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Investigation of a Variational Principle for  
Open Systems\*

by

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## ABSTRACT

This report describes an attempt to obtain information about the stationary nonequilibrium state of a fluid through which heat is flowing. The fluid is in contact with several heat reservoirs at different temperatures and is assumed to be described by an ensemble density  $\mu$  which satisfies a generalized Liouville equation. Our method consists of minimizing a positive functional  $W(\mu)$ , which vanishes only when  $\mu = \mu_s$ , the correct stationary  $\Gamma$ -space distribution, by assuming a particular form for the density  $\mu$ ,  $\mu = \hat{\mu}$ , with variable parameters. The  $\hat{\mu}$  we chose is essentially one representing a product of local equilibrium cononical ensembles which ~~are varied to minimize~~ with unspecified space dependent macroscopic parameters. These parameters are the density  $n(\underline{r})$ , mean velocity  $\underline{u}(\underline{r})$  and the temperature  $T(\underline{r})$ . The reservoirs determine the temperature on the boundaries. We show first that  $W(\hat{\mu})$  is related, somewhat indirectly, to the irreversible thermodynamic entropy production in the system and is naturally divided into parts related to the temperature and and velocity gradients. Considering then a situation in which only a temperature gradient is present  $T(\underline{r})$  is varied to minimize  $W$ . This leads to a differential equation for  $T(\underline{r})$  subject to boundary conditions specified by the reservoirs. It is then shown that the heat conductivity deduced from this equation does not agree, in the low density limit with that computed from kinetic theory. It is further shown that this difficulty is not alleviated when the class of distribution functions used in the variational principle is modified so as to include more realistic distributions. Our conclusion is then that  $W$  is not useful as a practical variational principle. The reason for this is that  $W$  looks at too fine details of  $\mu$  as is shown by the fact that it remains invariant in an isolated system.



## I. Introduction.

In a series of previous publications a model was developed for the description of the time evolution of an ensemble, representative of a "system" in contact with a number of idealized heat and particle "reservoirs".<sup>(1-4)</sup> The system Hamiltonian has the form

$$H(p_i, q_i) = \sum_{i=1}^N \left\{ \frac{p_i^2}{2m} + U_i(q_i) + \frac{1}{2} \sum_{i=2}^N \psi(q_i, q_j) \right\} \quad (1.1)$$

Here the cartesian position and momentum of the  $i$ 'th particle of the system are denoted by  $q_i$  and  $p_i$ ;  $U(q_i)$  is an external potential, such as might represent the effect of the walls;  $\psi(q_i, q_j)$  represents the interactions of the particles.

Let  $x$  stand for the set of variables  $\{p_i, q_i\}$  with the domain of integration  $\Gamma$  and let  $\mu(x)dx$  be the probability of the system being found with the set of variables having values in the region  $dx$  about  $x$ . It was shown by Bergmann and Lebowitz<sup>(1,2)</sup> that  $\mu(x, t)$  for their model satisfies the equation

$$\frac{\partial \mu(x, t)}{\partial t} + (\mu(x, t), H) = \int_{\Gamma} K(x, x') \mu(x', t) dx' - \int_{\Gamma} K(x', x) \mu(x, t) dx' \quad (1.2)$$

Here  $(\mu, H)$  denotes the Poisson Bracket of  $\mu$  and  $H$ , that is

$$(\mu, H) = \sum_{i=1}^N (\nabla_{q_i} \mu \cdot \nabla_{p_i} H - \nabla_{p_i} \mu \cdot \nabla_{q_i} H) \quad (1.3)$$

The "kernel"  $K(x, x')$  represents the effects of the reservoirs on the system. Specifically the quantity  $K(x, x') dx dt$  is the contingent probability that during a time interval  $dt$  the system, known to be in a configuration  $x'$ , suffers a "collision" with the reservoirs and as a result jumps discontinuously into the region  $dx$ . The general conditions

$$K(x, x') \geq 0, \quad \mu(x, t) \geq 0 \quad \text{and} \quad \int_{\Gamma} \mu(x, t) dx = 1$$

are to be imposed and are consistent with equation (1.2).

It was first shown<sup>(2,3)</sup> that if equation (1.2) possesses a time independent



solution  $\mu_s(x)$ , then any initial ensemble density  $\mu(x,0)$  will tend to  $\mu_s$  after a sufficiently long time. In order to demonstrate this fact a number of functionals of  $\mu(x,t)$  were considered which had the following properties:

$$\begin{aligned} \text{a) } F[\mu] &\geq 0 & \text{c) } \frac{d}{dt} F[\mu(t)] &\leq 0 \\ \text{b) } F[\mu_s] &= 0 \end{aligned} \quad (1.4)$$

A special example of such a functional is

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$$F(\mu) = \int \mu \ln(\mu/\mu_s) dx$$

All these functionals were constructed so as to compare the temporal evolution of two differing ensembles; either two arbitrary ensembles or an arbitrary ensemble with a stationary one as in the example given above. Bergmann and Morris<sup>(4)</sup> introduced a new functional  $W(\mu)$  defined as follows:

$$W(\mu) = \int \frac{1}{\mu} \left( \frac{\partial \mu}{\partial t} \right)^2 dx = \int \frac{1}{\mu} (K\mu - L\mu)^2 dx \quad (1.5)$$

where

$$\begin{aligned} L\mu &= (\mu, H) \\ K\mu &= \int K(x, x') \mu(x') dx' - \int K(x', x) \mu(x) dx' \end{aligned}$$

$W(\mu)$  is seen to be dependent on one ensemble function  $\mu(x,t)$  only, and has all the properties (1.4). These characteristics make  $W(\mu)$  suitable for use as measure of the closeness of  $\mu$  to the stationary ensemble  $\mu_s$ . Thus, if we are given two ensembles  $\mu_1$  and  $\mu_2$  and find that  $W(\mu_1) > W(\mu_2)$  then we will say that  $\mu_2$  is closer to  $\mu_s$  than  $\mu_1$  is to  $\mu_s$ . If  $\mu_2(t) = \mu_1(t + \tau)$  then property (1.4c) implies that  $W(\mu_2) < W(\mu_1)$  which we are interpreting as meaning that  $\mu_1(t + \tau)$  is closer to stationarity than  $\mu_1(t)$  is.

The explicit expression for the rate of change of  $W$  was shown to be

$$\frac{dW}{dt} = - \iint \mu(x) K(x, x') \left[ \frac{\partial \ln \mu(x)}{\partial t} - \frac{\partial \ln \mu(x')}{\partial t} \right]^2 dx dx' \quad (1.6)$$



This expression vanishes if the kernel  $K(x, x')$  becomes zero. Equation (1.1) then reduces to Liouville's equation and (1.6) is an expression of the fact that functionals of the type under consideration are invariant under the natural motion of a closed system. We stress that the change in  $W$  is "proportional" to the "size" of the kernels.

It is the object of this report to see if physically significant results obtain from the use of the criterion just described.

This introduction will end with a discussion of certain features of the kernels useful for the purposes of this report. The kernel  $K$  generally represents the combined action of several reservoirs at different temperatures. It was shown (1,2) that any given reservoir acting alone would tend to bring the system into equilibrium at its own temperature and thus the kernel relevant to a reservoir at a temperature  $T_\alpha (= 1/\beta_\alpha)$ ,  $K_\alpha(\beta_\alpha, x, x')$ , has the property

$$\int_{\Omega} K_\alpha(\beta_\alpha, x, x') e^{-\beta_\alpha H(x')} dx' = \int_{\Omega} K_\alpha(\beta_\alpha, x', x) dx' e^{-\beta_\alpha H(x')} \quad (1.7)$$

It is assumed here that

$$K(x, x') = \sum_{\alpha} K_\alpha(\beta_\alpha, x, x') \quad (1.8)$$

that is the kernel is composed of independent parts each of which obeys relation (1.7).

The detailed structure of the kernels has been discussed<sup>(2)</sup> and a satisfactory description is the following. The basic interaction between reservoir and system is a two body collision between a reservoir particle and a particle of the system. In such a collision the positions of the colliding particles remain unchanged while their momenta are altered discontinuously. Thus



$$K_{\alpha}(\beta, x, x') = \sum_{i=1}^N K'_{\alpha}(\beta, p_i, p_i') \delta(q_i - q_i') \delta(y_i - y_i') \quad (1.9)$$

where  $x = \{p_i, q_i, y_i\}$

and  $y_i = (q_1, \dots, q_{i-1}, q_{i+1}, \dots, q_N; p_1, \dots, p_{i-1}, p_{i+1}, \dots, p_N)$

It follows from the nature of two body collisions that  $K'_{\alpha}(\beta, p_i, p_i')$  does not depend on the configuration of the remainder of the system that is on  $y_i (=y_i')$ , but it may depend on  $q_i (=q_i')$ . This dependence is at our disposal. We have in mind that the reservoirs are external to the system and act only near to the surface of the system. In order to parallel this physical idea in the mathematical structure of the kernel, we could introduce a factor  $\exp(-r_{\alpha}(q_i)/\lambda_{\alpha})$  where  $\lambda_{\alpha}$  is a constant distance and  $r_{\alpha}(q_i)$  is the distance from  $q_i$  to the region of the surface at which the  $\alpha^{\text{th}}$  reservoir acts.

In this case

$$K_{\alpha}(\beta, x, x') = \sum_{i=1}^N K''_{\alpha}(\beta, p_i, p_i') e^{-r_{\alpha}(q_i)/\lambda_{\alpha}} \delta(q_i - q_i') \delta(y_i - y_i') \quad (1.10)$$

It is easy to envisage a situation, such as in a treatment of lattice-spin or lattice-electron interactions, where the relevant kernels would be independent of  $(q_i)$ .

We will call the region in which the action of the reservoirs is appreciable, the boundary of the system. It would be possible to regard the interaction as confined to the surface of the system but if that were done, it would be necessary to regard this interaction as a boundary condition to the Liouville equation<sup>(5)</sup> rather than as an additional term.



## II. The Locally Canonical Distribution

It is well known that a system in equilibrium at a temperature  $T$  can be adequately described by the canonical ensemble

$$\mu_e = \frac{\exp [-H/kT]}{Z} \quad (2.1)$$

$Z$  being a normalizing factor. The properties of a given system in equilibrium, i.e. a system with specified  $H$ , are thus completely determined by one parameter, the temperature.

It is natural to ask whether a system not in equilibrium can also be described by an ensemble which is a functional only of the macroscopic parameters describing the fluid. A single component fluid needs for its macroscopic specification a knowledge of at least the values of the temperature  $T$  ( $\frac{2}{3}$  mean kinetic energy per particle), local velocity  $\underline{u}$ , and density  $n$  at all points of the fluid. It is generally assumed that the correct non-equilibrium ensemble for small variations in the macroscopic parameter is made up of a local equilibrium ensemble  $\hat{\mu}$  plus corrections linear in the gradients of the macroscopic variables. The ensemble  $\hat{\mu}$  consists of a super-portion of canonical ensembles for each small region of the fluid,

$$\hat{\mu}(T, \underline{u}, n) = \left\{ \prod_{i=1}^N \left( \frac{m\beta_i}{2\pi} \right)^{3/2} / \hat{Z} \right\} \exp \left[ - \sum_{i=1}^N \beta_i p_i' - \varphi_i \right], \quad (2.2)$$

$\hat{Z}$  being a normalizing factor. Here

where

$$\beta_i \equiv \beta(q_i) = \frac{1}{kT(q_i)},$$

$$p_i' = (p_i - \underline{u}_i m)^2 / 2m + U_i + \frac{1}{2} \sum_{j=1}^N \psi_{ij}$$

is the energy of the  $i$ th particle and  $\varphi_i = \varphi(q_i)$  is to be chosen so as to give the correct value of  $n$ .  $\varphi$  may be related to the chemical potential by using a thermodynamic relationship which remains true even for this non-equilibrium case. (6)



The main defect of the locally canonical distribution is that it does not represent a stationary or even quasi-stationary state. It thus predicts the absence of any heat flow and that the stress deviator is always zero. It is believed, however, that the correct non-equilibrium distribution differs only slightly from the appropriate local equilibrium ensemble (i.e. one having the correct macroscopic parameter) though this deviation gives rise to all the transport processes.

The first question we ask, and try to answer by the use of criterion described in section 1, is this. What are the optimum values of the parameters ( $T$ ,  $u$  and  $n$ ) to be used in the locally canonical distribution for the stationary state of a system in contact with specified reservoirs? The answer will be in the form of a set of partial differential equations for the parameters, the boundary conditions being determined by the relevant features of the reservoirs.

In order to carry out this program we substitute from (2.2) into equation (1.5),

$$W(T, \hat{\mu}, n) = \int \frac{1}{\hat{\mu}} \left( \frac{\partial \hat{\mu}}{\partial t} \right)^2 dx \quad (2.4)$$

where

$$\frac{\partial \hat{\mu}}{\partial t} = K \hat{\mu} - L \hat{\mu} \quad (2.5)$$

The expression  $K \hat{\mu}$  will be evaluated first.

As mentioned in Section 1, we assume that the interaction between the fluid and the exterior, as represented by the reservoir, is confined to a narrow region of space, the "boundary" of the system. We also make the assumption that the temperature of this region is equal to the temperature of the reservoir with which it is in contact. This implies that there is no observable temperature drop between reservoir and fluid and that the temperature does not vary much over distances covering the extent of the action of the reservoirs.

By using these assumptions and equation (1.7) it is seen that the term  $K \hat{\mu}$  is zero for the choice of  $\hat{\mu}$  made here, i.e. the effect of the reservoirs is to



impose boundary conditions on T. The expression (2.5) now reduces to

$$\frac{\partial \hat{\mu}}{\partial t} = (H, \hat{\mu}). \quad (2.6)$$

In order to indentify this quantity we write (2.2) in the form

$$\log \hat{\mu} + \log \hat{Z} = - \int [\beta(r) h'(r, x) + \eta(r) n(r, x)] dr$$

where  $\eta(r) = \varphi(r) - (3/2) \ln \beta(r)$

and

$$n(r, x) = \sum_{i=1}^N \delta(r - q_i)$$

$$h'(r, x) = \sum_{i=1}^N \delta(r - q_i) h_i'$$

Thus the r.h.s. of (2.6) becomes

$$-\hat{\mu} \int [\beta(r) (H, h') + \eta(r) (H, n)] dr. \quad (2.7)$$

An interpretation of this type of expression is provided by the relation for a closed system which also holds in an open system for quantities not changed directly by the interaction with the reservoirs

$$\begin{aligned} \frac{\partial}{\partial t} \int \mu A(x) dx &= \int (H, \mu) A(x) dx \\ &= \int (A, H) \mu dx, \end{aligned} \quad (2.8)$$

which says that  $(A, H)$  is a phase function whose average is the rate of change of the average value of A in a closed system. We define  $\hat{S}$  as the ensemble average of the phase function  $-k \ln \hat{\mu}$ .

$$\hat{S} = -k \int \mu \ln \hat{\mu} dx$$

where  $\mu$  is the correct distribution function corresponding to a given quasi-hydrodynamic state, then from (2.7) and (2.8)



$$\dot{\hat{S}} = \int_V \frac{1}{T(r)} \left[ \frac{\partial h'}{\partial t} + \eta^T \frac{\partial n}{\partial t} \right] dr, \quad (2.9)$$

where  $h'(r)$  and  $n(r)$  are the macroscopic energy density and particle density, respectively.

The second law of thermodynamics may be extended and written in a form connecting the densities of entropy  $s(r)$  local energy  $h'(r)$  and particles  $n(r)$  as

$$ds = \frac{dh'}{T} + \bar{\alpha} dn.$$

Therefore, defining the thermodynamic entropy  $S$  as  $\int dr s(r)$ , then

$$\dot{\hat{S}} = \int \frac{dr}{T} \left( \frac{\partial h'}{\partial t} + T \bar{\alpha} \frac{\partial n}{\partial r} \right)$$

is identical with (2.7) when  $\bar{\alpha}$  is identified with  $\eta$  which is indeed the case. <sup>(6)</sup>

$(H, \ln \hat{\mu}) \equiv \sigma(x)$  can thus be identified as a phase function whose average is related to the rate of change of entropy in the system.

Since  $\int \hat{\mu}(H, \ln \hat{\mu}) dx$  vanishes, the use of  $\hat{\mu}$  as the ensemble density predicts a vanishing production of entropy in the system as might be expected from the previous comments.



Having made a physical identification of the expression (2.7) we can next put this term in the form most suitable for future calculation. This involves the quantities  $(H, h'(x))$  and  $(H, n(x))$ . Equations similar to (2.8) allow these quantities to be identified as phase functions whose average values are equal to the time derivatives of the local densities. On the other hand, the indicated Poisson brackets may be explicitly evaluated before averaging and thus relate these quantities to the divergences of energy and particle flux. In this way Kirkwood<sup>(7)</sup> derives the equations of hydrodynamics from Liouville's equation. It follows from the analyses of Kirkwood<sup>(7)</sup>, Mori<sup>(8)</sup> and Lebowitz<sup>(9)</sup> that the unaveraged expression (2.6) is equal, after some integration by parts in which surface terms are neglected, to

$$\int \left[ \underline{Q}(\underline{r}, x) \cdot \frac{\partial}{\partial \underline{r}} \beta(\underline{r}) + \underline{p}(\underline{r}, x) \frac{\partial \underline{u}}{\partial \underline{r}} \right] d\underline{r} = \sigma(\underline{r}, x) / k \quad (2.10)$$

where the vector  $\underline{Q}(\underline{r}, x)$  and the tensor  $\underline{p}(\underline{r}, x)$  are phase functions whose ensemble averages are the heat-flux and the stress deviator at the position  $\underline{r}$ , i.e.

$\underline{Q}(\underline{r}, x)$  and  $\underline{p}(\underline{r}, x)$  may be interpreted as these quantities for a system specified by the point  $x$  in  $\Gamma$  on which absolutely precise measurements are made.  $\sigma(\underline{r}, x)$  is similarly the function whose average is the thermodynamic entropy production.

We have

$$\underline{Q}(\underline{r}, x) = \sum_{i=1}^N \delta(\underline{r} - \underline{q}_i) \underline{Q}_i(\underline{p}_i, q) \quad (2.11)$$

where

$$\underline{Q}_i = \sum_{j=1}^N \underline{Q}_{ij}(\underline{p}_i, \underline{q}_i, \underline{q}_j) \quad (2.12)$$

and

$$\underline{Q}_{ij} = \begin{cases} \left[ \frac{1}{2m} (\underline{p}_i - m \underline{u}(\underline{q}_i))^2 - h(\underline{q}_i) \right] (\underline{p}_i - m \underline{u}(\underline{q}_i)) \frac{1}{m} & i = j \\ \frac{1}{2} \left[ \psi(\underline{r}_{ij}) \frac{1}{m} + (\underline{r}_{ij} \cdot \underline{r}_{ij} / r_{ij}) \psi'(\underline{r}_{ij}) \right] (\underline{p}_i - m \underline{u}(\underline{q}_i)) \frac{1}{m} & i \neq j \end{cases} \quad (2.13)$$



Here  $h(q_i)$  is the enthalpy per particle at  $q_i$ . The expression for  $\underline{p}(\underline{r}, x)$  may be written in a similar form

$$\underline{p} = \sum_{ij} \sum_j \delta(\underline{r} - q_i) \underline{p}_{ij} \quad (2.14)$$

$$\underline{p}_{ij} = \begin{cases} \frac{1}{m} [\underline{p}_i - \underline{m} \underline{u}(q_i)] (\underline{p}_i - \underline{m} \underline{u}(q_i)) - kT(q_i) \underline{1}], & i = j \\ -\frac{1}{2} \left[ \frac{\Psi'(q_{ij})}{q_{ij}} \underline{q}_{ij} \underline{q}_{ij} - \underline{p}_\Psi(q_i) \underline{1} \right], & i \neq j \end{cases} \quad (2.15)$$

where  $\underline{p}_\Psi$  is the potential contribution to the scalar pressure and we have neglected terms which depend linearly on  $\underline{c}$ , and will, thus, essentially vanish after integration. We note again that the ensemble average of  $\underline{Q}$  and  $\underline{p}$  with respect to  $\mu$  are zero.

Substituting (2.10) into (2.4) yields

$$W(T, \underline{u}, n) = \int d\underline{x} \hat{\mu} \left\{ \int d\underline{r} \left[ \underline{Q}(\underline{r}, x) \cdot \frac{d\underline{\beta}(\underline{r})}{d\underline{r}} + \beta \underline{p} \frac{\partial \underline{u}}{\partial \underline{r}} \right] \right\}^2 = \int d\underline{x} \hat{\mu} \left[ \frac{1}{k} \int \underline{\sigma}(\underline{r}, x) d\underline{r} \right]^2 \quad (2.16)$$

It follows from the symmetry of the functions  $\underline{Q}$  and  $\underline{p}$  that the average value of products of  $\underline{Q}$  and  $\underline{p}$  vanishes and that,

$$\int d\underline{x} \hat{\mu} \underline{Q}(\underline{r}, x) \underline{Q}(\underline{r}', x) = \lambda(\underline{r}) \delta(\underline{r} - \underline{r}') \underline{1}. \quad (2.17)$$

Similarly, the average of all cross-products of the components of  $\underline{p}$  will also vanish. The functional  $W$  of (2.16) will thus break up into two independent positive definite parts related to the irreversible entropy production due to the temperature and velocity gradient. We may, therefore, consider each part separately and shall, therefore, set  $\underline{u}$  equal to zero now, i.e. we will consider a pure heat flow problem. In order that  $\frac{d\underline{u}}{dt}$  also vanish, we must have the pressure constant<sup>(3)</sup>. We shall, therefore, assume that for a given temperature distribution  $T(\underline{r})$  the density  $n(\underline{r})$  is so adjusted that the pressure is indeed constant. Eq. (2.16) then becomes



$$W = \int_V d\mathbf{r} \lambda(\mathbf{r}) \left( \frac{\partial \beta(\mathbf{r})}{\partial \mathbf{r}} \right)^2 \quad (2.18)$$

Taking the variation of  $W$  with respect to  $\beta(\mathbf{r})$  and equating to zero we obtain

$$\begin{aligned} 0 &= \delta \int d\mathbf{r} \lambda \left( \frac{\partial \beta}{\partial \mathbf{r}} \right)^2 \\ &= \int d\mathbf{r} \delta \lambda \left( \frac{\partial \beta}{\partial \mathbf{r}} \right)^2 + 2 \int d\mathbf{r} \lambda \left( \frac{\partial \beta}{\partial \mathbf{r}_i} \right) \cdot \left( \frac{\partial \delta \beta}{\partial \mathbf{r}_i} \right) \\ &= \int d\mathbf{r} \frac{\partial \lambda}{\partial \beta} \delta \beta \left( \frac{\partial \beta}{\partial \mathbf{r}} \right)^2 - 2 \int d\mathbf{r} \frac{\partial}{\partial \mathbf{r}_i} \left( \lambda \frac{\partial \beta}{\partial \mathbf{r}_i} \right) \delta \beta \\ &= -2 \int d\mathbf{r} \delta \beta \lambda^{1/2} \frac{\partial}{\partial \mathbf{r}_i} \cdot \left( \lambda^{1/2} \frac{\partial \beta}{\partial \mathbf{r}_i} \right) \end{aligned}$$

for arbitrary  $\delta \beta$ , which vanishes on the surface. This leads to the partial differential equation

$$\text{div} \left( \lambda^{1/2} \text{grad } \beta(\mathbf{r}) \right) = 0, \quad (2.19)$$

subject to the boundary conditions imposed by the reservoirs.

This is to be compared with the equation derivable with the aid of the Fourier conduction law

$$\mathbf{Q}(\mathbf{r}) = -K \nabla T = \tilde{\mathcal{K}} \text{grad } \beta(\mathbf{r}) \quad (2.20)$$

which states the condition for a steady state

$$\text{div } \mathbf{Q} = \text{div} (\tilde{\mathcal{K}} \text{grad } \beta) = 0 \quad (2.21)$$

Equations (2.19) and (2.21) are only equivalent if  $(\tilde{\mathcal{K}} / \lambda^{1/2})$  is independent of  $\mathbf{r}$ . This would be the case if  $(\tilde{\mathcal{K}} / \lambda^{1/2})$  depended only on the pressure which we have assumed, since there is no flow, to be constant.

That this is unlikely is shown if we compare the value of  $\tilde{\mathcal{K}}$  ( $\tilde{\mathcal{K}}$  = conductivity  $\propto kT^2$ ) for a dilute gas with the value of  $\lambda$  for this model calculated from equation (2.13b). It follows from kinetic theory that  $(^{10}) \tilde{\mathcal{K}} \propto (kT)^{5/2} / m^{1/2} a^2$ , (2.22)



where  $a^2$  is the scattering cross-section, while (2.13b) yields in the low density limit,

$$\lambda = \frac{\frac{nm^2}{6} \iiint_{-\infty}^{+\infty} d\mathbf{c} \left( c^2 - 5/2\beta \right)^2 c^2 e^{-\frac{\beta mc^2}{2}}}{\iiint_{-\infty}^{+\infty} d\mathbf{c} e^{-\frac{\beta mc^2}{2}}} = \frac{n}{m} (kT)^3 \frac{14}{3} \quad (2.23)$$

Thus,  $\frac{\tilde{\mathcal{K}}}{\lambda^{1/2}} \propto \frac{kT}{a n^{1/2}}$

whereas  $p = nkT$ .

A similar situation appears when one attempts to use the irreversible thermodynamic principle of minimum entropy production to find  $T(\underline{r})$ . (11)

Minimizing the total entropy production in the system,  $\sigma_t$ , gives

$$\begin{aligned} \delta \sigma_t &= \delta \int \sigma(\underline{r}) d\mathbf{r} = k^{-1} \delta \int \underline{Q}(\underline{r}) \cdot \frac{d\beta}{d\mathbf{r}} d\mathbf{r} \\ &= k^{-1} \delta \int \mathcal{K}(\underline{r}) \left( \frac{d\beta}{d\mathbf{r}} \right)^2 d\mathbf{r} = -k^{-1} 2 \int d\mathbf{r} \delta \beta \mathcal{K}^{1/2} \frac{d}{d\mathbf{r}} \left( \mathcal{K}^{1/2} \frac{d\beta}{d\mathbf{r}} \right) = 0, \end{aligned}$$

or  $\text{div} \left( \mathcal{K}^{-1/2} \frac{d\beta}{d\mathbf{r}} \right) = 0,$

rather than eq. (2.21). The quantity actually minimized in the stationary state is clearly the integral of  $\underline{Q}^2$ .



### III. Ensembles Describing Transport Processes

Having failed in our objective of obtaining the transport coefficients by using the locally canonical ensemble  $\hat{\mu}$ , we will investigate whether it is possible to modify the ensemble used, to obtain the correct equation governing the distribution of temperature, that is Eq. (2.21). It is clear that to arrive at this result we must begin with a figure of merit proportional to

$$\int d\mathbf{r} (\tilde{\mathcal{K}}(\mathbf{r}) \nabla \beta(\mathbf{r}))^2 \quad (3.1)$$

This form ought to be derived using a distribution function capable of predicting a conductivity factor  $\tilde{\mathcal{K}}(\mathbf{r})$  for the system.

In order to see if this is possible a distribution function  $\mu(\tau_1)$  predicting the correct fluxes will be described. Starting with  $\hat{\mu}$  at some initial time, the ensemble at a later time is formally given by

$$\begin{aligned} \mu(t) &= e^{-(\mathcal{K} + L)t} \hat{\mu}(0) \\ &= -\int_0^t e^{-(\mathcal{K} + L)s} L \hat{\mu} ds + \hat{\mu}. \end{aligned} \quad (3.2)$$

Now  $\lim_{t \rightarrow \infty} \mu(t) = \mu_s$  if the latter exists, that is the initial dis-

tribution,  $\hat{\mu}$  in this instance, would eventually decay to the stationary distribution. However, there is a range of times  $\tau_1 \ll t < \tau_2$  for which on the one hand  $\tau_2$  is so small that the macroscopic parameters calculated from  $\mu(\tau_2)$  are not significantly different from those in  $\hat{\mu}$ , and on the other hand,  $\mu(t)$  is capable of giving the fluxes corresponding to the parameters of  $\hat{\mu}$  correctly. This is shown explicitly by Mori<sup>(12)</sup> for a dilute gas of hard spheres. There is a short relaxation time  $\tau_1 \ll \tau_2$  corresponding to a large eigenvalue of  $L$ ; this corresponds to the mean time between two body collisions and  $\mu(\tau)$



calculated by using this relaxation time gives the same value for the coefficient  $\mathcal{K}$  as found by Chapman-Enskog<sup>(11)</sup> theory.

This quick internal relaxation is in sharp contrast to the slow relaxation which is governed by the kernel  $K$ . Although the effect of the kernels is due to two body collisions with the reservoir, these take place only near the boundary; therefore, they have an overall frequency less than internal collisions, and correspond to a much longer relaxation time  $\tau_K$ .

The significance of this discussion for the present purpose is that changes in the functional  $W$  take place on a time scale  $\tau_K$  rather than  $\tau_1$ . This is because  $W$  is invariant to the internal motion of the system and is changed only by its interaction with the reservoirs. If  $\mu(\tau)$ ,  $\tau < \tau_2$  is used in place of  $\hat{\mu}$ , then  $W(\mu(\tau))$  would not be appreciably different from  $W(\hat{\mu})$ . Thus, if we approximate (3.2) by

$$\mu(\tau) = \hat{\mu} + \tau L \hat{\mu}, \quad (3.3)$$

then

$$W[\mu(\tau)] = W(\hat{\mu}) + O\left(\frac{\tau}{\tau_K}\right) \quad (3.4)$$

which leads to essentially the same equation for  $T$  as before.

The use of a  $\mu(\tau)$  for large  $\tau$  ( $\tau \gg \tau_2$ ) would be better, but this would involve the exact computation of the integral in (3.2) which is equivalent to a direct calculation of  $\mu_S$  and has never been done.

Our conclusion must be that we are unable to obtain a useful variational principle out of the use of  $W$ .



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