Stationary Nonequilibrium Gibbsian Ensembles*

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The general theory of a Gibbs ensemble representing a system in contact with its surroundings is applied to several concrete situations of interest. By an appropriate choice of heat reservoirs a simply modified Liouville equation is found to describe a heat conducting system. The stationary nonequilibrium Γ-space ensembles which describe such a system are found explicitly for some cases. In the simplest cases these ensembles turn out to be canonical with a temperature that is a weighted average of the reservoir temperatures. For other systems, such as Brownian particles inside a fluid whose temperature is not uniform, we find the stationary ensemble to terms linear in the temperature gradient. From this we are led to discuss ensembles that will approximately represent an arbitrary heat conducting fluid. A more general proof than previously given for the asymptotic approach of the Γ-space distribution to its stationary value is also presented.

I. INTRODUCTION

THE theoretical investigation of the nonequilibrium properties of macroscopic systems has proceeded, with varying degrees of success, along the lines used for the treatment of systems in equilibrium: thermodynamics, kinetic theory, and statistical mechanics.[1] However, only in the case of equilibrium are the relationships between these methods, and hence their consistency, completely established. In the domain of nonequilibrium processes only the kinetic theory method of Boltzmann has been exploited extensively. The application of statistical mechanics and irreversible thermodynamics has been confined mostly to systems not far from equilibrium. In this paper we continue our effort to develop a general Gibbsian statistical mechanics of nonequilibrium processes. We try to find Γ-space ensembles that will represent systems not in equilibrium in the same way that the microcanonical, canonical, and grand canonical ensembles represent systems in equilibrium. There is of course no *a priori* assurance that such a parallel can be made. After all, the class of nonequilibrium states is richer and much more varied than that encountered in equilibrium. Our main interest however lies mainly in those systems which though not in equilibrium are yet in a steady state, i.e., systems through which stationary currents are flowing or which, subject to externally imposed periodic forces, respond periodically. Since experimentally the behavior of a large class of such systems is describeable by a few characteristic parameters such as conductivity, viscosity, etc., we hope there may exist general Gibbsian ensembles representing these systems.

In practice it is not usually necessary to know the detailed Γ-space distribution of a system in order to find its macroscopic properties. These are mostly expressible in terms of the reduced single particle and two particle distribution functions. However, even aside from the theoretical importance of the Gibbs ensemble it might happen that, as in equilibrium, it will be more convenient to first find the N-particle distribution and then by integration the lower order distributions.

Our approach has been described previously[2,3] and we shall give only a very brief review here. We consider an arbitrary system in contact with several heat reservoirs. The reservoirs are idealized models which have the following properties: (1) They consist of an infinite number of identical noninteracting components. (2) Each component may interact with our system but once. (3) This interaction is impulsive. These idealizations permit us to describe the time evolution of the Gibbs-ensemble representing our system if we know the stochastic kernel $K(x,x')$. $K(x,x')dxdt$ is the conditional probability of a system located at the point x' in its Γ-space at time t to have a collision with a reservoir component, causing it to make a transition to the volume element $(x, x+dx)$, in the time interval $(t, t+dt)$.

The equation governing the time evolution of the ensemble density $\mu(x,t)$ is a generalization of the Liouville equation for isolated systems, taking account of changes in μ due to collision with reservoir components. It has the form

$$\frac{\partial \mu(x,t)}{\partial t} + (\mu, H) = \int [K(x,x')\mu(x',t) - K(x',x)\mu(x,t)]dx',$$

$$K(x,x') = \sum_{\alpha} K_{\alpha}(x,x'), \qquad (1.1)$$

where K_{α} represents the effect of the αth reservoir which in the cases we have considered is some kind of temperature bath at temperature T_{α}.

The remainder of this paper deals with a system placed between two specified reservoirs for which the kernels K_{α} can be explicitly written. Section II describes these reservoirs and finds the stationary ensemble when their temperatures are equal. In Sec.

[1] For review and bibliography see E. W. Montroll and M. S. Green, Ann. Rev. Phys. Chem. **5**, 449 (1954); also D. ter Haar, Revs. Modern Phys. **27**, 289 (1955).

[2] P. G. Bergmann and J. L. Lebowitz, Phys. Rev. **99**, 578 (1955); J. L. Lebowitz and H. L. Frisch, Phys. Rev. **107**, 917 (1957).

[3] J. L. Lebowitz and P. G. Bergmann, Ann. Phys. **1**, 1 (1957).

III we simplify the right side of the generalized Liouville equation changing it from an integral to a differential operator. In Sec. IV we solve this equation to yield stationary nonequilibrium ensemble for some very simple systems. The stationary ensemble for a general heat conducting system is treated in an approximate fashion in Sec. V. Appendix I extends the proof of the ensembles approach to a stationary state under the influence of the reservoirs, previously given, and Appendix II is an extension of the theory developed in Sec. IV.

II. DESCRIPTION OF THE RESERVOIRS

We consider an arbitrary physical system contained in a cylinder whose ends are closed by two movable pistons. The state of the inner system is specified by the variable $y = (\mathbf{r}_1, \cdots, \mathbf{r}_N, \mathbf{p}_1, \cdots, \mathbf{p}_N)$ that of the two pistons by (Q_1, P_1) and (Q_2, P_2) and the whole system by $x = (y, Q_1, P_1, Q_2, P_2)$, $Q_1 < Q_2$. To the left of Q_1 there is an ideal gas (heat reservoir) of particles having mass m_1, density c_1, and temperature T_1, while to the right of Q_2 there is a similar reservoir of particles having masses m_2, density c_2, and temperature T_2. It is clear that the only system variables which will change discontinuously during a collision with a component of reservoir one or reservoir two are P_1 and P_2, respectively. We shall thus have $K_1(x, x') = K_1(P_1, P_1') \times \delta(Q_1 - Q_1') \delta(y - y') \delta(Q_2 - Q_2') \delta(P_2 - P_2')$ and a similar expression for $K_2(x, x')$. Hence our basic equation, Eq. (1.1), will assume the form

$$\frac{\partial \mu(x,t)}{\partial t} + (\mu, H)$$

$$\int [K_1(P_1, P_1') \mu(y, Q_1, P_1', Q_2, P_2, t)] dP_1'$$

$$- \int K_1(P_1', P_1) \mu(x, t) dP_1'$$

$$+ \int [K_2(P_2, P_2') \mu(y, Q_1, P_1, Q_2, P_2', t)] dP_2'$$

$$- \int K_2(P_2', P_2) \mu(x, t) dP_2', \quad (2.1)$$

where

$$H(x) = H_S(y) + U(\mathbf{r}_1, \cdots \mathbf{r}_N, Q_1, Q_2)$$

$$+ P_1{}^2/(2M_1) + P_2{}^2/(2M_2). \quad (2.2)$$

We now assume that prior to collision the particles of each reservoir have a Maxwellian distribution of velocities with their respective temperature T_1 and T_2, and that the density of the particles is uniform everywhere outside the pistons. These assumptions are certainly not satisfied exactly by any real gas and neither is it possible to find a rigid piston, whose state is com-

pletely specified by its position and velocity, in nature. As was stated however in the introduction it is known experimentally, and we hope that it is possible also to prove mathematically for our model, that all the important features of the stationary state of a system conducting heat are independent of the details of the interaction with its surroundings.

Using the laws of conservation of energy and momentum during a collision,[4] we get

$$K(P_\alpha, P_\alpha') = \frac{A c_\alpha m_\alpha (M_\alpha + m_\alpha)^2}{(2\pi m_\alpha k T_\alpha)^{\frac{1}{2}} (2m_\alpha M_\alpha)^2}$$

$$\times \epsilon [(-1)^\alpha (P_\alpha' - P_\alpha)] |P_\alpha - P_\alpha'|$$

$$\times \exp \left\{ - \frac{[(P_\alpha - P_\alpha') + (m_\alpha/M_\alpha)(P_\alpha + P_\alpha')]^2}{8 m_\alpha k T} \right\}. \quad (2.3)$$

where $\alpha = 1, 2, A$ is the area of the piston and ϵ is Heaviside unit function

$$\epsilon(z) = 1, \quad z > 0,$$
$$= 0, \quad z < 0.$$

The presence of the unit function is due to the fact that during a collision P_1 can only increase and P_2 decrease.

This model can be made much more realistic if we imagine each piston to consist of N_α parts which are held tightly together by strong forces but are not rigidly fixed. The state of the αth piston would then be specified by $(\mathbf{Q}_\alpha, \mathbf{P}_\alpha) = (Q_\alpha', \cdots, Q_\alpha{}^{N_\alpha}, P_\alpha{}^1, \cdots, P_\alpha{}^{N_\alpha}, z_\alpha)$ where z_α stands for all those variables not affected during collisions. The momentum of each part of the piston would now change independently during a collision with a reservoir component. The stochastic kernel $K_\alpha(\mathbf{P}_\alpha, \mathbf{P}_\alpha')$ will now be a sum of N kernels $K_\alpha{}^{(i)}(P_\alpha{}^i, P_\alpha{}^{i'})$. When the area a and mass m_w of each part of the pistons is held constant then the total area and mass, A and M, are proportional to N_α. Such a piston will approximate a physical wall when the structure of the wall molecules is unimportant in collisions with reservoir components. We shall however not consider this more complicated model in detail but shall sometimes indicate how our formulas are to be modified to apply to this model.

When the temperatures of the two reservoirs are equal, $T_1 = T_2 = T$, we expect the stationary state of the system to be one of true equilibrium. We can indeed find the stationary solution of Eq. (2.2) for this case. It has the form

$$\mu_s = (Z^{-1}) e^{-\beta [H + p_2 A Q_2 - p_1 A Q_2]}, \quad (2.4)$$

where $p_\alpha = c_\alpha k T$ is the pressure of the αth reservoir and

$$Z(T, p_1, p_2) = \int_\Gamma e^{-\beta [H + p_2 A Q_2 - p_1 A Q_1]} dx. \quad (2.5)$$

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[4] See appendix of reference 3.

In order that Z be finite, i.e., μ_s normalizable, the system must be confined to a limited region of physical space. This is accomplished if there is some term in H which prevents Q_1, when $p_1 \leq p_2$, from assuming infinitely large negative values. If piston two has no external forces acting on it then the pressure inside the system, p, equals p_2 and μ_s has the form

$$\mu_s = (Z^{-1}) e^{-\beta[H + pV + (p - p_1)A Q_1]}, \qquad (2.6)$$

where $V = A(Q_2 - Q_1)$ is the volume of the system.

When $p_2 = p_1$, or when Q_1, is held fixed, μ_s has the form usually assumed for an ensemble representing a system at fixed pressure.[5] It is gratifying that we get this ensemble, approached asymptotically in time for arbitrary initial conditions. The fact that only the temperature and pressure of the reservoirs enter into the description of the stationary state of the system lends strength to our belief that the details of the interaction between system and reservoir are not important for the final state.[6]

It is interesting to note that the quantity

$$W = \int \mu \ln\left(\frac{\mu}{\mu_s}\right) dx$$

which we show in the appendix to decrease monotonically until the stationary state is reached is simply related to the Gibbs free energy $G(T, p)$. We have

$$W = \int \mu [\ln\mu + \beta(H + pV) + \ln Z] dx = [G - G_{eq}](kT)^{-1} \qquad (2.7)$$

This is completely analogous to the monotonic decrease of the Helmholtz free energy for a system whose stationary state is represented by a canonical ensemble.[2,3]

III. SIMPLIFICATION OF KERNELS

The solution of the time independent part of Eq. (2.2) becomes much more difficult to find when the temperature of the two reservoirs is not the same. Even the form of the solution will now necessarily depend somewhat on H. To take a very extreme example; let the system consist of two separate parts, each interacting with but one reservoir, i.e.,

$$H = H_1(y_1, Q_1, P_1) + H_2(y_2, Q_2, P_2), \quad y = (y_1, y_2).$$

The stationary ensemble would now be a product of two equilibrium ensembles,

$$\mu_s = (Z_1^{-1}) e^{-\beta_1[H_1 - p_1 A Q_1]} (Z_2^{-1}) e^{-\beta_2[H_2 + p_2 A Q_2]}$$

and no heat would be conducted across the system. This is of course not the kind of system we are interested in. To tackle the true nonequilibrium situation we simplify the structure of the right side of Eq. (2.2). First we make the hypothesis that the mass of the pistons is much greater than the mass of the reservoir particles, $\gamma_\alpha = (m_\alpha/M_\alpha) \ll 1$. We now use the known result that the integral operator on the right of Eq. (2.2) is equivalent to a differential operator of infinite order.[7] That is, for an arbitrary K,

$$\int [K(P, P')\mu(P') - K(P', P)\mu(P)] dP'$$
$$= \sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^n}{dP^n} [\mathcal{Q}^{(n)}(P)\mu(P)], \quad (3.1)$$

where

$$\mathcal{Q}^{(n)}(P) = \int K(P', P)(P - P')^n dP'.$$

The change from the integral to the differential operator can be made separately for each K_α. We have

$$\mathcal{Q}^{(n)}(P) = \sum_\alpha \mathcal{Q}_\alpha^{(n)}(P)$$
$$= \sum_\alpha \int K_\alpha(P_\alpha', P_\alpha)(P_\alpha - P_\alpha')^n dP_\alpha',$$

and for the kernels considered here

$$\mathcal{Q}_\alpha^{(n)}(P_\alpha) = [c_\alpha A \gamma_\alpha^{(n-1)/2}/4(2\pi k T_\alpha M_\alpha^3)^{\frac{1}{2}}]$$
$$\times \int_{-\infty}^{\infty} z^n |z| \, \epsilon[(-1)^\alpha z] \exp\left(-\frac{z^2}{8 M_\alpha k T_\alpha}\right)$$
$$\times \left[1 + \frac{(\gamma_\alpha)^{\frac{1}{2}} z P_\alpha}{2 M_\alpha k T_\alpha} + O(\gamma_\alpha)\right] dz. \quad (3.2)$$

When only terms of $O((\gamma_\alpha)^{\frac{1}{2}})$ are kept in the differential operator[8] above, then Eq. (2.2) assumes the form

$$\frac{\partial \mu(x, t)}{\partial t} + (\mu, H) = -p_1 A \frac{\partial \mu}{\partial P_1} + p_2 A \frac{\partial \mu}{\partial P_2}$$
$$+ \sum_{\alpha=1,2} \left[\frac{\partial}{\partial P_\alpha}(\lambda_\alpha P_\alpha \mu) + \frac{\partial^2}{\partial P_\alpha^2}(D_\alpha \mu)\right]. \quad (3.3)$$

where

$$\lambda_\alpha = c_\alpha A(8\gamma_\alpha k T_\alpha/\pi M_\alpha)^{\frac{1}{2}}, \quad D_\alpha = \lambda_\alpha M_\alpha k T_\alpha.$$

The right side of this equation has a structure similar to the usual Fokker-Planck equation where $p_1 A$ and $(-p_2 A)$ is the average force exerted by the reser-

[5] E. A. Guggenheim, J. Chem. Phys. **7**, 103 (1939); see also T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 60.

[6] If the pistons are tied down to some equilibrium positions by very strong forces, then our system would in effect have a constant volume and the stationary solution would be the canonical ensemble appropriate for such systems.

[7] J. Keilson and J. E. Storer, Technical Report No. 33, Cruft Laboratory, Harvard University (unpublished), or see M. C. Wang and G. E. Uhlenbeck, Revs. Modern Phys. **17**, 323 (1945).

[8] These are the lowest order terms which contain the essential features of the reservoirs.

voirs on pistons 1 and 2 and λ_α is the friction coefficient.[9] Note that if the αth reservoir were on both sides of the αth piston then the average force term would vanish and the friction constant would be $2\lambda_\alpha$. The average forces can be included in the Liouville term by defining a new Hamiltonian H', $H'=H+p_2AQ_2-p_1AQ_1$. The fundamental equation whose stationary solution we want is then

$$\frac{\partial\mu}{\partial t}+(\mu,H')=\sum_{\alpha=1,2}\frac{\partial}{\partial P_\alpha}\left\{\left[D_\alpha\exp\left(\frac{-\beta_\alpha P_\alpha^2}{2M_\alpha}\right)\right]\right.$$
$$\left.\times\frac{\partial}{\partial P_\alpha}\left[\exp\left(\frac{\beta_\alpha P_\alpha^2}{2M_\alpha}\right)\mu\right]\right\}, \quad (3.4)$$

where use has been made, in the last expression, of the relation between λ and D. After this simplification of the kernels the total entropy production σ can be written down easily. The entropy produced in the first reservoir is $\sigma_1=-(J_1'/T_1)$ where $J_1'=J_1-p_1Ad\langle Q_1\rangle/dt$ is the heat current flowing into the system from that reservoir; J_1 being the energy flux. Similarly for the second reservoir

$$\sigma_2=-(J_2'/T_2)=T_2^{-1}\left[-J_2-p_2A\frac{d\langle Q_2\rangle}{dt}\right],$$

while

$$\frac{d\langle H\rangle}{dt}=J_1+J_2; \quad \frac{d\langle H'\rangle}{dt}=J_1'+J_2'.$$

The rate of entropy change in the system is

$$\frac{dS_s}{dt}=-k\frac{d}{dt}\int\mu\ln\mu dx=-k\int\frac{\partial\mu}{\partial t}\ln\mu dx. \quad (3.5)$$

We find from Eq. (3.4) that

$$J_\alpha'=\lambda_\alpha[kT_\alpha-\langle P_\alpha^2\rangle/M_\alpha],$$

$$\sigma=\sigma_1+\sigma_2+\frac{dS_s}{dt}=k\sum_\alpha D_\alpha\int\left\{\exp(-\beta_\alpha P_\alpha^2/4M_\alpha)(\mu)^{-\frac{1}{2}}\right.$$
$$\left.\times\left[\frac{\partial}{\partial P_\alpha}[\exp(\beta_\alpha P_\alpha^2/2M_\alpha)\mu]\right]\right\}^2 dx\geq0. \quad (3.6)$$

In the stationary state

$$\frac{dS_s}{dt}=0; \quad \frac{d\langle H'\rangle}{dt}=0=J_1'+J_2'; \quad J_\alpha=J_\alpha', \quad (3.7)$$

so that

$$\sigma=-(J_1/T_1)-(J_2/T_2)=J_1(T_1-T_2)/(T_1T_2)\geq0, \quad (3.8)$$

and, if $T_1>T_2$,

$$J\equiv J_1=\lambda_1(kT_1-\langle P_1^2\rangle/M_1)=\lambda_2(\langle P_2^2\rangle/M_2-kT_2)\geq0. \quad (3.9)$$

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[9] S. Chandrasekhar, Revs. Modern Phys. **15**, 1 (1943).

is the heat current in the stationary state. We expect the following relation to hold in general $T_1\geq T_1^{(w)}\geq T_2^{(w)}\geq T_2$ where $M_\alpha kT_\alpha^{(w)}\equiv\langle P_\alpha^2\rangle$ is the wall temperature. The physical meaning of the expression for J' is obvious. J' is proportional to the deviation of the mean kinetic energy of the αth piston from the equilibrium value it would have if it were only in contact with the αth reservoir. It is a further consequence of Eq. (3.9) that, in the stationary state,

$$\sum_\alpha\lambda_\alpha T_\alpha^{(w)}=\sum_\alpha\lambda_\alpha T_\alpha=(\sum\lambda_\alpha)\bar{T}, \quad (3.10)$$

where $\bar{T}$ is the weighted average temperature of the two reservoirs.

It also follows from the definition of λ that J and σ are proportional to the area of the piston so that a heat flux per unit area, j, can be defined. The quantity (λ_α/A) plays the role of a heat conductivity across the interface between piston and reservoir. In the more realistic case described after Eq. (2.3), of a piston consisting of N_α parts, the mass of the piston M_α is replaced by $m_\alpha^{(w)}$ the mass of one segment of the piston, in the expression for the heat flux.

IV. SIMPLE STATIONARY ENSEMBLES

We consider here some very simple systems for which exact stationary nonequilibrium ensembles can be found. First we consider the case of one piston between two reservoirs. The position and momentum of this piston are designated by (Q,P), and its Hamiltonian is $h(Q,P)=P^2/2M+V(Q)$. Equation (3.4) will now have the form

$$\frac{\partial\mu(Q,P,t)}{\partial t}+(\mu,h')=\sum_\alpha\frac{\partial}{\partial P}\left\{D_\alpha\exp[-(\beta_\alpha P^2/2M)]\right.$$
$$\left.\times\frac{\partial}{\partial P}[\exp(\beta_\alpha P^2/2M)\mu]\right\}, \quad (4.1)$$

where $h'=h+(p_2-p_1)AQ$. Equation (4.1) has the time independent solution

$$\mu_s=(Z^{-1})\exp[-\bar{\beta}h'(Q,P)], \quad (4.2)$$

where

$$\bar{\beta}=(\sum D_\alpha\beta_\alpha/\sum D_\alpha)=(k\bar{T})^{-1}.$$
$$\bar{T}=[c_1(m_1T_1^3)^{\frac{1}{2}}+c_2(m_2T_2^3)^{\frac{1}{2}}]/$$
$$[c_1(m_1T_1)^{\frac{1}{2}}+c_2(m_2T_2)^{\frac{1}{2}}]. \quad (4.3)$$

The stationary heat flux J and the entropy production σ are, (for $T_1\geq T_2$)

$$J=\lambda_1k(T_1-\bar{T})=\lambda_2k(\bar{T}-T_2)(T_1-T_2)$$
$$=[\lambda_1\lambda_2/(\lambda_1+\lambda_2)]k(T_1-T_2),$$
$$\sigma=J(T_1-T_2)/T_1T_2$$
$$=[(\lambda_1\lambda_2k)/(\lambda_1+\lambda_2)T_1T_2](T_1-T_2)^2. \quad (4.4)$$

From the expression for λ given in Eq. (3.3) we get for the heat current per unit area

$$j = J/A = (8k^3/\pi M^2)^{\frac{1}{2}}(T_1 - T_2)$$
$$\times [c_1 c_2 (m_2 m_2 T_1 T_2)^{\frac{1}{2}}] / [(c_1^2 m_1 T_1)^{\frac{1}{2}} + (c_2^2 m_2 T_2)^{\frac{1}{2}}]. \quad (4.5)$$

The magnitude of J will be determined primarily by the reservoir with the lower value of λ. It is that reservoir which imposes the limit on the transport of heat.

The stationary nonequilibrium ensemble found here for a simple piston can be extended immediately to a piston consisting of N parts. The Hamiltonian of such a piston is

$$\mathfrak{IC} = \sum_{i=1}^{N} \frac{P_i^2}{2m_i^{(w)}} + U(Q_1, \cdots, Q_N, z), \quad (4.6)$$

where z stands for all those pairs of canonically conjugate variables which do not change during a collision. The equation governing the time evolution of this system's ensemble is similar to Eq. (4.1),

$$\frac{\partial \mu}{\partial t} + (\mu, \mathfrak{IC}') = \sum_{i=1}^{N} \sum_{\alpha=1,2} \frac{\partial}{\partial P_i} \left[D_\alpha^{\ i} \exp\left[-\left(\frac{\beta_\alpha P_\alpha^2}{2m_i^{(w)}} \right) \right] \right.$$
$$\left. \times \frac{\partial}{\partial P_i} \left(\exp\left(\frac{\beta_\alpha P_i^2}{2m_i^{(w)}} \right) \mu \right) \right], \quad (4.7)$$

where in order to get the right side of this equation we had to assume $m_\alpha \ll m_i^{(w)}$. Equation (4.7) again has the stationary solution

$$\mu_s = (Z^{-1}) \exp[-(\bar{\beta}\mathfrak{IC}')], \quad (4.8)$$

with $\bar{\beta}$ given by Eq. (4.3). This average temperature is the same for all parts of the piston being independent of the mass $m_i^{(w)}$ and the area a_i of each part. The heat flux j across this piston will be proportional to

$$\left[\sum_{i=1}^{N} a_i (m_i^{(w)})^{-2} / \sum a_i \right]$$

but will not depend otherwise on the structure of the piston.

The stationary ensembles found here for these simple systems may have some relevance to the kind of ensembles we may expect for a fluid between two temperature reservoirs. They suggest that, as a starting point, we might isolate (mentally) a narrow cylinder of fluid perpendicular to the temperature gradient and consider the fluid to the right and left of this cylinder as two temperature baths. These baths will tend to bring this cylinder of fluid into a canonical distribution with a temperature intermediate between those of the sides. Thus a kind of local equilibrium can exist in the fluid. This similarity will be clarified by treating a system whose surroundings have a continuously varying temperature.

Our system consists of a dilute concentration of large spheres, i.e., Brownian particles, embedded in a gas, treated as a reservoir, whose temperature varies with position. Since the concentration of the Brownian particles is assumed dilute we shall neglect the interaction among them and only consider the ensemble density in the Γ-space of a single such particle $\mu(\mathbf{R}, \mathbf{P}, t)$; $\mathbf{R} = (X, Y, Z)$. This distribution will change under the influence of the system Hamiltonian $H(\mathbf{R}, \mathbf{P})$ and due to collisions with the gas particles. Such a collision will occur whenever the distance between the centers of the Brownian particle and some reservoir particle is equal to σ, the sum of their radii. The velocity distribution of the gas particles just prior to a collision is again assumed to be Maxwellian with a temperature T, and concentration c, that depends on their position during a collision, i.e., on the surface of a sphere of radius σ centered at $\mathbf{R}$. In accordance with the approach of this article we shall not consider how such a reservoir could be maintained.

In order to treat this syetm by the methods developed before, we divide up the surface of the collision sphere of radius σ into small elements of area $dA_\alpha = \sigma^2 dw_\alpha$, where dw_α is an element of solid angle. All the gas particles which during collision, with a Brownian particle located at R, have their centers in dw_α will form one reservoir with temperature $T_\alpha(\mathbf{R}) = T(\mathbf{R} + \sigma \mathbf{n}_\alpha)$, where $\mathbf{n}_\alpha$ is a unit vector in dw_α. Evidently collisions with the αth reservoir will affect only the component of the systems momentum in the direction of $\mathbf{n}_\alpha$, i.e., $\mathbf{P} \cdot \mathbf{n}_\alpha$. We may now immediately write down the generalized Liouville equation for $\mu(\mathbf{R}, \mathbf{P}, t)$.

$$\frac{\partial \mu}{\partial t} + (\mu, H) = \sum_\alpha \int [K^\alpha(\mathbf{R} : \mathbf{P}, \mathbf{P}')\mu(\mathbf{R}, \mathbf{P}', t)$$
$$- K^\alpha(\mathbf{R} : \mathbf{P}', \mathbf{P})\mu(\mathbf{R}, \mathbf{P}, t)] d\mathbf{P}', \quad (4.9)$$

where

$$H = P^2/2M + U(\mathbf{R}),$$

$$K^\alpha(\mathbf{R} : \mathbf{P}, \mathbf{P}') = K_\alpha(\mathbf{R} : \mathbf{P} \cdot \mathbf{n}_\alpha, \mathbf{P}' \cdot \mathbf{n}_\alpha) \delta(\mathbf{P} \times \mathbf{n}_\alpha - \mathbf{P}' \times \mathbf{n}_\alpha),$$

and the summation is over all solid angle elements. The stochastic kernel K_α is essentially the same as the one in Eq. (2.3)

$$K_\alpha = \frac{\sigma^2 dw_\alpha m(m+M)^2 c_\alpha(\mathbf{R})}{(2\pi mkT_\alpha(\mathbf{R}))^{\frac{1}{2}}(2mM)^2} \epsilon[(\mathbf{P} - \mathbf{P}') \cdot \mathbf{n}_\alpha] |(\mathbf{P} - \mathbf{P}') \cdot \mathbf{n}_\alpha|$$
$$\times \exp\left\{ -\frac{[(\mathbf{P} - \mathbf{P}') \cdot \mathbf{n}_\alpha + (m/M)(\mathbf{P} + \mathbf{P}') \cdot \mathbf{n}_\alpha]^2}{8mkT_\alpha(\mathbf{R})} \right\}, \quad (4.10)$$

where m is the mass and $c_\alpha(\mathbf{R}) = C(R + \sigma \mathbf{n}\alpha)$ is the concentration of the gas particles.

When we convert the integral stochastic operator into a differential one and keep only the lowest order terms in (m/M), we get the following equation for

$\mu(R,P,t)$,

$$\frac{\partial \mu}{\partial t} + (\mu, H') = \sum_\alpha \sigma^2 dw_\alpha \{\lambda_\alpha \nabla_P(\bar{T} \cdot \mathbf{n}_\alpha \mathbf{n}_\alpha \mu) + D_\alpha \nabla_P, \nabla_P(\mathbf{n}_\alpha \mathbf{n}_\alpha \mu)\}, \quad (4.11)$$

where

$$H' = H + \sum_\alpha p_\alpha(\mathbf{R}) \sigma^2 dw_\alpha(\mathbf{R} \cdot \mathbf{n}_\alpha),$$

$$p_\alpha = c_\alpha k T_\alpha, \quad D_\alpha = M k T_\alpha \lambda_\alpha,$$

and λ_α is the friction constant for a plane piston per unit area given in Eq. (3.5),

$$\lambda_\alpha = (c_\alpha/M)(8mkT_\alpha/\pi)^{\frac{1}{2}}.$$

If it should happen that the temperature and concentration of the gas are the same everywhere then the summation over α, or integration over dw, can be performed explicitly, yielding the well known Fokker-Planck equation for a Brownian particle,[9,10]

$$\frac{\partial \mu}{\partial t} + (\mu, H) = \zeta M k T \nabla_P$$
$$\cdot \left\{ \exp\left(-\frac{\beta \mathbf{P}^2}{2M}\right) \nabla_P \left[\exp\left(\frac{\beta \mathbf{P}^2}{2M}\right) \mu \right] \right\}, \quad (4.12)$$

with $\zeta = (4/3)\pi\sigma^2\lambda$ the friction constant for a large sphere in an ideal gas also found by Green.[11] For comparison, the friction constant of a Brownian particle in a liquid is related to the viscosity of the liquid η by the well known Stokes relation $\zeta = 6\pi\sigma\eta/M$, but Eq. (4.12) is otherwise unchanged. The stationary solution of this equation, for constant T and c, is evidently the canonical ensemble at temperature T.

In general the temperature and concentration of the reservoir gas will vary but little over the distance σ. We may therefore expand these quantities about their value at the point R,

$$T_\alpha(\mathbf{R}) = T(\mathbf{R}) + \sigma \mathbf{n}_\alpha \cdot \frac{dT}{d\mathbf{R}} + O\left(\sigma \left|\frac{d \ln T}{d\mathbf{R}}\right|\right)^2,$$

$$c_\alpha(\mathbf{R}) = c(\mathbf{R}) = \sigma \mathbf{n}_\alpha \cdot \frac{dc}{d\mathbf{R}} + O\left(\sigma \left|\frac{d \ln c}{d\mathbf{R}}\right|\right)^2. \quad (4.13)$$

and keep only the terms linear in the gradients. When this is done in Eq. (4.11) we find the following equation for $\mu(R,P,t)$ to term linear in $\sigma |d \ln T/d\mathbf{R}|$,

$$\frac{\partial \mu}{\partial t} + (\mu, \mathfrak{H}) = \zeta(X) M k T(X) \nabla_P$$
$$\times \left[\exp\frac{(-\beta(X)\mathbf{P}^2)}{2M} \nabla_P \left(\exp\frac{(\beta(X)\mathbf{P}^2)}{2M} \mu \right) \right], \quad (4.14)$$

$$\mathfrak{H} = \frac{P^2}{2M} + V(X) = \frac{P^2}{2M} + U(X) + \frac{4}{3}\pi\sigma^3 X\frac{dp}{dX},$$

[10] J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946).
[11] M. S. Green, J. Chem. Phys. **19**, 1036 (1951).

where we have assumed for simplicity that the external forces are along the X-axis, the direction of the temperature and concentration gradients.

We shall now find the stationary solution of Eq. (4.14) for the situation in which the change of the reservoir temperature is very small in one "mean path" of the Brownian particle. In effect we will expand the stationary nonequilibrium ensemble density, which is a solution of Eq. (4.14), in powers of $|\tau v \cdot d \ln T/d\mathbf{R}|$ where $\tau(R) = [\zeta(\mathbf{R})]^{-1}$ is the relaxation time and v is some characteristic velocity of the Brownian particle.

We first write the stationary ensemble density $\mu(R,P)$ in the form

$$\mu(\mathbf{R},\mathbf{P}) = n(\mathbf{R})F(\mathbf{R},\mathbf{P}); \quad \int F(R,\mathbf{P})d\mathbf{P} = 1, \quad (4.15)$$

where $n(\mathbf{R})$ is the density and $F(\mathbf{R},\mathbf{P})$ the momentum distribution of the Brownian particles. Letting $\mathfrak{R}$ stand for differential operator on the right side of Eq. (4.14) we may rewrite the stationary part of Eq. (4.14) in the form

$$\tau(R)(nF, \mathfrak{H}) = n\mathfrak{R}(F - F_0), \quad (4.16)$$

where $F_0 = [2\pi M k T(R)]^{-\frac{3}{2}} \exp[-\beta(\mathbf{R})\mathbf{P}^2/2m]$. Here F_0 is the locally canonical distribution which is the zero order solution of Eq. (4.16). Writing in general

$$F = \sum_{i=0}^{\infty}(\tau)^i F_i, \quad n = \sum_{i=0}^{\infty}(\tau)^i n_i, \quad \mu = nF = \sum_{i=0}^{\infty}(\tau)^i \mu_i, \quad (4.17)$$

we find

$$F_1 = \mathfrak{R}^{-1}[F_0(\ln\mu_0, \mathfrak{H})], \quad \mu_0 = n_0 F_0. \quad (4.18)$$

The functions n_i as well as the integration constants appearing in Eq. (4.18) can be determined by consistency requirements. In particular we must have

$$\int F_i d\mathbf{P} = 0, \quad \nabla_R \cdot \int \mathbf{P} F_i d\mathbf{P} = 0, \quad i > 0. \quad (4.19)$$

This leads to the following expressions for the stationary ensemble density to first order in the gradients

$$\mu = \mu_0 + (\tau/3)\mu_0 \left\{ [P^2/2M - \tfrac{5}{2}kT(X)]P_X/M\frac{d\beta}{dX} \right\};$$

$$n_0 = B\beta(X) \exp\left[-\int \beta\frac{dV}{dX}dX \right]. \quad (4.20)$$

where B is a normalization constant. This n represents a balancing of the external forces by the pressure gradient of the Brownian particles, μ clearly reduces to the canonical distribution when the temperature gradient vanishes.

The form of the stationary ensemble (4.20) is remarkably independent of the detailed properties of the reservoir and its interaction with the system. Thus we would obtain the same stationary ensemble, (to first

order), if we had started [instead of Eq. (4.14)] with a relaxation type equation

$$\frac{\partial \mu}{\partial t} + (\mu, \mathfrak{IC}) = \frac{\mu_0 - \mu}{\tau'}, \quad \tau' = (\tau/3) = (3\zeta)^{-1}. \quad (4.21)$$

We shall use this fact to guide us in the construction of approximate stationary ensembles for a general heat conducting fluid which we shall do in the next section.

V. APPROXIMATE STATIONARY ENSEMBLE

In this section we will discuss some ensembles which we believe to be similar to the true stationary ensembles representing a system conducting heat. Restricting ourselves to a one component monatomic system, the Hamiltonian $H(x)$ [or $H'(x)$] has the form

$$H(x) = \sum_{i=1}^{N} \left\{ \frac{p_i^2}{2m} + \frac{1}{2} \sum_{j \neq i} V(u_{ij}) + \xi(x_i - Q_1) + \xi(Q_2 - x_1) \right\}$$

$$+ h^1(Q_1, P_1) + h^2(Q_2, P_2), \quad (5.1)$$

where ξ is the interaction potential between particles of the system and the pistons. Both ξ and V are assumed to have a range which is very small compared to any distances over which there is a variation in the bulk properties of the system. We always have $Q_1 \leq x_i \leq Q_2$; (x_i is the coordinate along the cylinder axis).

We have seen in Sec. III that when only piston 1 or piston 2 is in contact with its reservoir, then the system ensemble will approach and remain in a canonical distribution with temperature T_1 or T_2. The way in which this canonical distribution is approached will of course vary with the type of potentials ξ and V, the density and size of the system, as well as the form of the ensemble at $t=0$. However, except for a rarefied gas (Knudsen gas) where the mean free path is of the same length as the system, we may expect the evolution of the system to proceed as follows. First, collisions between the molecules will tend to set up a kind of local canonical distribution in each region of the system. These local distributions gradually become more exactly canonical at the temperature of the reservoir, as the effects of the reservoir are propagated via collisions between the molecules.

When the two pistons are in contact with different reservoirs, there is a competition between the efforts of each reservoir to bring the system to its own temperature This will lead to some new kind of stationary ensemble. The results of the last section suggest that if we look at some narrow region of our system, its distribution should be almost canonical with a temperature intermediate between those of its neighbors. The temperature gradually changing from nearly T_1 to nearly T_2 as we cross our system from left to right.

This idea can be made very precise when dealing with the lower order distribution functions. It forms the starting point of the Chapman-Enskog solution of the Boltzmann Equation,[12] of the Bogoliubov[13] virial expansion and the Born-Green[14] "normal solutions" for the n-particle distribution functions f_n, $n \ll N$. These authors were interested in the evolution of the general, even if not the most general, time dependent state of a system. They could therefore not say anything about the higher order, particularly the N-particle, or Γ-space distribution. These could be expected to depend sensitively on the initial conditions for very long times. Since our interest here lies in the stationary distribution which we have shown to be independent of the initial conditions we shall take for the zero order form of $\mu(x)$ something that corresponds to local equilibrium $\mu_l(x)$. The corrections to μ_l we have to get in a very rough way, but are probably qualitatively right. They are proportional to the temperature gradient. If the temperature of the two reservoirs is kept fixed while the length of the system and the number of particles in it are permitted to increase indefinitely, then we expect that μ_l will approach the true stationary distribution.

To represent explicitly our assumed local equilbrium solution, we write H as a sum of $N+2$ parts

$$H = \sum_{i=0}^{N+1} h_i(\mathbf{p}_i, \mathbf{r}^N, Q_1, Q_2), \quad (5.2)$$

where

$$h_i = \mathbf{p}_i^2/2m + \frac{1}{2} \sum_{j \neq i} V(r_{ij}) + \xi(x_i - Q_1) + \xi(Q_2 - x_i),$$

$$1 \leq i \leq N, \quad (5.3)$$

$$h_0 = h^1(Q_1, P_1), \quad h_{N+1} = h^2(Q_2, P_2), \quad \mathbf{r}^N = (\mathbf{r}_1, \cdots, \mathbf{r}_N).$$

h_i represents the energy of the ith molecule in the field of all the other molecules and the walls. Thus the mean internal energy per molecule at the position $\mathbf{r}$ is simply

$$U_1(\mathbf{r}) = \left[\int h_1 \mu(x) \delta(\mathbf{r}_1 - \mathbf{r}) dx \right] \bigg/ \left[\int \mu(x) \delta(\mathbf{r}_1 - \mathbf{r}) dx \right]. \quad (5.4)$$

The local equilibrium ensemble μ_l is of the following form:

$$\mu_l(x) = (Z_l^{-1}) \left[\prod_{i=1}^{N} (2\pi m k T(\mathbf{r}_i))^{-\frac{3}{2}} \right]$$

$$\times \exp\left\{ -\sum_{i=0}^{N+1} [\beta(\mathbf{r}_i) h_i + \phi(\mathbf{r}_i)] \right\}, \quad (5.5)$$

where Z_l is a normalization factor and ϕ is related to

[12] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases* (Cambridge University Press, London, 1939).
[13] N. Bogoliubov, J. Phys. U.S.S.R. **10**, 265 (1946).
[14] H. S. Green, *The Molecular Theory of Fluids* (Interscience Publishing Company, Inc., New York, 1952).

the density in physical space $n(\mathbf{r})$

$$n(\mathbf{r}_1) = e^{-\phi(r_1)} \int \exp\left\{-\left[\frac{1}{2}\sum_{i,j}\left(\frac{\beta(\mathbf{r}_i)+\beta(\mathbf{r}_j)}{2}\right)V(r_{ij})\right.\right.$$

$$\left.\left.+\sum_{i=2}^{N}\phi(\mathbf{r}_i)\right]\right\}d\mathbf{r}_2\cdots d\mathbf{r}_N \Big/$$

$$\int \exp\left\{-\left[\frac{1}{2}\sum_{i,j}\left(\frac{\beta(\mathbf{r}_i)+\beta(\mathbf{r}_j)}{2}\right)V(r_{ij})\right.\right.$$

$$\left.\left.+\sum_{i=1}^{N}\phi(\mathbf{r}_i)\right]\right\}d\mathbf{r}_1\cdots d\mathbf{r}_N, \quad (5.6)$$

where, for simplicity, the boundary terms have been omitted from the last expression. We will choose $\beta(\mathbf{r}_i)$ and $\phi(\mathbf{r}_i)$ later to satisfy certain consistency conditions.

We write now $\mu = \mu_l + \mu_1$ and substitute this into Eq. (3.4), giving us

$$\frac{\partial \mu_1}{\partial t} + (\mu_1, H) = \left\{(H, \mu_l) + \sum_{\alpha=1}^{2}\left[\frac{\beta_\alpha - \beta(Q_\alpha)}{M_\alpha}\right]\right.$$

$$\times\left[1 - \frac{\beta(Q_\alpha)P_\alpha^2}{M_\alpha}\right]\mu_l\Big\}$$

$$+ \sum_{\alpha=1}^{2}D_\alpha\frac{\partial}{\partial P_\alpha}\left\{\exp\left(\frac{-\beta_\alpha P_\alpha^2}{2M_\alpha}\right)\frac{\partial}{\partial P_\alpha}\right.$$

$$\times\left[\exp\left(\frac{\beta_\alpha P_\alpha^2}{2M_\alpha}\right)\mu_1\right]\Big\}. \quad (5.7)$$

The stationary solution $\mu_1(x)$ of Eq. (5.7) is

$$\mu_1(x) = \int_0^\infty dt \int_\Gamma dx' P(x,x'|t)\mu_l(x')\Big\{(H(x'), \ln\mu_l(x'))$$

$$+ \sum_{\alpha=1,2}D_\alpha\left[\frac{\beta(Q_\alpha')-\beta_\alpha}{M_\alpha}\right]\left[1 - \frac{\beta(Q_\alpha')P_\alpha'^2}{M_\alpha}\right]\Big\}, \quad (5.8)$$

where $P(x,x'|t)$ is the solution of Eq. (3.4) for $t \geq 0$ with the initial condition $P(x,x'/0) = \delta(x-x')$. "Forgetting" about the surface terms, we can rewrite the above equation as

$$\mu_1(x) = \sum_{i=1}^{N}\int_0^\infty dt \int_\Gamma dx'\left[P(x,x'|t)\mu_l(x')\right.$$

$$\times\left\{\frac{d\beta}{d\mathbf{r}_i'}(r_i')\left[h_i(x') - \tfrac{3}{2}kT(\mathbf{r}_i')\right] + \frac{d\phi}{d\mathbf{r}_i'}\right.$$

$$\left.+ \tfrac{1}{2}\sum_k\left[\beta(\mathbf{r}_i') - \beta(r_k')\right]\frac{\partial V(r_{ik}')}{\partial\mathbf{r}_i'}\right\}\cdot\frac{\mathbf{p}_i'}{m}\Big]. \quad (5.9)$$

What we have done so far has been completely formal and rigorous. We now make the drastic assumption that in *the integral* of (5.8) where very small weight is given to exceptional initial states x', we may approximate $P(x,x'/t)$ by some "relaxation time" type $P_\tau(x,x't)$. $P_\tau(x,x'/t)$ represents a system which forgets its initial state exponentially,

$$P_\tau(x,x'/t) = e^{-t/\tau}\delta(x-x') + \psi(x,t), \quad (5.10)$$

$\psi(x,t)$ can be arbitrary as far as we are concerned since it makes no contribution to (5.8). The time τ must be related to the macroscopic "relaxation time" of the system (i.e., mean time between collisions for gases and the reciprocal of the Kirkwood[9] friction constant for liquids.) This relaxation time is a local property and depends on the temperature and density in each region of the system. We shall therefore assume ad hoc a $\tau_i(\beta(\mathbf{r}_i), n(\mathbf{r}_i))$ for each term in the sum in Eq. (5.9).

These τ_i have no direct relation to the properties of the reservoirs. The reservoirs establish and maintain the stationary ensemble but, we believe, do not influence its actual form except near the boundaries. Their role is somewhat, but not completely, analogous to that of walls all at the same temperature in equilibrium. However, the distinction between the boundaries and the rest of the system can have meaning only for those properties of the system which can be associated with a definite position (or small region) in physical space. These include the lower order distributions f_n, after suitable subtraction of their asymptotic values. It is for the calculation of such quantities that our approximation might be valid.

Putting in our relaxation assumption in Eq. (5.9) we find to terms linear in the temperature gradient, which are the only ones we shall consider,

$$u_1(x) = \mu_l(x)\sum_{i=1}^{N}\tau_i\frac{d\beta}{d\mathbf{r}_i}\Big\{\left[h_i + \frac{d\eta(\beta(\mathbf{r}_i))}{d\beta}\right](\mathbf{p}_i/m)$$

$$+ \tfrac{1}{2}\sum_k(\mathbf{r}_k - \mathbf{r}_i)\left[\frac{\partial V(r_{ik})}{\partial\mathbf{r}_i}\cdot\frac{\mathbf{p}_i}{m}\right]\Big\}, \quad (5.11)$$

where $\eta = \phi(r_i) - \tfrac{3}{2}\ln\beta(r_i) = \eta(\beta)$ to first order in the temperature gradient. The term μ_1 will give rise to small correction terms for the macroscopic properties of the system whenever $|\tau v| \ll |d\ln T/dr|$, v being a representative molecular velocity. For a gas this amounts to having a very small change in temperature within one mean free path.

In order to make Eq. (5.11) definite, we have to determine $\beta(\mathbf{r})$ and $n(\mathbf{r})$ [or $\eta(\mathbf{r})$] within our approximation. We find $n(\mathbf{r})$ by requiring that the pressure p be uniform inside our system. [We shall see later that this also makes the mean flow velocity $\mathbf{u}(\mathbf{r})$ calculated from Eq. (5.10) vanish.] The temperature $T(\mathbf{r})$ must

be such as to make the heat flux **j** constant. This flux is equal to the energy flowing from the reservoir at the left into piston 1 and from this piston to the molecules adjoining it, flowing out again into the second reservoir through the second piston. These conditions are sufficient to determine the temperature (mean kinetic energy) of the pistons and the system inside.

It is easy to see from symmetry considerations that neither the density $n(\mathbf{r})$ nor the two body position distribution $n_2(\mathbf{r}_1, \mathbf{r}_2)$ can have any terms linear in the temperature gradient. Hence, they will not depend on μ_1. We then have for the pressure tensor Π[14]

$$\Pi(r_1) = n^0(\mathbf{r}_1)kT(\mathbf{r}_1)\mathbf{1}$$

$$-\tfrac{1}{2}\int\left[n_2^0(\mathbf{r}_1-\tfrac{1}{2}\mathbf{r}, \ r_1+\tfrac{1}{2}\mathbf{r})\frac{V'(r)}{r}\mathbf{rr}\right]d^3r = p\mathbf{1}, \quad (5.12)$$

where the superscript zero designates quantities calculated from μ_l only to terms of zero order in the temperature gradient. We shall usually omit the superscript on those quantities which have no terms linear in the gradient. It follows further from symmetry considerations that the pressure tensor will be equal to its equilibrium value at $T = T(\mathbf{r})$, $n = n(\mathbf{r})$

$$\Pi(\mathbf{r}_1) = \Pi_{\text{eq}}.(n(\mathbf{r}_1), T(\mathbf{r}_1)) = p_{\text{eq}}.\mathbf{1}. \quad (5.13)$$

The density is therefore determined by the equation

$$\frac{dn(r_i)}{d\mathbf{r}_1} = -\left(\frac{\partial p}{\partial T} \Big/ \frac{\partial p}{\partial n}\right)_{\text{eq}.} \frac{dT(\mathbf{r}_1)}{d\mathbf{r}_1} = \left(\frac{dn}{dT}\right)_{p=\text{const}.} \frac{dT}{d\mathbf{r}_1}. \quad (5.14)$$

The relation between the different order configurational distributions $n_q(\mathbf{r}_1, \cdots, \mathbf{r}_q)$, calculated from μ_l can be expressed by integro-differential equations of the type derived by Bogoliubov for equilibrium. This leads to an explicit equation for η

$$\frac{\partial \eta}{\partial \beta} = -U_1(n,T) - p(n,T)/n. \quad (5.15)$$

which together with Eq. (5.13) determines $\eta(\beta)$. These integro-differential equations also permit a virial expansion of the n_q in powers of the average density $\bar{n}$.

It is interesting to note that for a gas of hard spheres the configurational part of μ_l is equal to what it would be if this gas were in equilibrium at a temperature T_0 in an external force field derivable from a potential Φ

$$\Phi = kT_0 \sum_{i=1}^{N} \phi(r_i). \quad (5.16)$$

The single particle distribution $f_1(\mathbf{r}_1, \mathbf{p}_1)$ is found in our approximation $= f_1^0 + f_1^1$

$$f_1^0 = n(\mathbf{r}_1)[2\pi m kT(\mathbf{r}_1)]^{-\frac{3}{2}} \exp[-\beta(\mathbf{r}_1)\mathbf{p}_1^2/2m], \quad (5.17)$$

$$f_1^1 = f_1^0 \tau_1 [n(\mathbf{r}_1)mkT(\mathbf{r}_1)]^{-1} \frac{dT}{d\mathbf{r}_1} \cdot \left\{\left[\mathbf{p}_1^2/2m + \frac{\partial \eta}{\partial \beta}\right]n(\mathbf{r}_1)\right.$$

$$+ \frac{1}{2}\int n_2(\mathbf{r}_1,\mathbf{r}_2)V(r_{12})d\mathbf{r}_2$$

$$\left. - \frac{1}{6}\int n_2(\mathbf{r}_1, \ \mathbf{r}_1+\mathbf{r})\mathbf{r}V'(r)d\mathbf{r}\right\}\frac{\mathbf{p}_1}{m}.$$

For a gas the potential energy terms are negligible and f_1 is equal to that gotten from the solution of Boltzmann's Equation by a relaxation method.

The requirement that there be no net mass flow in the stationary state gives

$$\int \mathbf{p}_1 f_1(\mathbf{r}_1,\mathbf{p}_1)d\mathbf{p}_1$$

$$= -\tau_1\left\{\frac{d}{d\mathbf{r}_1}(nkT) + \frac{1}{2}\int \frac{\partial}{\partial\mathbf{r}_1}V(r_{12})n_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2\right\}$$

$$= -\tau_1\frac{dp}{d\mathbf{r}_1} = 0. \quad (5.18)$$

where we have used the integro-differential relations between n_1 and n_2 mentioned before. Hence, the requirement that the pressure be constant insures that there is no mass flow.

The two particle distribution function $f_2(\mathbf{r}_1, \mathbf{r}_q, \mathbf{p}_1, \mathbf{p}_2)$ is symmetric in the indices 1 and 2. It is given to first order in the temperature gradient by $f_2^0 + f_2^1$

$$f_2^0 = f_1^0(\mathbf{r}_1,\mathbf{p}_1)f_1^0(\mathbf{r}_2,\mathbf{p}_2)g_0(r_{12},\bar{\beta},\bar{n}), \quad (5.19)$$

where g_0 is the equilibrium radial distribution at a temperature and density which is a symmetrical average between their values at $\mathbf{r}_1$ and $\mathbf{r}_2$,

$$f_2' = I(\mathbf{r}_1,\mathbf{r}_2,\mathbf{p}_1,\mathbf{p}_2) + I(\mathbf{r}_2,\mathbf{r}_1,\mathbf{p}_2,\mathbf{p}_1),$$

$$I = f_2^0(n_2^{-1})\tau_1\frac{d\beta}{d\mathbf{r}_1}\left[\left\{\left[\mathbf{p}_1^2/2m_1 + \tfrac{1}{2}V(r_{12})\right.\right.\right.$$

$$+ \frac{\partial\eta[\beta(\mathbf{r}_1)]}{\partial\beta}\right]n_2 + \frac{1}{2}\int V(r_{13})n_3^0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_3$$

$$+ \frac{1}{2}\int(\mathbf{r}_2-\mathbf{r}_1)\frac{\partial}{\partial\mathbf{r}_1}V(r_{13})n_3^0 d\mathbf{r}_3\right\}\frac{\mathbf{p}_1}{m}$$

$$+ \frac{1}{4}(\mathbf{r}_2-\mathbf{r}_1)\frac{\partial}{\partial\mathbf{r}_1}V(r_{12})\left[\frac{\mathbf{p}_1+\mathbf{p}_2}{m}\right]n_2\right]. \quad (5.20)$$

From this expression we can calculate the heat flux **j** and hence determine $T(\mathbf{r})$. We can also find from μ the higher order distributions f_n but we shall not give any details of those calculations here.

APPENDIX I

It was shown in reference 3 that the quantity W, defined as

$$W(t) = \int_\Gamma \mu(x,t) \ln\phi(x,t)dx; \quad \phi(x,t) = \mu(x,t)/\mu_s(x),$$

(A1.1)

where μ_s is a stationary solution of Eq. (1.1), is greater than zero when $\mu(x,t) \neq \mu_s$ and has the property that

$$\frac{dW}{dt} = -\int\int K(x,x')\mu(x',t)$$

$$\times \left\{ \ln\left[\frac{\phi(x',t)}{\phi(x,t)'}\right] + \frac{\phi(x,t)}{\phi(x',t)} - 1 \right\}dxdx' \leq 0. \quad (A1.2)$$

The integrand in (A1.2) will be zero only for those pairs of points x,x' for which either $K(x,x')$ vanishes or $\phi(x) = \phi(x')$. This implies that W will continue to decrease towards its minimum value until ϕ is constant, or $\mu(x,t)$ is proportional $\mu_s(x)$, inside those regions A_i of Γ-space where $K(x,x') \neq 0$ for x,x' both in the same A_i. This by itself is clearly insufficient to show an over-all asymptotic approach of $\mu(x,t)$ towards $\mu_s(x)$ when, as in the case considered in this paper, the sets A_i are of a much lower dimensionality than the whole Γ-space (i.e., of measure zero). It was therefore argued there that W should continue to decrease until ϕ is constant inside all regions B_i, defined by the property that a system starting at a point in some B_i can reach any other point in the same B_i region under the *combined action* of its natural motion and collisions with reservoir components. In this appendix we formalize and make more rigorous the arguments given in reference 3.

The proof given here will also apply directly when the stochastic operator on the right side of Eq. (1.1) reduces to a Fokker-Planck type differential operator. For the kernels considered in this paper Eq. (1.1) is then transformed into Eq. (3.4) and (A.2) assumes the form, after some integration by parts,

$$\frac{dW}{dt} = -\sum_\alpha D_\alpha \int \mu_s(x)[\phi(x,t)]^{-1}\left[\frac{\partial}{\partial P_\alpha}\phi\right]^2 dx \leq 0. \quad (A1.3)$$

This quantity will vanish whenever $\partial\phi(x)/\partial P_\alpha = 0$.

Since Eq. (1.1) is of first order in time and H and K are time independent the probability density $\mu(x,t)$ behaves like a Markoff process. Hence the conditional probability $P(x,x'/t)dx$ of finding the system in $(x, x+dx)$ at time t if at $t=0$ it was known to be at x' will satisfy the Chapman-Kolmogoroff equation

$$P(x,x'|t) = \int P(x,x''|t-t')P(x'',x'|t')dx'', \quad t \geq t' \geq 0.$$

(A1.4)

$$P(x,x'|t) \geq 0, \quad \int P(x,x'|t)dx = 1.$$

We further have from the linearity of the equation for μ that

$$\mu(x,t) = \int P(x,x'|t-t')\mu(x',t')dx', \quad t-t' \geq 0. \quad (A1.5)$$

and by definition, $\mu_s(x)$ must have the property

$$\mu_s(x) = \int P(x,x'|t)\mu_s(x')dx'. \quad (A1.6)$$

Let us define a new function:

$$\bar{W}(t) = \int \mu(x,t)\phi(x,t)dx \quad (A1.7)$$

The difference between $\bar{W}_{n+1} \equiv \bar{W}(t_{n+1})$ and $\bar{W}_n \equiv \bar{W}(t_n)$ for $t_{n+1} \geq t_n$, can now be written in the following form.

$$\bar{W}_{n+1} - \bar{W}_n$$

$$= \int \mu(x,t_{n+1})\phi(x,t_{n+1})dx - \int \mu(x,t_n)\phi(x,t_n)dx$$

$$= 2\int\int P(x,x'|t_{n+1}-t_n)\mu_s(x')\phi(x,t_{n+1})\phi(x,t_n)dxdx'$$

$$- \int\int P(x,x'|t_{n+1}-t_n)\mu_s(x')\phi^2(x,t_{n+1})dxdx'$$

$$- \int\int P(x,x'|t_{n+1}-t_n)\mu_s(x')\phi^2(x',t_n)dxdx'$$

$$= -\int\int P(x,x'|t_{n+1}-t_n)\mu_s(x')$$

$$\times [\phi(x,t_{n+1}) - \phi(x',t_n)]^2 dxdx'$$

$$\leq 0.$$

The integrand will vanish only if $\phi(x,t_{n+1})$ is constant and equal to $\phi(x,t_n)$ in each set B_i, for if x, x' and x'' are all in the same set B_i then for some value of $(t_{n+1}-t_n)$ $P(x, x'|t_{n+1}-t_n)$ and $P(x'', x'|t_{n+1}-t_n)$ are both greater than zero and we must have $\phi(x,t_{n+1}) = \phi(x',t_n) = \phi(x'',t_{n+1})$ if $\bar{W}_{n+1}$ is to equal $\bar{W}_n$. This shows that $\bar{W}(t)$ will continue to decrease until $\mu(x,t) = a_i\mu_s(x)$, a_i constant, in each B_i. In general we expect there to be only one set, B_1, consisting of the whole phase space. When that happens the constant of proportionality will be unity because of normalization. When there are several B_i there will be a different stationary ensemble for each different initial distribution of systems over the B_i. Inside each B_i the different densities will be proportional to each other.

APPENDIX II

In this appendix we consider in more generality than done in Section IV, the problem of a simple system,

like a Brownian particle, interacting with several reservoirs when the effect of the reservoirs on the time evolution of the distribution function of the system is expressible as a Fokker-Planck type differential operator. A possible example of such a system might be an atomic particle moving in a plasma of ions and electrons which have different temperatures for times sufficiently long for this particle to come to a stationary state. A different example, may be found in the case where the different degrees of freedom of the molecules of the medium through which our particle is moving are not in equilibrium with each other.

Consider a particle moving in such a three dimensional isotropic medium. Calling the distribution function of our system, (particle), $f(\mathbf{Q},\mathbf{P},t)$ and its Hamiltonian h, $h(\mathbf{Q},\mathbf{P})=\mathbf{P}^2/2M+V(\mathbf{Q})$ we will have the following equation for f

$$\frac{\partial f}{\partial t}+\frac{\mathbf{P}}{M}\cdot\frac{\partial f}{\partial \mathbf{Q}}-\frac{\partial V}{\partial \mathbf{Q}}\cdot\frac{\partial f}{\partial \mathbf{P}}=\sum_\alpha \nabla_{\mathbf{P}}\cdot[\lambda_\alpha f+\nabla_{\mathbf{P}}(D_\alpha f)]. \quad (A2.1)$$

where $(\lambda_\alpha)_{x_i}=\lambda_\alpha(P^2,P_{x_i})$, $i=1, 2, 3$ and $D_\alpha=D_\alpha(P^2)$ have essentially the same interpretation as the quantities defined in Eq. (3.2) except that we now permit them to depend explicitly on $\mathbf{Q}$ and $\mathbf{P}$. Further we do not require that the reservoirs themselves be in true equilibrium, it is sufficient that they have a stationary (or approximately stationary) distribution.

In many cases the Liouville term in Eq. (A2.1) is zero because there are no external forces and f is spatially homogeneous. In any case, let $f_\alpha=e^{-\phi_\alpha}$ be the solution of the equation

$$\nabla_{\mathbf{P}}\cdot[\lambda_\alpha f+\nabla_{\mathbf{P}}(D_\alpha f)]=0, \quad f_\alpha=f_\alpha(P^2,\mathbf{Q}). \quad (A2.2)$$

This implies, by the condition of isotropy and normalizability, that

$$\lambda_\alpha f_\alpha=-\nabla_{\mathbf{P}}(D_\alpha f_\alpha). \quad (A2.3)$$

Hence the right side of Eq. (A2.1) can be written in the form

$$\sum_{i=1}^3 \frac{\partial}{\partial P_{x_i}}\left\{\sum_\alpha\left[D_\alpha e^{-\phi_\alpha}\frac{\partial}{\partial P_{x_i}}(e^{\phi_\alpha}f)\right]\right\}. \quad (A2.4)$$

It is now our result, which is a generalization of Eq. (4.2), that the curly bracket in the above equation will vanish for

$$f=\exp(-\bar\phi),$$

when

$$\bar\phi=\int\left[\sum_\alpha D_\alpha\frac{d\phi_\alpha(P^2)}{dP^2}\Big/\sum_\alpha D_\alpha\right]d(P^2). \quad (A2.5)$$

The constant of integration can depend on $\mathbf{Q}$. We therefore have that when $\bar\phi$ can be chosen to be a function of h only, or if the Liouville term vanishes, and D_α is independent of $\mathbf{Q}$, then $\exp(-\bar\phi)$ is the stationary solution of Eq. (A2.1).

When $\lambda_\alpha(\mathbf{P})=\lambda_\alpha\mathbf{P}$ then $\phi_\alpha=\beta_\alpha h+$constant, and Eq. (A2.5) reduces to the stationary solution μ_s of Sec. IV,

$$\mu_s=(Z^{-1})\exp[-\bar\beta h(\mathbf{Q},\mathbf{P})]. \quad (A2.6)$$

The heat fluxes J_α are now given by

$$J_\alpha=3\lambda_\alpha[(\beta_\alpha)^{-1}-(\bar\beta)^{-1}], \quad \sum_\alpha J_\alpha=0. \quad (A2.7)$$

The Onsager relations for the type of flows encountered here were discussed in reference 2. It was proven there that, in the stationary state,

$$L_{\delta\gamma}\equiv\frac{\partial J_\delta}{\partial\beta_\gamma}\bigg|_{\text{all }\beta_\alpha=\beta}=\frac{\partial J_\gamma}{\partial\beta_\delta}\bigg|_{\text{all }\beta_\alpha=\beta}\equiv L_{\gamma\delta}, \quad \gamma\neq\delta. \quad (A2.8)$$

From Eq. (A2.7) we get for the case considered here

$$\frac{\partial J_\gamma}{\partial\beta_\delta}=\frac{3\lambda_\gamma}{\lambda}\left\{\left[\frac{\sum_\alpha(\lambda_\alpha|\beta_\alpha)}{\lambda}-\frac{1}{\beta_\delta}\right]\frac{\partial\lambda_\delta}{\partial\beta_\delta}+\frac{\lambda_\delta}{\beta_\delta}\right\}; \quad \lambda=\sum\lambda_\alpha, \quad (A2.9)$$

which, when all β_α are set equal to some β, gives

$$L_{\gamma\delta}=\frac{3\lambda_\gamma\lambda_\delta}{\lambda\beta^2}=L_{\delta\gamma}. \quad (A2.10)$$

We see from (A2.9) that in the nonlinear region, where the heat fluxes J_α are not proportional to the thermodynamic driving forces, $(\beta-\beta_\alpha)$, then $\partial J_\gamma/\partial\beta_\delta\neq\partial J_\delta/\partial\beta_\gamma$ so that the J_α cannot be derived from a potential, which has sometimes been suggested as a generalization of the Onsager relations.