the complex conductivity of a Lorentz gas. We also obtain an expression for the stationary nonequilibrium distribution of a system in contact with several reservoirs at slightly differing temperatures and chemical potentials. The Onsager coefficients, which relate the heat and particle fluxes to the differences among the reservoir parameters, are then explicitly expressed in terms of suitable time-correlation functions and their symmetry is exhibited. The validity of perturbation theory in finding the linear deviation from equilibrium of the Γ-space ensemble density is also discussed.

1. INTRODUCTION

IN this paper the general problem of investigating the nonequilibrium properties of a system in contact with reservoirs will be simplified in two ways. First, we shall consider only those nonequilibrium states which are in some clear sense "close" to equilibrium. And second, we shall employ a model which gives an idealized but very convenient representation of the interaction between the system and the reservoirs.

The model has been described in detail by Bergmann and Lebowitz,[1] and a brief recapitulation of its properties will suffice for our purposes. Each reservoir is assumed to consist of an infinite number of non-interacting components distributed prior to interaction with the system according to a Maxwell-Boltzmann distribution at a temperature characteristic of the reservoir. Each component is assumed to interact with the system at most once, and the interaction is impulsive. It follows from these assumptions that each reservoir always presents the same statistical appearance to the system. The interaction of the rth reservoir with the system can therefore be represented by a stochastic kernel $K_r(x,x')$, where $K_r(x,x')dxdt$ is the conditional probability that a system located at the point x' in its phase space will interact with the rth reservoir during an interval dt and as a result arrive at

a phase point in the volume element dx. $K_r(x,x')$ is assumed to be a differentiable function of the temperature T_r of the rth reservoir, but to be independent of the temperature of the other reservoirs. The evolution of the distribution function $\mu(x,t)$ in the system phase space is the result of both the natural motion of the system and the interactions with the reservoirs, and therefore the equation governing this evolution is

$$\frac{\partial \mu(x,t)}{\partial t} = \{H(x),\mu(x,t)\}$$
$$+ \sum_{r=1}^{R} \int [K_r(x,x')\mu(x',t) - K_r(x',x)\mu(x,t)]dx'. \quad (1.1)$$

Here R is the number of reservoirs, $H(x)$ is the system Hamiltonian, and the curly brackets in the first term on the right represent the Poisson bracket operation. The assumption that a Maxwell-Boltzmann distribution is maintained in each reservoir, together with considerations of mechanical time reversibility in the system plus reservoirs, imply the following "time-reversed symmetry condition":

$$\exp[-\beta_r H(x)]K_r(x',x) = \exp[-\beta_r H(x')]K_r(\bar{x},\bar{x}'). \quad (1.2)$$

In this equation $\beta_r = (kT_r)^{-1}$, and $\bar{x}$ is the point corresponding to x under time reversal, i.e., $\bar{x}$ has the same position coordinates as x but momentum coordinates of opposite sign. It is assumed here that $H(x) = H(\bar{x})$. Finally, if the volume of the system is kept constant, it is natural to require that the canonical distribution $Z_r^{-1} \exp[-\beta_r H(x)]$, where $Z_r = \int \exp[-\beta_r H(x)]dx$, be a stationary distribution when the system interacts only with the rth reservoir. By (1.1) this requirement implies

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[1] P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955); J. L. Lebowitz and P. G. Bergmann, Ann. Phys. (New York) **1**, 1 (1957); J. L. Lebowitz, Phys. Rev. **114**, 1192 (1959); in *Ergodic Theory*, edited by P. Caldirola (Academic Press Inc., New York, 1962).

the "integral condition"

$$\int \exp[-\beta_r H(x)] K_r(x',x) dx'$$

$$= \int \exp[-\beta_r H(x')] K_r(x,x') dx'. \quad (1.3)$$

A simple but powerful method for treating irreversible processes in the neighborhood of equilibrium has been developed by Kubo.[2] The method is essentially a perturbation treatment of the Liouville equation, and it is therefore directly applicable only to closed systems, in which the total Hamiltonian (including terms due to external mechanical disturbances) completely determines the evolution of a distribution in phase space. We shall adapt Kubo's method to Eq. (1.1), which is a stochastic modification of the Liouville equation, and in this way we may obtain information about the behavior of open systems without explicitly considering the Hamiltonian of the environment.

In Sec. 2 we assume that the system interacts only with one reservoir and that the deviation from equilibrium is due to an external mechanical disturbance. A macroscopic quantity of the system is related to the external disturbance by a "response function," and it is shown that response functions can be expressed in the familiar form of time correlations in the equilibrium ensemble, and that under certain circumstances they satisfy reciprocal relations. In Sec. 3 a fluctuation-dissipation theorem is demonstrated, i.e., a theorem relating certain time correlations in the equilibrium ensemble to the rate at which energy is dissipated into the reservoir when the system is driven by a periodic external field. The theorem is similar to results of Callen and Welton[3] and of Kubo,[2] but differs from those results since contact of the system with the reservoir is explicitly considered here; in other words, the theorem of Sec. 3 is an isothermal rather than an adiabatic version of the fluctuation-dissipation theorem.[4] In Sec. 4 we consider the stationary nonequilibrium state of a system in contact with a number of reservoirs at different temperatures. Explicit expressions are derived for the coefficients relating the heat flow into the various reservoirs to the reservoir temperatures, and it is shown that the cross coefficients satisfy the Onsager reciprocal relations. Section 5 outlines an extension of this result to the situation in which the reservoirs can exchange particles as well as energy with the system. In Sec. 6 we shall make several applications of the general formulas to the calculation of electrical conductivity and the rate of dissipation in some simple systems. Section 7 briefly discusses the validity of perturbation methods in dealing with distributions in phase space. The proofs of several auxiliary theorems are given in the Appendix.

[2] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957).
[3] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).
[4] J. M. Blatt and T. Matsubara, Progr. Theoret. Phys. **21**, 696 (1959).

2. RESPONSE OF AN OPEN SYSTEM TO A MECHANICAL DISTURBANCE

We consider a system in contact with a single reservoir at temperature T, with which it can exchange energy but not particles. Furthermore, we assume that there is a mechanical disturbance of the system due to an external field, such that the total Hamiltonian of the system is the sum of an unperturbed part $H_0(x)$ and an interaction part $-h(t)A(x)$, where $h(t)$ is independent of x. Some of the results below hold when $A(x)$ is an arbitrary function of position in system phase space, but the most useful expression for the response function presupposes a limitation on $A(x)$ which will be stated later. It will be convenient to assume that $h(t) \rightarrow 0$ as $t \rightarrow -\infty$, for then the system can be pictured as evolving from a state of Maxwellian equilibrium in the infinitely distant past, i.e.,

$$\mu(x, -\infty) = \mu_0(x), \quad (2.1)$$

where

$$\mu_0(x) = Z^{-1} \exp[-\beta H_0(x)],$$
$$Z = \int \exp[-\beta H_0(x)] dx. \quad (2.2)$$

Since there is only one reservoir, the subscripts in Eq. (1.1) may be dropped, and this equation becomes

$$\partial \mu(x,t)/\partial t = \mathcal{K}\mu(x,t) - h(t)\mathcal{F}\mu(x,t), \quad (2.3)$$

where $\mathcal{K}$ and $\mathcal{F}$ are linear operators such that for an arbitrary function ψ on the phase space

$$\mathcal{K}\psi(x) = \{H_0(x), \psi(x)\}$$
$$+ \int [K(x,x')\psi(x') - K(x',x)\psi(x)] dx', \quad (2.4)$$

and

$$\mathcal{F}\psi(x) = \{A(x), \psi(x)\}. \quad (2.5)$$

Equation (2.3) and the initial condition (2.1) imply the integral equation

$$\mu(x,t) = \mu_0(x) - \int_{-\infty}^{t} dt' \, h(t') \exp[(t-t')\mathcal{K}]\mathcal{F}\mu(x,t'), \quad (2.6)$$

as can be checked by differentiation. An infinite series, which is obtained by an iteration process beginning with $\mu_0(x)$, is a formal solution to Eq. (2.6). The term in this series which is obtained for the first time at the ith iteration will be designated by $\mu_i(x,t)$. In particular,

$$\mu_1(x,t) = -\int_{-\infty}^{t} dt' \, h(t') \exp[(t-t')\mathcal{K}]\{A(x), \mu_0(x)\}$$

$$= -\int_{0}^{\infty} dt' \, h(t-t') \exp(t'\mathcal{K})$$

$$\times \int dx' \, \delta(x-x')\{A(x'), \mu_0(x')\}. \quad (2.7)$$

The distribution $\exp(t'\mathcal{K})\delta(x-x')$ is the probability density that the system at time t' will be located at point x in phase space, if at time 0 it is located at point x' and if the external field were not present; this is evident from Eq. (2.3), if the second term on the right is set equal to 0. We shall therefore use the transition probability notation

$$P(x,x'|t) \equiv \exp(t\mathcal{K})\delta(x-x') \quad (t \geqslant 0). \tag{2.8}$$

Using this notation and the fact that $\exp(t\mathcal{K})$ is a linear operator, we can write Eq. (2.7) as

$$\mu_1(x,t) = -\int_0^\infty dt'\, h(t-t')$$

$$\int dx' P(x,x'|t)\{A(x'),\mu_0(x')\}. \tag{2.9}$$

Because the Poisson bracket is a differential operation it follows that $\{A(x),\mu_0(x)\} = -\beta\mu_0(x)\{A(x),H_0(x)\}$. A further simplification would be obtained immediately if the system were closed, for then the rate of change of any quantity of the system, in the absence of the external disturbance, would be determined by H_0, specifically, $\dot{A}(x) = \{A(x),H_0(x)\}$. In an open system, however, the rate of change of A at the phase point x is not uniquely determined, because of the possibility of interaction with the reservoir. Consequently, we let $\dot{A}(x)$ designate the average rate of change of A, i.e.,

$$\dot{A}(x) \equiv \left[\frac{\partial}{\partial t}\int dx' A(x')P(x',x|t)\right]_{t=0}. \tag{2.10}$$

By (2.8) and (2.4) we find

$$\dot{A}(x) = \{A(x),H_0(x)\}$$

$$+ \int dx' K(x',x)[A(x')-A(x)], \tag{2.11}$$

which shows that in the limiting case of a closed system, when $K(x,x')=0$, the standard expression for $\dot{A}(x)$ is recovered. Furthermore, if $A(x)$ is a quantity which is not instantaneously changed by an interaction with the reservoir—e.g., if $A(x)$ is a function of position in configuration space only—then again one obtains the equation

$$\dot{A}(x) = \{A(x),H_0(x)\}. \tag{2.11'}$$

Since interactions between the system and components of the reservoir were assumed in Sec. 1 to be impulsive, $A(x)$ can change instantaneously if it depends upon the momenta of particles in the system, as in the case of a disturbance by an external magnetic field. However, if the interaction between the system and the reservoir is weak, or if $A(x)$ is essentially a volume-dependent quantity while the reservoir affects the system directly only at its boundaries, then the second term on the right-hand side (rhs) of Eq. (2.11) may be negligible

even though it does not vanish. In the remainder of Sec. 2 and in Sec. 3, $A(x)$ will be assumed to be such that Eq. (2.11') holds, so that (2.9) becomes

$$\mu_1(x,t) = \beta\int_0^\infty dt'\, h(t-t')$$

$$\times \int dx' P(x,x'|t')\dot{A}(x')\mu_0(x'). \tag{2.12}$$

In the Appendix it is proved that

$$P(x,x'|t)\mu_0(x') = P(\bar{x}',\bar{x}|t)\mu_0(x), \tag{A2}$$

which enables us to obtain from Eq. (2.12) the alternative formula

$$\mu_1(x,t) = \mu_0(x)\beta\int_0^\infty dt'\, h(t-t')$$

$$\times \int dx'\, P(x',\bar{x}|t')\dot{A}(\bar{x}'). \tag{2.13}$$

Now let $B(x)$ be any dynamical variable of the system, and consider the average of this variable in the ensemble representing the perturbed system:

$$\langle B(t)\rangle = \int B(x)\mu(x,t)dx. \tag{2.14}$$

The contribution to this average from the ith term in the iteration expression for $\mu(x,t)$ is

$$\langle B(t)\rangle_i = \int B(x)\mu_i(x,t)dx, \tag{2.15}$$

and it may be called the *ith order response*. Substitution of (2.12) into (2.15) yields for the first order or linear response the formula

$$\langle B(t)\rangle_1 = \int_0^\infty dt'\, h(t-t')\phi_{BA}(t'), \tag{2.16}$$

where

$$\phi_{BA}(t) = \beta\int dx\int dx'\, B(x)P(x,x'|t)\dot{A}(x')\mu_0(x'). \tag{2.17}$$

If we introduce the usual notation for a time-correlation function in the equilibrium ensemble, namely

$$\langle R(t)S(0)\rangle_0$$

$$= \int dx\int dx'\, R(x)P(x,x'|t)S(x')\mu_0(x'), \tag{2.18}$$

then

$$\phi_{BA}(t) = \beta\langle B(t)\dot{A}(0)\rangle_0. \tag{2.19}$$

The function $\phi_{BA}(t)$ is known as the *linear response function*, and Eq. (2.16) together with (2.17) or (2.19) constitute the response function theorem for a classical

open system. The theorem expresses the first-order response of a system to an external mechanical disturbance in terms of a correlation function in an equilibrium ensemble. It is clear that formal expressions can be written for the higher order response terms (and, in fact, in Sec. 3 we shall find such an expression for the second-order response quite useful), but these expressions do not have the intuitive physical meaning of the expression for the linear response. Equation (2.19) agrees with Kubo's formula (3.20) for a response function in a classical system,[2] but its range of applicability is wider, since we have considered systems which interact with a reservoir. It should be emphasized, however, that Eq. (2.19) is valid only for those quantities $A(x)$ which satisfy (2.11').

A valuable concept in considerations of systems subject to external disturbances is the *complex admittance* $\chi_{BA}(\omega)$, which is defined as

$$\chi_{BA}(\omega) = \lim_{\epsilon \to 0} \int_0^\infty \phi_{BA}(t) e^{-i\omega t - \epsilon t} dt. \qquad (2.20)$$

If $h(t)$ has the form

$$\begin{aligned} h(t) &= h_0 \cos\omega t e^{\epsilon t} \quad \text{for} \quad t < 0 \\ &= h_0 \cos\omega t \quad \text{for} \quad t \geqslant 0, \end{aligned} \qquad (2.21)$$

then in the limit of $\epsilon \to 0$ we can express the first-order response as

$$\langle B(t) \rangle_1 = b(\omega) \exp i\omega t, \qquad (2.22)$$

where

$$b(\omega) = h_0 \operatorname{Re}\chi_{BA}(\omega).$$

The factor $\exp\epsilon t$ provides that the periodic disturbance is gradually "switched on", and it guarantees that $h(t) \to 0$ as $t \to -\infty$, which would not be the case if $h(t)$ were strictly periodic.

The results above, with the exception of Eq. (2.13), do not depend upon the time-reversed symmetry condition (1.2). It is desirable, however, to establish a reciprocal relation between ϕ_{BA} and ϕ_{AB}, and any such relation depends on the time-reversal theorem (A2), which is derived in the Appendix from Eq. (1.2). We suppose that both A and B satisfy (2.11'), and that both have definite signs under time reversal, i.e.,

$$\begin{aligned} A(\bar{x}) &= \epsilon_A A(x), \quad \epsilon_A = \pm 1 \\ B(\bar{x}) &= \epsilon_B B(x), \quad \epsilon_B = \pm 1. \end{aligned} \qquad (2.24)$$

It will be shown that

$$\phi_{BA}(t) = \epsilon_A \epsilon_B \phi_{AB}(t). \qquad (2.25)$$

To prove this, first note that because of (2.11')

$$\dot{A}(\bar{x}) = -\epsilon_A \dot{A}(x) \qquad (2.26)$$

and

$$\dot{B}(\bar{x}) = -\epsilon_B \dot{B}(x). \qquad (2.27)$$

Using (2.26), (A2), and (A7) we have

$$\int dx \int dx' B(x) P(x,x'|t) \dot{A}(x') \mu_0(x')$$

$$= -\epsilon_A \epsilon_B (d/dt) \int dx \int dx' A(x') P(x',x|t)$$

$$\times B(x)\mu_0(x). \qquad (2.28)$$

Similar reasoning, using (2.27), yields

$$\int dx \int dx' A(x) P(x,x'|t) \dot{B}(x)\mu_0(x')$$

$$= -(d/dt) \int dx \int dx' A(x') P(x',x|t)$$

$$\times B(x)\mu_0(x). \qquad (2.29)$$

The reciprocal relations (2.25) follow immediately from (2.28) and (2.29).

3. THE FLUCTUATION-DISSIPATION THEOREM

Since the system considered in Sec. 2 is coupled both with an external field and a reservoir, it is possible for energy to be dissipated from the field into the reservoir via the system. Particularly simple and useful expressions can be found for the average heat flow when the external field is periodically varying.

The average rate of increase of energy of the system when it is located at point x in phase space will be denoted by $j(x)$, and it follows from the meaning of the stochastic kernel $K(x,x')$ that

$$j(x) = \int dx' K(x',x)[H(x') - H(x)]. \qquad (3.1)$$

[The same expression follows from Eq. (2.11) if $j(x)$ is identified with $\dot{H}_0(x)$.] The heat flow into the system at time t, denoted by $J(t)$, can be expressed as the ensemble average of $j(x)$ at time t,

$$J(t) \equiv \int dx \, j(x)\mu(x,t)dx. \qquad (3.2)$$

The contribution to $J(t)$ from the term $\mu_i(x,t)$ is

$$J_i(t) \equiv \langle j(t) \rangle_i = \int dx \, j(x)\mu_i(x,t). \qquad (3.3)$$

It follows immediately from the integral condition (1.3) that

$$J_0(t) \equiv \int dx \, j(x)\mu_0(x) = 0. \qquad (3.4)$$

By (2.16) and (2.19)

$$J_1(t) = \beta \int_0^\infty dt'\, h(t-t')\langle j(t')\dot{A}(0)\rangle_0, \qquad (3.5)$$

which in general is nonvanishing. However, if $h(t)$ is the asymptotically periodic function given in Eq. (2.21), then in the limit of $\epsilon \to 0$ the time average of $J(t)$ over a period vanishes, i.e.,

$$(J_1)_{\mathrm{av}} \equiv \tau^{-1} \int_{t_0}^{t_0+\tau} J_1(t)dt = 0, \qquad (3.6)$$

where

$$\tau = 2\pi/\omega. \qquad (3.7)$$

The lowest order contribution to the heat flow which does not vanish on the average when the external field is periodic is $J_2(t)$. To obtain an expression for this quantity we first return to (2.6) and carry out the iteration process to second order, making use of (2.8), (2.9) and (2.11'). We obtain

$$\mu_2(x,t) = -\int_{-\infty}^{t} dt'\, h(t')\, \exp[(t-t')\mathfrak{K}]\mathfrak{F}\mu_1(x,t')$$

$$= -\beta \int_0^\infty dt'\, h(t-t')\int_0^\infty dt''\, h(t-t'-t'')$$

$$\times \int dx'\, P(x,x'|t')\int dx''\, \{A(x'),P(x',x''|t'')\}$$

$$\times \dot{A}(x'')\mu_0(x''). \qquad (3.8)$$

From (3.3), (3.8), and the relation

$$\int dx\, H_0(x)(\partial/\partial t)P(x,x'|t)$$

$$= \int dx\, H_0(x)\partial/\partial t\, \exp(t\mathfrak{K})\delta(x-x')$$

$$= \int dx \int dx''\, P(x,x'|t)K(x'',x)$$
$$\times [H_0(x'')-H_0(x)], \qquad (3.9)$$

we obtain

$$J_2(t) = \beta \int_0^\infty dt'\, h(t-t')\int_0^\infty dt''\, h(t-t'-t'')$$

$$\times \int dx' \int dx\, H_0(x)(\partial/\partial t')P(x,x'|t')$$

$$\times \int dx''\, \{A(x'),P(x',x''|t'')\}$$

$$\times \dot{A}(x'')\mu_0(x''). \qquad (3.10)$$

Now let $h(t)=h_0\cos\omega t$ [the limit of (2.21) as $\epsilon \to 0$] and calculate the average of $J_2(t)$ over a period τ,

$$(J_2)_{\mathrm{av}} = -\frac{\omega}{2\pi}h_0^2\beta \int_{t_0}^{t_0+\tau} dt \int_0^\infty dt'\, \cos\omega(t-t')$$

$$\times \int_0^\infty dt''\, \cos\omega(t-t'-t'')$$

$$\times \int dx \int dx'\, H_0(x)\frac{\partial P(x,x'|t')}{\partial t'}$$

$$\times \int dx''\, \{A(x'),P(x',x''|t'')\}$$

$$\times \dot{A}(x'')\mu_0(x''). \qquad (3.11)$$

The integrations with respect to t and t' in (3.11) can be performed, yielding

$$(J_2)_{\mathrm{av}} = -\tfrac{1}{2}\beta h_0^2 \int_0^\infty \cos\omega t \int dx\, H_0(x)$$

$$\times \int dx'\, [P(x,x'|\infty)-P(x,x'|0)]$$

$$\times \int dx''\, \{A(x'),P(x',x''|t)\}$$
$$\times \dot{A}(x'')\mu_0(x''). \qquad (3.12)$$

$P(x,x'|\infty)=\mu_0(x)$, since it has been shown that in the absence of the disturbance the stationary distribution is approached asymptotically regardless of the initial distribution.[1] Therefore, in the term containing $P(x,x'|\infty)$ the integrand of the integration with respect to x is a Poisson bracket, and hence this term vanishes. Furthermore, $P(x,x'|0)=\delta(x-x')$. Consequently,

$$(J_2)_{\mathrm{av}} = \tfrac{1}{2}\beta h_0^2 \int_0^\infty dt\, \cos\omega t$$

$$\times \int dx \int dx'\, H_0(x)\{A(x),P(x,x'|t)\}\dot{A}(x')\mu_0(x')$$

$$= -\tfrac{1}{2}\beta h_0^2 \int_0^\infty dt\, \cos\omega t\langle \dot{A}(t)A(0)\rangle_0. \qquad (3.13)$$

It is convenient to have a notation for the average rate at which heat flows from the system into the reservoir, and in order to emphasize that this quantity is a function of the frequency of the external field we shall denote it by $Q(\omega)$. In the second-order approximation $Q(\omega)$ is evidently the negative of $(J_2)_{\mathrm{av}}$. It is

also convenient to introduce a notation for the Fourier cosine transform of $\langle A(t)A(0)\rangle_0$,

$$G(\omega) \equiv \int_0^\infty dt \, \cos\omega t \langle \dot{A}(t)\dot{A}(0)\rangle_0. \qquad (3.14)$$

We can now express the second-order approximation to the average heat flow into the reservoir as

$$Q(\omega) = h_0^2 G(\omega)/2kT. \qquad (3.15)$$

This formula is a form of the fluctuation-dissipation theorem: $Q(\omega)$ expresses the dissipation of energy, while $G(\omega)$ is related to the fluctuations of the system in the absence of the driving field, for the auto-correlation function $\langle \dot{A}(t)\dot{A}(0)\rangle_0$ expresses the strength and mode of relaxation of spontaneous fluctuations of the quantity $\dot{A}(x)$.

We may also derive the fluctuation-dissipation theorem by another argument. The rate at which energy passes into the system from the driving field, when the system is at phase point x, is

$$-[dh(t)/dt]A(x). \qquad (3.16)$$

When $h(t)$ is asymptotically periodic, as in Eq. (2.21), the total average energy passing into the system in a single period is

$$-\int_{t_0}^{t_0+\tau} dt \int dx \, \mu(x,t)\frac{dh(t)}{dt}A(x). \qquad (3.17)$$

Since $\mu(x,t)$ is asymptotically periodic with the same period as $h(t)$, the ensemble average of the energy of the system will be the same at the end as at the beginning of a period, and, therefore, the expression (3.17) represents the heat dissipated into the reservoir.[1] As (3.17) contains a factor $h(t)A(x)$ in the integrand, the lowest order contribution to the average heat flow into the reservoir will be obtained by using $\mu_0(x)+\mu_1(x,t)$:

$$Q(\omega) = -\frac{\omega}{2\pi}\int_{t_0}^{t_0+\tau} dt \int dx \, [\mu_0(x)+\mu_1(x,t)]\frac{dh(t)}{dt}A(x)$$

$$= -\frac{\omega\beta}{2\pi}\int_{t_0}^{t_0+\tau} dt \, \frac{dh(t)}{dt}\int_0^\infty dt' \, h(t-t')$$

$$\times \int dx \int dx' \, P(x,x'|t')A(x)\dot{A}(x')\mu_0(x'). \qquad (3.18)$$

Taking the expression (2.21) for $h(t)$, letting $t_0=0$, using the fact that the factor $\exp\epsilon(t-t')$ is virtually unchanged in a single period and almost equal to

$\exp-\epsilon t'$, and integrating by parts, we obtain

$$Q(\omega) = \tfrac{1}{2}\omega\beta h_0^2 \left\{ \left[-\omega^{-1}\cos\omega t \exp-\epsilon t \int dx \int dx' \right. \right.$$

$$\left. \times P(x,x'|t)A(x)\dot{A}(x')\mu_0(x') \right]_0^\infty$$

$$+\omega^{-1}\int_0^\infty \cos\omega t \exp-\epsilon t \int dx \int dx'$$

$$\times \frac{\partial}{\partial t}(x,x'|t)A(x)\dot{A}(x')\mu_0(x')$$

$$\left. -\omega^{-1}\epsilon\int_0^\infty \cos\omega t \exp-\epsilon t \int dx \int dx' \right.$$

$$\left. \times P(x,x'|t)A(x)\dot{A}(x')\mu_0(x') \right\}. \qquad (3.19)$$

The first term on the rhs receives no contribution at $t=\infty$ because of the exponential damping factor; nor at 0 because $P(x,x'|0)=\delta(x-x')$, and $A(x)\dot{A}(x)$ changes sign under the transformation $x \to \bar{x}$. The third term goes to 0 as $\epsilon \to 0$. The second term can be simplified by means of formula (A7) of the Appendix, so that in the limit of $\epsilon \to 0$

$$Q(\omega) = \frac{h_0^2}{2kT}\int_0^\infty dt \, \cos\omega t \int dx \int dx'$$

$$\times P(x,x'|t)\dot{A}(x)\dot{A}(x')\mu_0(x'), \qquad (3.20)$$

which is identical with the fluctuation-dissipation theorem, Eq. (3.15). Using (2.19) and (2.20) we can also rewrite Eq. (3.18) as

$$Q(\omega) = -\tfrac{1}{2}\omega\beta h_0^2 \, \mathrm{Im}\chi_{AA}(\omega), \qquad (3.21)$$

thus expressing the rate of dissipation of energy in terms of the imaginary part of the susceptibility.

It should be noted that the name "fluctuation-dissipation theorem" is used by Callen and Welton[3] and by Kubo[2] to refer to a result which is essentially the Fourier-transformed version of Eq. (2.19) and to the quantum mechanical generalization of this Equation. Their use of this name is justified by the fact that the response function $\phi_{AA}(t)$ determines the susceptibility, which in turn determines the rate of dissipation of energy. However, it seems equally or more appropriate to refer to (3.15) as a "fluctuation-dissipation theorem", because in this formula the rate of dissipation of energy is explicitly given. The nature of the dissipation of energy is somewhat obscure in the work of Callen and Welton and of Kubo, since the systems they consider are closed systems. Roughly speaking, dissipation in the situations which they consider is the transfer of energy from a few macroscopic degrees of freedom to

very many microscopic degrees of freedom of the system. Such a process cannot be isothermal, and the assumption which is implicit in their formalism, that after the removal of the driving field the system would relax to equilibrium at its initial temperature, is not rigorously true.[4] It is a justifiable assumption in many practical problems, however, because the energy absorbed by the system in the time intervals which are relevant may be much smaller than the internal energy of the system.[5] The advantage of the derivation given above of the fluctuation-dissipation theorem is that the obscurity regarding the dissipation of energy is removed. The energy is dissipated into an infinite reservoir, and the entire process is isothermal.

4. HEAT FLOW IN THE PRESENCE OF SEVERAL RESERVOIRS

It has been shown[1] under very general conditions that when the system is in contact with several reservoirs at different temperatures, as described in Sec. 1, the distribution approaches a stationary distribution which is independent of the initial distribution function. We shall now examine the stationary distribution under the condition that the reservoir temperatures T_r differ only slightly from each other.[6] The meaning of this condition depends upon the physical quantities which are under consideration. If these quantities (e.g., the heat flow from each reservoir into the system) are expressed as power series in $\beta_r - \beta_s$, and if truncating the series after the first-order terms provides sufficiently good approximations to these quantities, then the temperatures may be said to "differ slightly" from each other. It will be convenient in the following calculations to choose some T close to the T_r, and possibly equal to one of them, and to express all series expansions in powers of $(\beta_r - \beta)$, where $\beta = 1/kT$.

In particular, the kernels $K_r(x,x')$ can be expanded about $\beta_r = \beta$. If only terms to first order in $(\beta_r - \beta)$ are retained, then (1.1) becomes

$$\frac{\partial \mu(x,t)}{\partial t} = \{H_0(x), \mu(x,t)\}$$

$$+ \sum_{r=1}^{R} \int [\tilde{K}_r(x,x')\mu(x',t) - \tilde{K}_r(x',x)\mu(x,t)]dx'$$

$$+ \sum_{r=1}^{R} (\beta_r - \beta) \int \left[\frac{\partial K_r(x,x')}{\partial \beta_r}\mu(x',t)\right.$$

$$\left. - \frac{\partial K_r(x',x)}{\partial \beta_r}\mu(x,t)\right]_{\beta_r=\beta} dx'. \quad (4.1)$$

where

$$\tilde{K}_r(x,x') = K_r(x,x')|_{\beta_r=\beta}, \quad (4.2)$$

[5] U. Fano, Phys. Rev. **96**, 869 (1954).
[6] This problem has also been considered by J. A. McLennan, Phys. Fluid **3**, 493 (1960), who does not adopt a special physical model, but instead makes certain simplifying mathematical assumptions.

and where $H_0(x)$ is written in place of $H(x)$, since no interaction with an external field is assumed. It is convenient to rewrite (4.1) in operator notation as

$$\frac{\partial \mu(x,t)}{\partial t} = \mathcal{K}\mu(x,t) + \sum_{r=1}^{R} (\beta_r - \beta)\mathcal{F}_r(x,t), \quad (4.3)$$

where $\mathcal{K}$ and $\mathcal{F}_r$ are linear operators such that for an arbitrary function $R(x)$

$$\mathcal{K}R(x) = \{H_0(x), R(x)\}$$

$$+ \sum \int [\tilde{K}_r(x,x')R(x') - \tilde{K}_r(x',x)R(x)]dx', \quad (4.4)$$

and

$$\mathcal{F}_r R(x) = \int \left[\frac{\partial K_r(x,x')}{\partial \beta_r}R(x')\right.$$

$$\left. - \frac{\partial K_r(x',x)}{\partial \beta_r}R(x)\right]_{\beta_r=\beta} dx'. \quad (4.5)$$

The operator $\mathcal{K}$ of (4.4) is essentially the same as the operator $\mathcal{K}$ introduced in Sec. 2, for when all the reservoirs have the same temperature T, they constitute a single composite reservoir, and the stochastic kernel $K(x,x')$ of this composite reservoir is simply $\sum K_r(x,x')$. By the result cited at the beginning of this Section, if $\mu(x,t)$ is any solution of (4.1) with an arbitrary initial condition, then it asymptotically approaches the unique stationary solution $\mu^s(x)$ as t increases to infinity. In particular, therefore, we may specify $\mu(x,0) = \mu_0(x)$, where $\mu_0(x)$ is defined in (2.2). We shall seek only an approximation to the true stationary solution $\mu^s(x)$ by investigating the solution to the approximate equation (4.3). By (1.4) and the properties of the Poisson bracket it follows that

$$\mathcal{K}\mu_0(x) = 0. \quad (4.6)$$

It may be checked by differentiation and the use of (4.6) that a formal solution to (4.3) which satisfies the initial condition $\mu(x,0) = \mu_0(x)$ is

$$\mu(x,t) = \mu_0(x) + \sum_{r=1}^{R} (\beta_r - \beta) \int_0^t dt'$$

$$\times \exp[(t-t')\mathcal{K}]\mathcal{F}_r\mu(x,t'). \quad (4.7)$$

The first-order term in the iteration solution of this integral equation is

$$\mu_1(x,t) = \sum_{r=1}^{R} (\beta_r - \beta) \int_0^t dt' \int dx' P(x,x'|t')\mathcal{F}_r'\mu_0(x'), \quad (4.8)$$

where $\mathcal{F}_r'$ is the linear operator of (4.5), except that it operates on functions of x', and where the transition probability notation of (2.8) has been used. We now proceed to find a simple expression for $\mathcal{F}_r\mu_0(x)$. By

(2.2) and (4.5)

$$\mathfrak{F}_r\mu_0(x) = \left\{ \frac{\partial}{\partial\beta_r} \int dx' \left[K_r(x,x')\frac{1}{Z_r} \exp[-\beta_r H_0(x')] - K_r(x',x)\frac{1}{Z_r} \exp[-\beta_r H_0(x)] \right] \right\}_{\beta_r=\beta}$$

$$- \left(\frac{\partial}{\partial\beta_r}\frac{1}{Z_r} \right)_{\beta_r=\beta} \int dx' \left[\tilde{K}_r(x,x') \exp[-\beta H_0(x')] - \tilde{K}_r(x',x) \exp[-\beta H_0(x)] \right]$$

$$+ \int dx' \left[\tilde{K}_r(x,x')Z^{-1} \exp[-\beta H_0(x')]H_0(x') - \tilde{K}_r(x',x)Z^{-1} \exp[-\beta H_0(x)]H_0(x) \right]. \quad (4.9)$$

The first two terms on the rhs of (4.9) vanish by (1.4), and therefore

$$\mathfrak{F}_r\mu_0(x) = \int dx' \left[\tilde{K}_r(x,x')\mu_0(x')H_0(x') \right.$$
$$\left. - \tilde{K}_r(x',x)\mu_0(x)H_0(x) \right]. \quad (4.10)$$

This equation may be transformed by using (1.2), (1.4), and $H_0(\bar{x})=H_0(x)$ to

$$\mathfrak{F}_r\mu_0(x) = \mu_0(x) \int \tilde{K}_r(x',\bar{x})[H_0(x')-H_0(\bar{x})]dx'. \quad (4.11)$$

Generalizing the notation of Sec. 3, we express the average rate of increase of the energy of the system due to interaction with the rth reservoir, when the system is located at phase point x, as

$$j^r(x) = \int dx' \, K_r(x',x)[H_0(x')-H_0(x)]. \quad (4.12)$$

When the rth reservoir has the temperature T, we shall use the notation

$$\tilde{j}^r(x) \equiv j^r(x)|_{\beta_r=\beta}$$

$$= \int dx' \, \tilde{K}_r(x',x)[H_0(x')-H_0(x)]. \quad (4.13)$$

From (4.8), (4.11), (4.12), and (4.13) it follows that

$$\mu_1(x,t) = \sum (\beta_r-\beta) \int_0^t dt' \int dx'$$
$$\times P(x,x'|t')\tilde{j}^r(\bar{x}')\mu_0(x'). \quad (4.14)$$

An expression for the first-order term $\mu_1{}^s(x)$ in the stationary solution $\mu^s(x)$ is obtained by letting $t \to \infty$ in Eq. (4.14):

$$\mu_1{}^s(x) = \sum (\beta_r-\beta) \int_0^\infty dt \int dx'$$
$$\times P(x,x'|t)\tilde{j}^r(\bar{x}')\mu_0(x'). \quad (4.15)$$

Using (A2) of the Appendix, we obtain an interesting alternative expression for $\mu_1{}^s(x)$ (which will not,

however, be used in the following considerations):

$$\mu_1{}^s(x) = \mu_0(x) \sum (\beta_r-\beta) \int_0^\infty dt \int dx'$$
$$\times P(x',\bar{x}|t)\tilde{j}^r(x'). \quad (4.16)$$

We shall now consider the heat flow from the rth reservoir into the system when the stationary state has been attained, which may be expressed as the ensemble average of $j^r(x)$:

$$J^r \equiv \int j^r(x)\mu^s(x)dx. \quad (4.17)$$

Because of the flow of heat in the stationary non-equilibrium state, there will be a steady rate of entropy production. The entropy of the system itself is constant, because the distribution does not change, and hence the entropy production is due entirely to the exchange of energy among the reservoirs through the medium of the system. If a quantity of heat ΔQ_r passes into the rth reservoir, the entropy increase is

$$\Delta S_r = (1/T_r)\Delta Q_r = k\beta_r\Delta Q_r. \quad (4.18)$$

Since J^r is the rate of heat flow from the rth reservoir into the system, the rate of entropy production in the system plus reservoirs is

$$\sigma = -\sum k\beta_r J^r. \quad (4.19)$$

Since $\sum J^r = 0$ in the stationary state, (4.19) can be rewritten as

$$\sigma = -\sum k(\beta_r-\beta)J^r. \quad (4.20)$$

In Onsager's treatment of irreversible thermodynamics[7] the thermodynamic "forces" ϕ_r and "flows" J^r are related to the rate of entropy production by the relation

$$\sigma = \sum \phi_r J^r.$$

Clearly this relation is satisfied in (4.20) if the thermodynamic force ϕ_r conjugate to the flow J^r is taken to be

$$\phi_r = -k(\beta_r-\beta). \quad (4.21)$$

Onsager's theory of irreversible thermodynamics is concerned with phenomena in which the flows are approximately linear in the thermodynamic forces, and

[7] L. Onsager, Phys. Rev. 37, 405 (1931); 38, 2265 (1931).

his reciprocity theorem applies to the coefficients of this set of linear relations. Bergmann and Lebowitz[1] have established previously that in the present model the Onsager reciprocal relations hold when the J^r are expressed as linear functions of the ϕ_q. We shall now derive their result in a new way, which has the advantage of providing explicit expressions for the coefficients.

We first return to Eq. (4.17) in order to find the first-order term in an expansion of J^r in powers of $(\beta_q - \beta)$. It is clear that for this purpose we may substitute $\mu_0(x) + \mu_1{}^s(x)$ for the exact stationary distribution $\mu^s(x)$. Furthermore, by expanding the kernel $K_r(x,x')$ about $\beta_r = \beta$ we may use (4.12) and (4.13) to obtain

$$j^r(x) = \tilde{j}^r(x) + (\beta_r - \beta) \int dx' \, [H_0(x') - H_0(x)]$$

$$\times \left[\frac{\partial K_r(x',x)}{\partial \beta_r} \right]_{\beta_r = \beta} + \cdots . \quad (4.22)$$

From (4.15), (4.17), and (4.22) we find, to first order in $(\beta_q - \beta)$,

$$J^r = (\beta_r - \beta) \int dx \int dx' \, \mu_0(x) [H_0(x') - H_0(x)]$$

$$\times \left[\frac{\partial K_r(x',x)}{\partial \beta_r} \right]_{\beta_r = \beta} + \sum_{q=1}^{R} (\beta_q - \beta) \int_0^\infty dt \int dx \int dx'$$

$$\times \tilde{j}^r(x) P(x,x' \mid t) \tilde{j}^q(\bar{x}') \mu_0(x'). \quad (4.23)$$

The first term in (4.23) can be transformed by the method of (4.9), and the second term can be written compactly by introducing for arbitrary $R(x)$ the notation

$$R_{\mathrm{tr}}(x) = R(\bar{x}), \quad (4.24)$$

(where the subscript tr denotes "time reversed") and by using the time-correlation notation of (2.18). Hence, to first order,

$$J^r = (\beta_r - \beta) \int dx \int dx'$$

$$\times \mu_0(x) \tilde{K}_r(x',x) H_0(x) [H_0(x') - H_0(x)]$$

$$+ \sum (\beta_q - \beta) \int_0^\infty dt \, \langle \tilde{j}^r(t) \tilde{j}_{\mathrm{tr}}{}^q(0) \rangle_0. \quad (4.25)$$

Using (4.21) and (4.25) we can express the linear relations between the J^r and the ϕ_q by

$$J^r = \sum_{r=1}^{R} L_q{}^r \phi_q, \quad (4.26)$$

where the coefficients of these linear relations are

$$L_q{}^r = -\frac{1}{k} \left\{ \int_0^\infty dt \, \langle \tilde{j}^r(t) \tilde{j}_{\mathrm{tr}}{}^q(0) \rangle_0 + \delta_q{}^r \int dx \int dx' \right.$$

$$\left. \times \mu_0(x) \tilde{K}_r(x',x) H_0(x) [H_0(x') - H_0(x)] \right\}. \quad (4.27)$$

Using the time-reversal theorem (A7) we obtain

$$L_q{}^r = L_r{}^q. \quad (4.28)$$

Thus, the Onsager reciprocal relations hold in the situation which we are considering. There is an analogy between Eq. (4.28) and Eq. (2.25), and in particular both of these reciprocity theorems rest upon time-reversal invariance. However, it does not seem correct to call Eq. (2.25) a generalization of Onsager's theorem, as sometimes is done, since the thermodynamic forces considered by Onsager cannot in general be represented as mechanical disturbances.

5. HEAT AND MATTER FLOW IN THE PRESENCE OF SEVERAL RESERVOIRS

The model described in Sec. 1 has been generalized by Bergmann and Lebowitz[1] in order to represent a system which exchanges particles as well as energy with several reservoirs. When there are n particles in the system, the state of the system can be specified by a point x_n in a phase space of $2nf$ dimensions, where f is the number of degrees of freedom of each particle. The phase space will be taken to be a generic phase space, in which microstates differing by a permutation of particles are considered to be identical. The grand ensemble density is represented by a family of functions $\mu_n(x_n,t)$, one in each $2nf$-dimensional generic phase space, and the evolution of the ensemble is governed by the following generalization of (1.1):

$$\frac{\partial \mu_n(x_n,t)}{\partial t} = \{ H(x_n), \mu_n(x_n,t) \}$$

$$+ \sum_{r=1}^{R} \sum_{i=0}^{\infty} \int dx_i' \, [K_{ni}{}^r(x_n,x_i') \mu_i(x_i',t)$$

$$- K_{in}{}^r(x_i',x_n) \mu_n(x_n,t)]. \quad (5.1)$$

Here $K_{ni}{}^r(x_n,x_i')$ is the probability per unit time that the system at x_i' will make the transition to x_n (which involves gaining $n-i$ particles) due to interaction with the rth reservoir. The rth reservoir is assumed to be characterized by a temperature T_r and in addition by a chemical potential ν_r. If the volume of the system is kept constant, it is natural to require that the following grand canonical distribution be stationary when the system is in contact only with the rth reservoir:

$$\mu_{n0}(x_n) = \mathfrak{z}_r{}^{-1} \exp[-\beta_r H(x_n) + \gamma_r n], \quad (5.2)$$

where

$$\mathfrak{z}_r \equiv \sum_{n=0}^{\infty} \int dx_n \exp[-\beta_r H(x_n) + \gamma_r n],$$

and

$$\gamma_r \equiv \beta_r \nu_r = (kT_r)^{-1}\nu_r.$$

In order to satisfy this requirement, an obvious generalization of (1.4) is required. Furthermore, the "time-reversed symmetry condition" (1.2) can also be generalized.

If the temperatures T_r are all close to each other, and hence close to some temperature T, and if in addition the chemical potentials ν_r are all close to some ν, it is possible to obtain generalizations of all the results of Sec. 4. The procedure is exactly the same as before except somewhat more cumbersome, and it suffices here to write down the main results.

The first-order term in the stationary solution $\mu_n{}^s(x_n)$ is found to be

$$\mu_{n1}{}^s(x_n) = \sum_{r=1}^{R} (\beta_r - \beta) \int_0^{\infty} dt \sum_{i=0}^{\infty} \int dx_i'$$

$$\times P(x_n, x_i' | t) \bar{j}^r(\bar{x}_i') \mu_i(x_i')$$

$$- \sum_{r=1}^{R} (\gamma_r - \gamma) \int_0^{\infty} dt \sum_{i=0}^{\infty} \int dx_i'$$

$$\times P(x_n, x_i' | t) \tilde{g}^r(\bar{x}_i') \mu_i(x_i'). \quad (5.3)$$

Here $\gamma = \beta\nu$, $P(x_n, x_i' | t)$ is the transition probability density in time t from x_i' to x_n when all the reservoirs

have temperature T and chemical potential ν, and $\bar{j}^r(x_n)$ has the same meaning as the similar expression in Eq. (4.13) except for an additional specification that the chemical potential of the rth reservoir is set equal to ν. Similarly $\tilde{g}^r(x_n)$ is the average rate of increase of the number of particles in the system due to interaction with the rth reservoir, when the system is at phase point x_n and the temperature and the chemical potential of the rth reservoir have, respectively, been set equal to T and ν, i.e.,

$$\tilde{g}^r(x_n) = [g^r(x_n)]_{\beta_r = \beta, \gamma_r = \gamma}$$

$$= \sum_{i=0}^{\infty} \int dx_i' \tilde{K}_{in}{}^r(x_i', x_n)[i - n]. \quad (5.4)$$

The heat and particle flows in the stationary state are the grand ensemble averages of $j^r(x_n)$ and $g^r(x_n)$, respectively:

$$J^r = \sum_{n=0}^{\infty} \int j^r(x_n) \mu_n{}^s(x_n) dx_n, \quad (5.5)$$

$$G^r = \sum_{n=0}^{\infty} \int g^r(x_n) \mu_n{}^s(x_n) dx_n, \quad (5.6)$$

where $\mu_n{}^s(x_n)$ is the exact stationary distribution in the presence of the reservoirs at different temperatures and chemical potentials. The approximations to J^r and G^r which are correct to first power in $(\beta_q - \beta)$ and $(\gamma_q - \gamma)$ are obtained by substituting $\mu_{n0}(x_n) + \mu_{n1}{}^s(x_n)$ for $\mu_n{}^s(x)$ and by expanding $j^r(x_n)$ and $g^r(x_n)$ about β and γ. The results are

$$J^r = (\beta_r - \beta) \sum_{n=0}^{\infty} \int dx_n \sum_{i=0}^{\infty} \int dx_i' \, \mu_{n0}(x_n) \tilde{K}_{in}{}^r(x_i', x_n) H(x_n)[H(x_i') - H(x_n)]$$

$$- (\gamma_r - \gamma) \sum_{n=0}^{\infty} \int dx_n \sum_{i=0}^{\infty} \int dx_i' \, \mu_{n0}(x_n) \tilde{K}_{in}{}^r(x_i', x_n) n [H(x_i') - H(x_n)] + \sum_{q=1}^{R} (\beta_q - \beta) \int_0^{\infty} dt \, \langle \bar{j}^r(t) \bar{j}^q{}_{tr}(0) \rangle_0$$

$$- \sum_{q=1}^{R} (\gamma_q - \gamma) \int dt \, \langle \bar{j}^r(t) \tilde{g}^q{}_{tr}(0) \rangle_0, \quad (5.7)$$

and

$$G^r = (\beta_r - \beta) \sum_{n=0}^{\infty} \int dx_n \sum_{i=0}^{\infty} dx_i' \, \mu_{n0}(x_n) K_{in}{}^r(x_i', x_n) H(x_n)[i - n]$$

$$- (\gamma_r - \gamma) \sum_{n=0}^{\infty} \int dx_n \sum_{i=0}^{\infty} dx_i' \, \mu_{n0}(x_n) \tilde{K}_{in}{}^r(x_i', x_n) n [i - n] + \sum_{q=1}^{R} (\beta_q - \beta) \int_0^{\infty} dt \, \langle \tilde{g}^r(t) \bar{j}^q{}_{tr}(0) \rangle_0$$

$$- \sum_{q=1}^{R} (\gamma_q - \gamma) \int_0^{\infty} dt \, \langle \tilde{g}^r(t) \tilde{g}^r{}_{tr}(0) \rangle_0. \quad (5.8)$$

The thermodynamic forces will be taken to be

$$\phi_r = -k(\beta_r - \beta), \quad r = 1, \cdots, R, \quad (5.9a)$$

$$\phi_r = k(\gamma_{r'} - \gamma), \quad r = R+1, \cdots, 2R \text{ and } r' = r - R, \quad (5.9b)$$

and we introduce the notation

$$J^r = G^{r'}, \quad \text{for} \quad r = R+1, \cdots, 2R \quad \text{and} \quad r' = r - R. \quad (5.10)$$

We can then express the rate of entropy production by

$$\sigma = \sum_{r=1}^{2R} \phi_r J^r. \quad (5.11)$$

It is clear that linear relations hold between the J^r and the ϕ_q (for $r = 1, \cdots, 2R$),

$$J^r = \sum_{q=1}^{2R} L_q{}^r \phi_q, \quad (5.12)$$

where the coefficients $L_q{}^r$ can be read from (5.7) and (5.8). Finally, it can be checked that

$$L_q{}^r = L_r{}^q, \quad (5.13)$$

so that the Onsager relations hold in the present model when there are simultaneous flows of heat and matter.

6. APPLICATIONS TO KINETIC THEORY

We can apply the formal results of Secs. 1–3 to the following problem considered by Chang and Uhlenbeck[8] and others.[9] A particle of mass M and charge e is bound harmonically to a fixed center, with potential $\frac{1}{2}M\omega_0^2 R^2$. It is subject to elastic collisions with a gas of neutral molecules of mass m, and this gas is assumed to be unaffected statistically by collisions with the particle and always to have a Maxwellian distribution at temperature T. Finally, there is an alternating external electric field $E(t) = E_0 \cos\omega t$ in the X direction. The particle is driven by the field and dissipates energy by colliding with the gas molecules. In a number of important cases Chang and Uhlenbeck calculate $Q(\omega)$, the rate at which the dissipation of energy occurs, by finding solutions to the Boltzmann equation. We shall rederive two of their results by use of the fluctuation-dissipation theorem, and in addition we shall give a proof of a sum rule which they noticed but did not prove.

In Sec. 3 we found that

$$Q(\omega) = \frac{h_0^2}{2kT} \int_0^\infty dt \cos\omega t \langle \dot{A}(t)\dot{A}(0)\rangle_0. \quad (6.1)$$

In the present problem the perturbation term of the total Hamiltonian is $-XeE_0 \cos\omega t$, so that we can

write

$$h_0 = eE_0 \quad \text{and} \quad A(x) = X. \quad (6.2)$$

Since the position of the particle is not instantaneously changed by a collision with the gas molecules (which constitute the reservoir) the condition (2.11′) is satisfied, and we have

$$\dot{A} = \{X, H\} = V_X \quad (6.3)$$

Hence, the correlation function of interest is

$$\langle \dot{A}(t)\dot{A}(0)\rangle_0 = \langle V_X(t)V_X(0)\rangle_0. \quad (6.4)$$

The first case we shall consider is the Brownian motion limit, in which $m/M \ll 1$. The correlation function (6.4) in the case of a harmonically bound Brownian particle was found by Wang and Uhlenbeck[10] to be

$$\langle V_X(t)V_X(0)\rangle_0 = \frac{2kT\eta}{\pi M} \int_0^\infty \frac{d\omega\,\omega^2 \cos\omega t}{(\omega_0^2 - \omega^2)^2 + \eta^2\omega^2}, \quad (6.5)$$

where η is a friction constant depending on the density of the gas and the law of interaction between the particle and the gas molecules. [It has been convenient in Eq. (6.5), and also later, to change their notation slightly.] From (6.1)–(6.5) we have

$$Q(\omega) = \frac{e^2 E_0^2 \eta}{M} \frac{\omega^2}{(\omega^2 - \omega_0^2)^2 + \eta^2\omega^2}, \quad (6.6)$$

which agrees with the result of Chang and Uhlenbeck.[8]

The second case we shall consider is that in which $m/M \gg 1$ (the "Lorentz limit"), the interaction between the particle and the gas molecules is a hard sphere collision, and $\omega_0 = 0$. We calculate the correlation function (6.4) as follows:

$$\langle V_X(t)V_X(0)\rangle_0$$

$$= \int V_X' P(\mathbf{V}', \mathbf{R}'; \mathbf{V}, \mathbf{R}|t) V_X \mu_0(\mathbf{V}, \mathbf{R}) d\mathbf{V}' d\mathbf{R}' d\mathbf{V} d\mathbf{R}$$

$$= \int V_X' W(\mathbf{V}, t)\delta(\mathbf{V} - \mathbf{V}')\delta(\mathbf{R}' - \mathbf{R} - \mathbf{V}t)$$
$$\times V_X \mu_0(\mathbf{V}, \mathbf{R}) d\mathbf{V}' d\mathbf{R}' d\mathbf{V} d\mathbf{R}. \quad (6.7)$$

The second equation of (6.7) results from writing $P(\mathbf{V}', \mathbf{R}'; \mathbf{V}, \mathbf{R}|t)$ as

$$P(\mathbf{V}', \mathbf{R}'; \mathbf{V}, \mathbf{R}|t) = W(\mathbf{V}, t)\delta(\mathbf{V} - \mathbf{V}')\delta(\mathbf{R}' - \mathbf{R} - \mathbf{V}t)$$
$$+ P'(\mathbf{V}', \mathbf{R}'; \mathbf{V}, \mathbf{R}|t), \quad (6.8)$$

where $W(\mathbf{V}, t)$ is the probability that the particle with velocity $\mathbf{V}$ will not suffer a collision with a gas molecule in time t, and $P'(\mathbf{V}', \mathbf{R}'; \mathbf{V}, \mathbf{R}|t)$ the transition probability density from $(\mathbf{V}, \mathbf{R})$ to $(\mathbf{V}', \mathbf{R}')$ in time t if at least

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[9] J. H. Van Vleck and V. Weisskopf, Revs. Modern Phys. **17**, 227 (1945); E. P. Gross and J. L. Lebowitz, Phys. Rev. **104**, 1528 (1956), and references cited there.

[10] Ming Chen Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945).

one collision has occurred in the interval; the contribution of the second term on the rhs of (6.8) to the correlation function (6.7) is zero, because there is zero "correlation of velocities" when a small hard sphere is scattered by a very large one.[11] From the assumption of hard-sphere scattering

$$W(\mathbf{V},t) = \exp(-Vt/\lambda), \tag{6.9}$$

where λ is the mean free path of the particle. Therefore

$$\langle V_x(t)V_x(0)\rangle_0$$

$$= \int d\mathbf{V}\ V_x{}^2 \exp(-Vt/\lambda)(2\pi kT/M)^{-3/2}$$

$$\times\exp(-MV^2/2kT) = \tfrac{4}{3}\pi(2\pi kT/M)^{-3/2}\int_0^\infty dV$$

$$\times V^4 \exp(-Vt/\lambda)\ \exp(-MV^2/2kT). \tag{6.10}$$

From (6.1), (6.4), and (6.10) we obtain

$$Q(\omega) = \tfrac{4}{3}\pi^{-1/2}\frac{e^2 E_0{}^2 \tau_0}{M}\int_0^\infty dc\ \frac{c^5}{c^2+\tau_0{}^2\omega^2}\exp(-c^2), \tag{6.11}$$

where $\tau_0 = (M/2kT)^{1/2}\lambda$. Again this agrees with the result of Chang and Uhlenbeck.

We can go one step beyond the work of Chang and Uhlenbeck by proving (to second order in accuracy) a sum rule which they noted without proof. From (6.1)–(6.4) we have

$$\int_{-\infty}^\infty Q(\omega)d\omega = \frac{e^2 E_0{}^2}{2kT}\int_{-\infty}^\infty d\omega \int_0^\infty dt\ \cos\omega t\langle V_x(t)V_x(0)\rangle_0$$

$$= (\pi e^2 E_0{}^2/2kT)\langle V_x{}^2\rangle_0. \tag{6.12}$$

But by the equipartition theorem

$$\langle V_x{}^2\rangle_0 = kT/M. \tag{6.13}$$

Hence,

$$\int_{-\infty}^\infty Q(\omega)d\omega = \pi e^2 E_0{}^2/M. \tag{6.14}$$

Related sum rules have been proved by Kubo.[2]

The above calculation can be used to determine the conductivity of a slightly ionized gas, in which only collisions between electrons and neutral molecules need be taken into account, and in which the electrons are represented as small hard spheres and the molecules as large hard spheres (the Lorentz model). If the density of electrons is N, then the current density in the X direction is

$$j_X(t) = eN\langle V_X(t)\rangle, \tag{6.15}$$

where the average $\langle V_X(t)\rangle$ is taken in the perturbed ensemble. The complex conductivity $\sigma(\omega)$ is defined by

$$j_X(t) = \sigma(\omega)E_0 e^{i\omega t}, \tag{6.16}$$

where $E_0\exp i\omega t$ is the electric field in the X direction. If the quantity B of Sec. 2 is identified with eNV_X, and the quantity A with eX, then clearly

$$\sigma(\omega) = \chi_{BA}(\omega), \tag{6.17}$$

where $\chi_{BA}(\omega)$ is the susceptibility defined in Eq. (2.20). From Eq. (2.19) and Eq. (2.20) we then have

$$\sigma(\omega) = e^2 N\beta \int_0^\infty \langle V_X(t)V_X(0)\rangle_0 e^{-i\omega t}dt. \tag{6.18}$$

Inserting the expression for $\langle V_X(t)V_X(0)\rangle_0$ from Eq. (6.10) yields

$$\sigma(\omega) = \frac{8Ne^2\tau_0}{3\pi^{1/2}M}\int_0^\infty dc\ \frac{c^4}{c+i\tau_0\omega}\exp(-c^2). \tag{6.19}$$

This formula agrees with a result of Margenau,[12] but our derivation uses a more specialized model than the one which he assumes.

7. VALIDITY OF THE PERTURBATION PROCEDURE

Approximate solutions of a modified Liouville equation were found in Secs. 2 and 4 by means of a perturbation procedure. No attempt was made in those sections to justify the procedure rigorously, nor shall we undertake to do this now. In particular, we shall not deal with the difficult problem of the convergence of the iteration solutions of the integral Eqs. (2.6) and (4.7). However, we wish to discuss a particular difficulty which arises from the fact that $\mu(x,t)$ is a function in phase space, which in the case of a system with many degrees of freedom is a space of high dimensionality. When the phase space has many dimensions, it is very likely that the first approximation $\eta(x,t) \equiv \mu_0(x) + \mu_1(x,t)$ will be a very bad approximation to $\mu(x,t)$, in the sense that $\eta(x,t)$ will have negligible values at those phase points at which $\mu(x,t)$ is large and conversely.[13] A more formal expression of this difficulty is that the functions

$$\left\{\int [\mu(x,t)]^2 dx\right\}^{-1/2}\mu(x,t), \quad \left\{\int [\eta(x,t)]^2 dx\right\}^{-1/2}\eta(x,t)$$

[which are, respectively, the distributions $\mu(x,t)$ and $\eta(x,t)$ normalized so as to be square integrable to

[11] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, New York, 1939), p. 99.

[12] H. Margenau, Phys. Rev. **69**, 508 (1946).

[13] This difficulty and its consequences were pointed out to the authors by Professor E. P. Wigner. Similar problems occur in the quantum mechanical many-body problem, see, e.g., Van Hove, Hugenholtz, and Howland, *Quantum Theory of Many-Body Systems* (W. A. Benjamin Inc., New York, 1961).

unity] may very well be almost orthogonal to each other, i.e.,

$$\frac{\displaystyle\int \mu(x,t)\eta(x,t)dx}{\left\{\displaystyle\int [\mu(x,t)]^2 dx \int [\eta(x,t)]^2 dx\right\}^{1/2}} \ll 1. \qquad (7.1)$$

The difficulty may be illustrated by a simple example. Let the system consist of N noninteracting harmonically bound Brownian particles, each as described at the beginning of Sec. 6: i.e., each of charge e and mass M and bound with a potential $\frac{1}{2}M\omega_0^2 R_i^2$, where $R_i = (X_i, Y_i, Z_i)$ is the displacement from the ith binding center. The reservoir, consisting of neutral gas molecules of mass $m \ll M$, will also be as described in Sec. 6. Instead of an alternating external field, however, we now assume a constant uniform field of strength E in the X direction. A phase point x in the system phase space is a point in a $6N$-dimensional space, but because the N particles are noninteracting, the physically significant distributions are products of single-particle distributions. Thus, the equilibrium distribution in the absence of the external field is

$$\mu_0(x) \propto \prod_{i=1}^{N} \exp\left\{-\beta\left[\frac{P_i^2}{2M}+\frac{M}{2}\omega_0^2 R_i^2\right]\right\}. \qquad (7.2)$$

The distribution in the presence of the external field at time $t=0$ (when the field has been present and constant for an infinitely long time, so that equilibrium has been established) is

$$\mu(x,0) \propto \exp\{-\beta[H_0(x)-\sum_i eEX_i]$$
$$=\prod_i \exp\{-\beta[(P_i^2/2M)+\frac{1}{2}M\omega_0^2 R_i^2-eEX_i]\}, \qquad (7.3)$$

while

$$\eta(x,0)=\mu_0(x)[1+\beta eE\sum_j X_j]. \qquad (7.4)$$

It follows that

$$\frac{\displaystyle\int \mu(x,0)\eta(x,0)dx}{\left\{\displaystyle\int [\mu(x,0)]^2 dx \int [\eta(x,0)]^2 dx\right\}^{1/2}}$$

$$=\left\{\frac{1+(eE/\omega_0)^2 N\beta/2M}{\exp[(eE/\omega_0)^2 N\beta/2M]}\right\}^{1/2}. \qquad (7.5)$$

Hence, for given E_0 and sufficiently large N the ratio in (7.5) is $\ll 1$, thus confirming (7.1).

Although in the foregoing example $\mu(x,0)$ and $\eta(x,0)$ are almost orthogonal for large N, there is nevertheless a clear sense in which the latter is a good approximation to the former: namely, the single-particle distribution $\eta^{(1)}(x,t)$ derived from $\eta(x,0)$ is close to the single-particle distribution $\mu^{(1)}(x,t)$ derived from $\mu(x,0)$, at least when E is sufficiently small. Thus,

$$\mu^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)$$

$$\equiv \int d\mathbf{R}_2 d\mathbf{P}_2 \cdots \int d\mathbf{R}_N \int d\mathbf{P}_N \,\mu(x,0)$$

$$\propto \exp[-\beta(P_1^2/2M+\frac{1}{2}M\omega_0^2 R_1^2-eEX_1)], \qquad (7.6)$$

because of Eq. (7.3), while

$$\eta^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)$$

$$=\int d\mathbf{R}_2 \int d\mathbf{P}_2 \cdots \int d\mathbf{R}_N \int d\mathbf{P}_N \,\eta(x,0)$$

$$\propto \exp[-\beta(P_1^2/2M+\frac{1}{2}M\omega_0^2 R_1^2)]$$
$$\times(1+\beta eEX_1), \qquad (7.7)$$

from Eq. (7.4).

One sees that for a field sufficiently weak that

$$(eE/\omega_0)^2\beta/2M \ll 1,$$

the functions $\mu^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)$ and $\eta^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)$ are very close to each other, i.e.,

$$\frac{\displaystyle\int \eta^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)\mu^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)d\mathbf{R}_1 d\mathbf{P}_1}{\left\{\displaystyle\int [\eta^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)]^2 d\mathbf{R}_1 d\mathbf{P}_1 \int [\mu^{(1)}(\mathbf{R}_1,\mathbf{P}_1,0)]^2 d\mathbf{R}_1 d\mathbf{P}_1\right\}^{1/2}} \approx 1. \qquad (7.8)$$

Similarly, all the n-particle distributions derived from $\mu(x,0)$ and $\eta(x,0)$, for small n, are close to each other. Since physical quantities of interest, such as energy, heat flow, entropy, depend most strongly on the n particle distributions with n small, the deviation of the N-particle distributions from each other causes no serious difficulty in interesting calculations.

Caution is necessary, however, in adopting this solution to the difficulty. In the example considered above it was easy to demonstrate that the single-particle distributions are close to each other, since the system consists of noninteracting components. In more realistic situations, in which there is interaction between the components, the question of the character of the single-particle distributions would have to be re-examined, and, in general, it would be a difficult question. It is reasonable that when the physical characteristics of the system do not change radically

in the presence of the disturbance (whether thermal or mechanical) the single-particle distribution obtained by the perturbation method in first order is indeed a good approximation to the exact single-particle distribution. On the other hand, in the neighborhood of a critical point or a phase transition, the perturbation method may be extremely inaccurate, not merely in the sense of (7.1), but in the sense that the first-order approximation to the single-particle distribution will be very inaccurate.

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APPENDIX

We wish to state and prove several theorems concerning the transition probability density $P(x,x'|t)$ and the time-correlation function $\langle R(t)S(0)\rangle_0$.

The first theorem is that $P(x,x'|t)$ obeys the Chapman-Kolmogoroff equation

$$P(x,x'|t+t') = \int dx'' \, P(x,x''|t)P(x'',x'|t'), \quad (A1)$$

for t and $t' \geqslant 0$, where $P(x,x'|t)$ is the transition probability density for a system in contact with a single reservoir. This follows directly from the definition

$$P(x,x'|t) = \exp(t\mathcal{K})\delta(x-x'), \quad (2.8)$$

by using the properties of the δ function and the fact that $\mathcal{K}$ is a linear operator on functions of x.

The second theorem is that $P(x,x'|t)$ has the time-reversal property

$$P(x,x'|t)\mu_0(x') = P(\bar{x}',\bar{x}|t)\mu_0(x). \quad (A2)$$

This is an integral form of the "time-reversed symmetry condition" given by Eq. (1.2) and states that in an equilibrium ensemble as many systems move in a time interval from the region dx' to dx go from $d\bar{x}$ to $d\bar{x}'$. The reason for this "detailed balance" is clearly the basic mechanical reversibility of system-reservoir combination and the assumption that the reservoir components have a Maxwell-Boltzmann distribution prior to collision, which are the properties assumed by Bergmann and Lebowitz[1] in order to establish conditions (1.2) and (1.4). To prove (A2) we first rewrite Eq. (2.8) as

$$P(x,x'|t) = \exp[t\mathcal{K}(x,x')],$$

where the matrix element $\mathcal{K}(x,x')$ is defined in terms of the operator $\mathcal{K}$ (operating on functions of y) as

$$\mathcal{K}(x,x') \equiv \int dy \, \delta(y-x)\mathcal{K}\delta(y-x').$$

Then

$$\mathcal{K}(x,x') = \{\delta(y-x'),H_0(y)\}_{y=x}$$

$$+ K(x,x') - \delta(x-x') \int K(x'',x')dx''. \quad (A3)$$

A formal expansion of P in powers of t is then

$$P(x,x'|t) = \delta(x-x') + t\mathcal{K}(x,x')$$

$$+ \tfrac{1}{2}t^2 \int \mathcal{K}(x,x'')\mathcal{K}(x'',x')dx'' + \cdots. \quad (A4)$$

The symmetry relation (A2) may now be shown to hold for the coefficient of t^n in (A4) for each $n=0, 1, 2, \cdots$. This is obvious for $n=0$. For $n=1$ we must examine each of the three terms of (A3) separately: The invariance of $\{\delta(y-x'), H_0(y)\}_{y=x}\mu_0(x')$ under $(x,x') \to (\bar{x}',\bar{x})$ follows from time reversal of a trajectory in the isolated system (in the absence of the reservoir); the validity of (A2) for the second and third terms of (A3) follows from conditions (1.2) and (1.4). Finally, the validity of (A2) for the coefficients of t^n with $n \geqslant 2$ follows recursively from the case of $n=1$.

A time-reversal theorem for time-correlation functions follows immediately from (A1) and from the definition of time-correlation functions: By (A1) and the change of variables $x \to \bar{x}$, $x' \to \bar{x}'$, (2.18) becomes

$$\langle R(t)S(0)\rangle_0 = \int dx \int dx' \, R(\bar{x})P(x',x|t)S(\bar{x}')\mu_0(x). \quad (A5)$$

Using the notation of Eq. (4.24), we obtain the theorem

$$\langle R(t)S(0)\rangle_0 = \langle S_{tr}(t)R_{tr}(0)\rangle_0. \quad (A6)$$

Finally, we can show that

$$\frac{d}{dt}\langle R(t)S(0)\rangle_0 = \langle \dot{R}(t)S(0)\rangle_0, \quad (A7)$$

by using (A1) as follows:

$$\frac{d}{dt}\int dx \int dx' \, R(x)P(x,x'|t)S(x')\mu_0(x')$$

$$= \lim_{\tau \to 0} \frac{d}{d\tau} \int dx \int dx' \, R(x)P(x,x'|t+\tau)S(x')\mu_0(x')$$

$$= \lim_{\tau \to 0} \frac{d}{d\tau} \int dx \int dx' \int dx''$$

$$\times R(x)P(x,x''|\tau)P(x'',x'|t)S(x')\mu_0(x')$$

$$= \int dx \int dx'' \, \dot{R}(x'')P(x'',x'|t)S(x')\mu_0(x').$$