WASHINGTON UNIVERSITY

Department of Physics

Dissertation Committee:

Edwin T. Jaynes, Chairman
Eugene Feenberg
J. Ely Shrauner

STATISTICAL MECHANICS OF THERMALLY DRIVEN SYSTEMS

by

William Cobbey Mitchell

A dissertation presented to the
Graduate Board of Washington
University in partial fulfillment
of the requirements for the
degree of Doctor of Philosophy

May, 1967

Saint Louis, Missouri

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

This thesis is concerned with the development of a statistical mechanics formalism for treating thermally driven systems.

Consider the production of non-equilibrium behavior in a closed isolated system. In general the system is driven by bringing some external mechanism into interaction with it, thereby violating internal conservation laws, such as conservation of energy, momentum, or particle number. It is the goal of statistical mechanics to predict the macroscopic behavior of a system from the dynamics of its constituent particles; in this case we want to calculate the response of the system to the external driving mechanism. If we have a detailed microscopic model for the interaction this can be achieved in a straightforward fashion simply by applying dynamical perturbation theory to our usual statistical mechanics ensemble. In particular if the driving mechanism is an applied potential, then one immediately finds the Kubo expressions for linear response. However in general we do not have this detailed microscopic knowledge of the driving process. Instead we have only macroscopic information on the effect of the interaction on system variables such as local energy, momentum, or particle density; i.e., in the language of hydrodynamics, we know source terms.

Systems driven by transport mechanisms of this sort rather than known potentials are called "thermally driven" as opposed to "dynamically driven".[1] The problem is this: to find a general characterization of thermally driven processes so that we can treat the effects of transport across the boundaries of a system, without going into the microscopic details of this transport.

Such a characterization is offered. In first order it leads to response functions of the Kubo type for thermally driven processes, in agreement with a half dozen other schemes.[2] Relative to the other methods its advantages are these: greater generality, no low frequency restrictions, no assumption of an a priori form for the macroscopic laws, and clear cut interpretation of the driving terms. It is also unique in that the higher order corrections are clear. In a sense it is the formal complement of dynamical perturbation theory. Dynamical perturbation theory can treat dynamically driven systems directly to all orders, and by making low frequency and first order approximations can treat thermally driven systems as well. This new approach treats both thermally and dynamically driven systems directly to all orders, without the need for low frequency and first order approximations (although, of course, approximations may greatly simplify the calculations). A further advantage is that non-equilibrium thermo-hydrodynamics can be derived from it.

Our treatment of thermally driven systems is based on Jaynes' Maximum Entropy Estimate (MEE) formalism.[3] MEE provides a very general solution to the fundamental problem of statistical mechanics, that of picking the proper ensemble to represent given experimental information. Since specification of a microstate requires $\sim 10^{23}$ conditions, while the macroscopic information furnishes ~ 1, obviously the information determines a set of microstates rather than a particular one. Consequently we need a prescription for weighting the possibilities. This is what MEE does. Jaynes showed that there exists a unique measure of the information contained in an ensemble. By minimizing this information measure (maximizing the information entropy) subject to the macroscopic constraints one picks out the least biased ensemble containing the given information. Of course, the derivation from some general principle of a prescription for going from experimental information to an ensemble is formally unnecessary. Once one has a prescription its merit must be judged solely on the following empirical condition: if, experimentally, fixing one set reproducibly, then the ensemble constructed by the prescription from the first set must predict the second set. Jaynes' arguments serve to convince one that MEE ought to do this. Such calculations as have been done bear this out.[4] For the case of known energy and particle number, the MEE prescription gives the usual grand canonical ensemble, and the information entropy is the Gibbs entropy. But with the MEE method it is just as easy to set up non-equilibrium ensembles as equilibrium ensembles. In fact one can set up an ensemble based on information gathered in an arbitrary space-time interval, and use it to predict behavior outside this region.[5] This is not the same problem as treating thermally driven systems, however, for variables obtained from ensembles of this kind are constrained to obey the conservation laws of the closed system, while it is precisely the violation of these conservation laws by the external mechanism which we consider as driving the system.

CHAPTER II

DEFINITION OF THE THERMAL DRIVING PROCESS

In hydrodynamics, dynamic and thermal driving terms are treated on an equal footing. When attempting to formulate the problem in statistical mechanics one soon discovers that there is a fundamental difference between the two concepts. Whereas dynamic driving has a well defined microscopic meaning, the concept of thermal driving has an inherent vagueness.

It is necessary to remove this ambiguity by formulating a precise definition of the thermal driving process. To do this we will need the MEE prescription for converting macroscopic information into an ensemble.

1. Brief Discussion of MEE Method

Consider an experimental procedure for preparing systems in some macrostate. Although in any particular case the rules of preparation result in a single microstate, we know that in repeating the preparation we will in general not produce the same microstate. In this sense the description of system preparation corresponds to specifying an "experimental" ensemble, which may then be identified as the "macrostate" of the system. The task of statistical mechanics is to find this ensemble.

Suppose we are given the average values of some set of physical variables over this experimental ensemble. The MEE density matrix containing this information, and nothing more, is obtained by maximizing the information entropy, $S_I = -\mathrm{Tr}[\rho \ln \rho]$, subject to the constraints on the ensemble averages. Given the values of A and B the resulting ensemble is

$$\rho = \frac{e^{\alpha A + \beta B}}{Z} \tag{2.1}$$

with the Lagrange multipliers α and β determined by the conditions

$$Z = \mathrm{Tr}\,[\rho]$$

$$\langle A \rangle_\rho \equiv \mathrm{Tr}\,[A\rho] = [A]$$

$$\langle B \rangle_\rho \equiv \mathrm{Tr}\,[B\rho] = [B] \tag{2.2}$$

where [A] and [B] denote averages over the experimental ensemble. We can use this ensemble to predict values of other variables:

$$\langle C \rangle \equiv \mathrm{Tr}\,[C\rho] \tag{2.3}$$

This prediction of C is the "best" prediction of C from the values of A and B in the information theory sense that no arbitrary assumptions are involved.

By introducing additional variables we could include any information obtained from the experimental ensemble. In fact, by measuring a complete set of commuting variables we could in principle determine the experimental ensemble exactly.

Of course we have nowhere near the complete information necessary to determine the experimental ensemble exactly. The problem is really to approximate this ensemble. More precisely, we want the MEE ensemble to yield the proper values of a relatively small number of experimentally accessible physical variables.

Now if we had to specify the observed values of all our experimental parameters this would be a worthless approximation. But we know from experience that our physical variables are usually functionally related; experimentally the system is often characterized by some set of variables (A, B) in the sense that specification of this set determines the values of a second set (C, D, E).

This leads to the expectation that our MEE ensemble determined by A and B also has this property; i.e., since the experimental ensemble is characterized by A and B with respect to C, D and E, then the MEE ensemble incorporating only the information on A and B should yield accurate predictions of C, D and E.

2. Definition of Thermal Driving for Discrete Transfers

Let the macrostate of an isolated system be characterized by values of A and B in the sense that experimental knowledge of A and B determines the values of some set D, E, F. The MEE ensemble is

$$\rho_1 = \frac{e}{Z_1}^{\alpha_1 A + \beta_1 B} \tag{2.4}$$

where α and β are determined by the measured values of A and B, denoted [A] and [B], through the relations

$$\begin{aligned} \mathrm{Tr}\ [A\rho_1] &\equiv \langle A\rangle_1 = [A] \\ \mathrm{Tr}\ [B\rho_1] &\equiv \langle B\rangle_1 = [B] \end{aligned} \tag{2.5}$$

and we assume the values of D, E, F to be given correctly by this ensemble. Suppose now we let the system interact with its surroundings so that [ΔA[and [ΔB] flow in.

A reasonable choice for the new ensemble is

$$\rho_2 = \frac{e}{Z_2}^{\alpha_2 A + \beta_2 B} \tag{2.6}$$

with α_2 and β_2 determined by

$$\begin{aligned} \langle A \rangle_2 &= [A] + [\Delta A] \\ \langle B \rangle_2 &= [B] + [\Delta B] \end{aligned} \qquad (2.7)$$

In picking this ensemble we have actually assumed that after the interaction we can still characterize the macrostate of the system experimentally by A and B for predictions of D, E and F. Some transfer mechanisms violate this. Let us take as part of the definition of thermally driven processes that <u>no new variables are required to characterize the system.</u> Then specifying [Δ A] and [Δ B] and that the variables are driven thermally leads to ρ_2 .

Now consider the case where [B] [B] + [Δ B], but the change in A is unspecified. Requiring thermal driving leads to

$$\rho_2 = \frac{e^{\alpha_2 A + \beta_2 B}}{Z_2} \qquad (2.8)$$

with $\langle B \rangle_2 = [B] + [\Delta B]$. This is obviously insufficient to determine the ensemble. We must know how A changes during the process.

At this point it might seem necessary that the experimenter specify the change in A as well as B. For many situations this is certainly the right attitude; if the experimenter imposed conditions on the A transfer then we should expect to get bad results by ignoring them.

On the other hand there is nothing wrong with singling out a particular type of A change with a special name in the hope that it will be useful. In particular it seems that for many transfer processes of physical interest the change of A associated with the transfer of B is determined by the state of the system. Guided by this consideration, we make the following definition.

. . .

The transfer of a specified variable is said to be "thermally driven" if no new variables are needed to characterize the new macrostate, and if the Lagrange multipliers corresponding to variables other than the driven one remain constant.

. . .

In the present case this means $\alpha_1 = \alpha_2$, so the new ensemble is

$$\rho_2 = \frac{e^{\alpha_2 A + \beta_2 B}}{Z_2} \tag{2.9}$$

with $\langle B \rangle_2 = [B] + [\Delta B]$, and $\alpha_1 = \alpha_2$

This definition is equivalent to two other possible definitions for the thermal transfer process, as will now be shown.

Returning to the original ensemble, notice that there is nothing special about the variable A; we can replace it by a linear combination of A and B and still have the same ensemble. Thus, if

$$A' \equiv A - \epsilon B,$$

then

$$\rho_1 = e^{\alpha_1 A' + \beta_1' B} \tag{2.10}$$

with

$$\beta_1' \equiv \beta_1 + \alpha_1 \epsilon$$

Driving this ensemble thermally to [B] + [Δ B], we obtain the ensemble

$$\rho_2 = \frac{e^{\alpha_1 A' + \beta_2' B}}{Z_2'} \tag{2.11}$$

with

$$\langle B \rangle_2 = [B] + [\Delta B] ,$$

or using the definition of A$'$,

$$\beta_2' = \beta_2 + \alpha\epsilon \qquad (2.12)$$

Now expand ρ_2 to first order in $\beta_2 - \beta_1$, about ρ_1 . Then to first order (indicated by dot),

$$\langle B\rangle_2 \doteq \langle B\rangle_1 + (\beta_2 - \beta_1) K_{BB} \qquad (2.13)$$

$$\langle A'\rangle_2 \doteq \langle A'\rangle_1 + (\beta_2 - \beta_1) K_{A'B} \qquad (2.14)$$

where

$$K_{A'B} \equiv \int_0^1 dx \; Tr\left[e^{-x\ln\rho_1} B e^{x\ln\rho_1} A'\rho_1\right] - \langle B\rangle_1 \langle A'\rangle_1$$

$$\equiv \langle \overline{B} A'\rangle_1 - \langle B\rangle_1 \langle A\rangle_1 \qquad (2.15)$$

Solving equation (2.13) for $\beta_2 - \beta_1$, and using this in (2.14),

$$\langle A'\rangle_2 - \langle A'\rangle_1 \doteq (\langle B\rangle_2 - \langle B\rangle_1) \frac{K_{A'B}}{K_{BB}} \qquad (2.16)$$

Now set $\epsilon = \dfrac{K_{AB}}{K_{BB}}$ so that A$'$ is defined as

$$A' \equiv A - \frac{K_{AB}}{K_{BB}} B \qquad (2.17)$$

With this definition

$$K_{A'B} = 0 \qquad (2.18)$$

so

$\langle A'\rangle_2 = \langle A'\rangle_1$, i.e., A$'$ is not changed in first order by the thermally driven transfer of B. Hence, instead of defining thermally driven processes by the condition ($\alpha \equiv$ constant), we could have used the condition

$$\left(\frac{\partial\langle A'\rangle}{\partial\langle B\rangle}\right)_{\substack{\text{Thermally}\\ \text{Driven}\\ \text{Process}}} = 0 \qquad (2.19)$$

with A' defined by (2.17). But $K_{A'B}$ has the physical significance of the covariance of the fluctuations of A' with fluctuations of B in the initial ensemble. Hence the thermal transfer process has the property that the unspecified variables change with the driven terms exactly as they do for fluctuations in the initial ensemble. In particular, variables uncorrelated with B remain constant.

A third property of this α or A' constant process is that it minimizes the net entropy transfer. Assume that the driving system is arbitrarily close to equilibrium under thermal transfer of B with our driven system. For the driven system the equilibrium parameter is

$$\left(\frac{\partial S_1}{\partial B}\right)_\alpha = \left(\frac{\partial S_1}{\partial B}\right)_{A'} = -\beta_1' \tag{2.20}$$

$$= -\beta_1 - \alpha_1 \frac{K_{AB}}{K_{BB}}$$

while for the driving system

$$\left(\frac{\partial S_D}{\partial B}\right)_{A'} = -\beta_D' \tag{2.21}$$

The condition for the transfer process to go in the direction of 1 is that the net entropy should increase, or $-\beta_1' > -\beta_D'$. However we can consider making the difference arbitrarily small, so that the second order terms in the expansion of the entropy about the ΔB transfer become important.

$$\Delta S = \Delta S_1 + \Delta S_D \tag{2.22}$$

$$= \left(\frac{\partial S_1}{\partial B}\right)_{A'} \Delta B + \left(\frac{\partial^2 S_1}{\partial B^2}\right)_{A'} \frac{(\Delta B)^2}{2!} + \cdots$$

$$+ \left(\frac{\partial S_D}{\partial B}\right)_{A'} (-\Delta B) + \left(\frac{\partial^2 S_D}{\partial B^2}\right)_{A'} \frac{(-\Delta B)^2}{2!} + \cdots$$

$$\Delta S \simeq \left(\frac{\partial^2 S_1}{\partial B^2}\right)_{A'} \frac{(\Delta B)^2}{2!} + \left(\frac{\partial^2 S_D}{\partial B^2}\right)_{A'} \frac{(\Delta B)^2}{2!}$$

Both second derivatives of the entropy are >0. Since we don't want to assume any microscopic knowledge about the reservoir, let us just consider the contribution from the driven system. Then in this case with $K_{A'B} = 0$,

$$\left(\frac{\partial^2 S_1}{\partial B^2}\right)_{A'} = -\frac{1}{K_{BB}} \tag{2.23}$$

If we had considered processes with some A other than A' constant, then

$$\left(\frac{\partial^2 S_1}{\partial B^2}\right)_{A} = -\frac{1}{K_{BB} - \frac{K_{AB}^2}{K_{AA}}} \tag{2.24}$$

Since $K_{AA} K_{BB} - K_{AB}^2 \geqslant 0$ it follows that $\left|\left(\frac{\partial S_1^2}{\partial B^2}\right)_A\right|$ is a minimum for A = A'. So in this sense the process we have chosen also corresponds to a minimum change in entropy. If we interpret $e^{\Delta S}$ as proportional to the probability of observing a fluctuation of magnitude Δ B between the two systems, then

$$P_{A'} \sim e^{-\frac{(\Delta B)^2}{2K_{BB}}}$$

for the thermally driven (i.e., A' = constant) process, and

$$P_A \sim e^{-\frac{(\Delta B)^2}{2\left(K_{BB} - \frac{K_{AB}^2}{K_{AA}}\right)}}$$

for the (A = constant) process. If (Δ B) is taken $\gg \sqrt{K_{BB}}$ then

$$\frac{P_A}{P_{A'}} \lesssim e^{-\frac{(\Delta B)^2}{2K_{BB}}\left(\frac{K_{AB}^2}{K_{AA} K_{BB}}\right)}$$

so that unless $\frac{K_{AB}^2}{K_{AA}K_{BB}}$ is correspondingly small, the thermally driven fluctuation ΔB is far more likely.

3. Thermal Driving With Explicit Constraints

So far we have merely defined a particular mechanism for driving systems and shown that it has some appealing properties. Certainly there exist processes which occur in the "thermally driven" fashion and others which do not. In fact all we have to do is to impose some experimental constraint on the transfer and our general considerations are inappropriate. If A is held constant, then it is quite irrelevant that A' constant is the "natural" constraint. But this is not a real restriction on the usefulness of our theory, for we can now extend the definition of "thermally driven" to include transfer mechanisms which impose constraints.

. . .

The transfer of a specified variable is said to be "thermally driven" if no new variables *other than those constrained experimentally* are needed to characterize the new state, and if the Lagrange multipliers corresponding to variables other than those specified remain constant.

. . .

Returning to our original ensemble, suppose that in addition to specifying the change in B we also include information that the interaction was constrained to constant C. Then the initial MEE ensemble is as before,

$$\rho_1 = \frac{e^{\alpha_1 A + \beta_1 B}}{Z_1} \qquad (2.25)$$

with $\langle A \rangle_1 = [A]$ and $\langle B \rangle_1 = [B]$

If $[B] \rightarrow \langle B \rangle_1 + [\Delta B]$ by a thermally driven process, then the clause "no new variables other than those constrained experimentally" means that the new ensemble has the form

$$\rho_2 = \frac{e^{\alpha_2 A + \beta_2 B + \gamma_2 C}}{Z_2}$$

with

$$\langle c \rangle_2 = \langle c \rangle_1 \qquad (2.26)$$

and

$$\langle B \rangle_2 = \langle B \rangle_1 + [\Delta B]$$

The change in A is not specified so we apply our "thermally driven" assumption to it;

$$\alpha_2 = \alpha_1 \qquad (2.27)$$

There is no restriction to the three variable case. In general let $[\Delta F_n]$ be added to a system characterized by values of $F_1 \cdots F_n$, with experimental constraints $G_1 \cdots G_m$. The MEE ensemble for this system is

$$\rho_{\text{initial}} = \frac{e^{+\sum_{j=1}^{n} \lambda_j F_j}}{Z_{\text{initial}}} \qquad (2.28)$$

Where as usual the λ's are determined by

$$\langle F_j \rangle_{\text{initial}} \equiv Tr\,[F_j\, \rho_{\text{initial}}] \qquad (2.29)$$

$$= [F_j],\ 1 \leq j \leq n$$

Assuming the system to be thermally driven from $\langle F_n \rangle$ initial to $\langle F_n \rangle$ initial + $[\Delta F_n]$ with $G_1 \cdots G_m$ held constant leads to

$$\rho_{\text{final}} = \frac{1}{Z_{\text{final}}} \exp \left[+ \sum_{i=1}^{m} \gamma_i G_i + \sum_{j=1}^{n-1} \lambda_j F_j + \lambda_{n_{\text{final}}} F_n \right] \tag{2.30}$$

with

$$\langle F_n \rangle \text{ final} = \langle F_n \rangle \text{ initial} + [\Delta F_n]$$

and

$$\langle G_i \rangle \text{ final} = \langle G_i \rangle \text{ initial}, \quad 1 \leq i \leq m$$

The generalization of "thermally driven" to include constraints was relatively simple, but it provides a powerful extension to our theory. The original singling out of a particular process to expect in the absence of detailed knowledge was based on the assumption that the state of the system determined the process. This is not necessarily the case. But our extended definition incorporates all the constraints in the transfer mechanism; it applies the assumption of a particular process only to those variables whose changes must in fact be determined by the state of the system, *if they are determined by the experimental process at all*; i.e., if there is a reproducible phenomenon to predict. Hence we have good reason to believe that any non-dynamically driven process should in fact be well described by assuming it "thermally driven". At least by assuming a system to be "thermally driven" we have a general prescription for converting information on source terms into an ensemble, and can then see whether predictions using this ensemble agree with experimental observation. To be more precise, in experiments where a driven change in some variable produces reproducible changes in some other set of variables, the "thermally driven" assumption allows us to set up an ensemble from the driven variable. We then expect this ensemble to correctly predict the second set of experimentally reproducible variables.

4. Time Dependent Thermal Driving

We have a reasonable prescription for the new ensemble produced by forcing a discrete change in some system variable. The next step is to extend this to systems driven continuously as a function of time. The instantaneous ensemble for a continuously driven system is easily obtained by a limiting process involving repeated application of the basic definition of "thermally driven". Note that the ensemble for a system with time dependent externally driven terms must be a function of time, incorporating the information on all driving applied to it up to the present instant.

Consider a sequence of density matrices obtained by adding $[\Delta F_1]$ with G_1 constant to ρ_0 to form ρ_1, then adding $[\Delta F_2]$ with G_2 constant to ρ_1 to form ρ_2, etc.

$$\rho_0 = \frac{e^{\alpha A}}{Z_0}$$

with

$$\langle A \rangle_0 = [A], \tag{2.31}$$

$$\rho_1 = \frac{e^{\alpha A + \gamma_1 G_1 + \lambda_1 F_1}}{Z_1}$$

with

$$\begin{aligned} \langle A\rangle_0 &= [A] \\ \langle G_1\rangle_1 &= \langle G_1\rangle_0 \\ \langle F_1\rangle_1 &= \langle F_1\rangle_0 + [\Delta F_1] \end{aligned} \tag{2.32}$$

$$\bullet\ \bullet\ \bullet$$

$$\rho_n = \frac{e}{Z_n}^{\alpha A + \sum_{i=1}^{n} \gamma_i G_i + \lambda_i F_i}$$

with

$$\begin{aligned} \langle A\rangle_0 &= [A] \\ \langle G_i\rangle_i &= \langle G_i\rangle_{i-1} \\ \langle F_i\rangle_i &= \langle F_i\rangle_{i-1} + [\Delta F_i], \quad 1 \leq i \leq n \end{aligned} \tag{2.33}$$

The F_i are any operators we control, and G_i is a constraint imposed on the transfer of F_i. In particular we can choose the F_i and G_i to be the Heisenberg operators for the physical quantities F and G at the time t_i,

$$\begin{aligned} F_i \equiv F_{t_i} &\equiv e^{\frac{iHt}{\hbar}} F_0 e^{-\frac{iHt}{\hbar}}, \\ G_i \equiv G_{t_i} &\equiv e^{\frac{iHt}{\hbar}} G_0 e^{-\frac{iHt}{\hbar}}, \end{aligned} \tag{2.34}$$

where H is the Hamiltonian of the isolated, non-driven system. Further specialize by taking the t_i to be ordered and at constant intervals, $t_i - t_{i-1} = \Delta t$. Define

$$\begin{aligned} \lambda_i &\equiv \Delta t \ \lambda(t_i) \\ \gamma_i &\equiv \Delta t \ \gamma(t_i) \end{aligned} \tag{2.35}$$

Then

$$\rho_{t_n} = Z^{-1} \exp \left[\alpha A + \sum_{i=1}^{n} \Delta t \left[\gamma(t_i) G_{t_i} + \lambda(t_i) F_{t_i} \right] \right] \tag{2.36}$$

with

$$\langle A \rangle_0 = [A_{t=0}] \tag{2.37}$$

$$\langle F_{t_i} \rangle_{t_i} = \langle F_{t_i} \rangle_{t_{i-1}} + [\Delta F_{t_i}] , \quad 1 \leq i \leq n \tag{2.38}$$

and

$$\langle G_{t_i} \rangle_{t_i} = \langle G_{t_i} \rangle_{t_{i-1}} , \quad 1 \leq i \leq n . \tag{2.39}$$

Condition (2.38) can be written

$$\langle F_{t_i} \rangle_{t_i} = [F_{t_i}] \tag{2.40}$$

where [F_{t_i}] is the experimental value of F at time ti, since

$$[\Delta F_{t_i}] \equiv [F_{t_i}] - \langle F_{t_i} \rangle_{t_{i-1}} .$$

Expand ρ_{t_i} about $\rho_{t_{i-1}}$ finding to first order in

$$\Delta t \, \lambda(t_i) + \Delta t \, \gamma(t_i), \tag{2.41}$$

$$0 = \langle G_{t_i} \rangle_{t_i} - \langle G_{t_i} \rangle_{t_{i-1}} \doteq \Delta t \, \lambda(t_i) K^{t_i}_{G_{t_i} F_{t_i}} + \Delta t \, \gamma(t_i) K^{t_i}_{G_{t_i} G_{t_i}}$$

or

$$\gamma(t_i) = - \lambda(t_i) \frac{K^{t_i}_{G_{t_i} \; F_{t_i}}}{K^{t_i}_{G_{t_i} \; G_{t_i}}}$$

where $K^{t_i}_{G_{t_i} F_{t_i}}$ is the covariance of the operators G_{t_i} and F_{t_i} evaluated in the ensemble ρ_{t_i};

$$K^{t_i}_{G_{t_i} F_{t_i}} \equiv Tr\left[\int_0^1 dx\, e^{-x\ln\rho_{t_i}} F_{t_i}\, e^{+x\ln\rho_{t_i}} G_{t_i}\,\rho_{t_i}\right] - Tr\left[F_{t_i}\,\rho_{t_i}\right] Tr\left[G_{t_i}\,\rho_{t_i}\right] \equiv \langle \overline{F_{t_i}}\; G_{t_i}\rangle_{t_i} - \langle F_{t_i}\rangle_{t_i}\langle G_{t_i}\rangle_{t_i}. \tag{2.42}$$

Now take the limit $n \longrightarrow \infty$, $\Delta t \longrightarrow 0$, $n\Delta t \longrightarrow t$.

Then

$$\rho_t = Z_t^{-1} \exp\left[\alpha A + \int_0^t \gamma(t')\,G(t') + \int_0^t \lambda(t')\,F_{t'}\,dt'\right] \tag{2.43}$$

with

$$\langle A\rangle_0 = [A_{t=0}] \tag{2.44}$$

$$\langle F_{t'}\rangle_{t'} = [F_{t'}] \tag{2.45}$$

and

$$0 = \frac{d}{dt'}\langle G_{t'}\rangle_{t'} - \langle \dot{G}_{t'}\rangle_{t'} = \lambda(t')\,K^{t'}_{G_{t'} F_{t'}} + \gamma(t')\,K^{t'}_{G_{t'} G_{t'}} \tag{2.46}$$

or

$$\gamma(t') = -\lambda(t')\,\frac{K^{t'}_{G_{t'} F_{t'}}}{K^{t'}_{G_{t'} G_{t'}}}\,. \tag{2.47}$$

Although (2.41) is a first order approximation, in the limit $\Delta t \longrightarrow 0$ it becomes exact, equation (2.46).

Expression (2.43) with α, $\gamma(t')$ and $\lambda(t')$ determined by equations (2.44) - (2.47) is the formally exact density matrix for the instantaneous state of a system with a time-dependent "thermally driven" variable. Equations (2.43) - (2.47) represent a considerable simplification of the general problem; they involve only the dynamics of the isolated system, with the actual details of the driving interaction replaced by source terms. Of course whether the "formally exact" density matrix (2.43) has anything to do with experimental physics depends on assuming that the experimental process is characterized as thermally driven. Above I argued for this assumption. If we accept it, then the density matrix (2.43) should predict any experimentally reproducible effect with no additional restrictions. In particular (2.43) - (2.47) are not limited to first order departures from equilibrium, or to slowly varying disturbances; nor was local equilibrium assumed.

For simplicity the derivation of expressions (2.43) - (2.47) was carried out with a single driven variable and constraint. The generalization to n spatially dependent source terms with m constraints is straightforward.

The density matrix for this general situation is (sum over repeated indices) (2.48)

$$\rho_t = Z_t^{-1} \exp\left[\alpha A + \int_0^t dt' \int_R dx' \, \gamma_l(x',t') G_l(x',t') + \int_0^t dt' \int_R dx' \, \lambda_i(x',t') F_i(x',t')\right]$$

with

(2.49)

$$\langle A_{t=0} \rangle_{t=0} = \left[A_{t=0} \right]_{t=0}$$

$$\langle F_i(x',t')\rangle_{t'} = [F_i(x',t')]_{t'}\ ,\ \forall i \tag{2.50}$$

$$\frac{d}{dt'}\langle G_l(x',t')\rangle_t - \langle \dot{G}_l(x',t')\rangle_{t'} = 0,\ \forall l \tag{2.51}$$

where (2.50) and (2.51) are required to hold in the region

$$\begin{aligned} &x' \in R \\ &t' \in [0,t] \end{aligned} \tag{2.52}$$

Equivalent forms for (2.50) and (2.51) are obtained by differentiating $\langle F_i(x',t')\rangle_t$ and $\langle G_l(x',t')\rangle_{t'}$:

$$\begin{aligned} \overset{\circ}{\sigma}_{F_i(x,t)} &\equiv \frac{d}{dt}\langle F_i(x,t)\rangle_t - \langle \overset{\circ}{F}_i(x,t)\rangle_t \\ &= \int dx'\, K^t_{F_i(x,t)F_j(x',t)}\lambda_j(x',t) \\ &\quad + \int dx'\, K^t_{F_i(x,t)G_k(x',t)}\gamma_k(x',t),\ \forall i \end{aligned} \tag{2.53}$$

and

$$\begin{aligned} 0 &= \int dx'\, K^t_{G_l(x,t)F_j(x',t)}\lambda_j(x',t) \\ &\quad + \int dx'\, K^t_{G_l(x,t)G_k(x',t)}\gamma_k(x',t),\ \forall l \end{aligned} \tag{2.54}$$

As before, the definition of the covariance functions is

$$\begin{aligned} K^t_{G_l(x,t)F_j(x',t')} \equiv \mathrm{Tr}\Big[\int_0^1 dx\, e^{-x\ln\rho_t} F_j(x',t') \\ \times e^{+x\ln\rho_t}\, G_l(x,t)\,\rho_t\Big] \end{aligned} \tag{2.55}$$

$$- \mathrm{Tr}\left[F_j(x',t')\rho_t\right] \mathrm{Tr}\left[G_\ell(x,t)\rho_t\right]$$

$$= \langle \overline{F_j(x',t') \quad} G_\ell(x,t)\rangle_t \qquad \text{(2.55) cont.}$$

$$- \langle F_j(x',t')\rangle_t \langle G_\ell(x,t)\rangle_t$$

5. Interpretation of the λ's

All the information on the driving process is contained in the λ's and γ's. Formally these are determined by the macroscopic information through equations (2.50) and (2.51). The exact solutions of these equations would be difficult. However, the $\lambda_{F_i}(x,t)$ have a clear physical meaning implied by the expressions (2.54) and (2.55).

Consider first the limiting case of a single driven variable with no space dependence and no explicit constraints. Then

$$\begin{aligned} \mathring{\sigma}_F(t) &\equiv \frac{d}{dt}\langle F(t)\rangle - \langle \mathring{F}(t)\rangle \\ &= \lambda(t)\, K^t_{F(t)F(t)} \end{aligned} \qquad (2.56)$$

The quantity $\frac{d}{dt}\langle F(t)\rangle$ is the total rate of change of F in the system; the quantity $\langle \mathring{F}(t)\rangle$ is the rate of change of F determined by the ensemble from the past behavior of the system. $\mathring{\sigma}_F(t)$ is then the total rate of change of F at t minus the rate of change produced by internal relaxation; i.e. it must be the rate at which F is supplied to the system by an external source, and is thus appropriately called the source strength. In the usual experimental situation it is this source strength which is directly measured.

The equal time covariance function $K^t_{F(t)F(t)}$ also has a simple physical interpretation: it is essentially the mean square fluctuation of F at the time t in the ensemble ρ_t. Hence $\lambda_F(t)$ is essentially the source strength at t "normalized" by the mean square fluctuations of F at t.

Suppose the transfer of F takes place with the explicit constraint that no G is transfered; i.e. the source strength of G is set equal to zero. Then

$$\overset{\circ}{\sigma}_F(t) \equiv \frac{d}{dt}\langle F(t)\rangle - \langle \overset{\circ}{F}(t)\rangle \tag{2.57}$$

$$= \lambda_F(t) K^t_{F(t)F(t)} + \lambda_G(t) K^t_{F(t)G(t)}$$

and

$$0 = \frac{d}{dt}\langle G(t)\rangle - \langle \dot{G}(t)\rangle \tag{2.58}$$

$$= \lambda_F(t) K^t_{G(t)F(t)} + \lambda_G(t) K^t_{G(t)G(t)}$$

Solving the second equation for $\lambda_G(t)$, we could write this as (2.59)

$$\overset{\circ}{\sigma}_F(t) = \lambda_F(t) K^t_{F(t)F(t)} \left[1 - \frac{{K^t_{F(t)G(t)}}^2}{K^t_{F(t)F(t)} K^t_{G(t)G(t)}}\right].$$

The additional term $\frac{{K^t_{F(t)G(t)}}^2}{K^t_{F(t)F(t)} K^t_{G(t)G(t)}}$ is a measure of the strength of the correlation of F and G in the ensemble ρ_t. It is convenient to introduce a new variable F':

$$F'(t) \equiv F(t) - \frac{K^t_{G(t)F(t)}}{K^t_{G(t)G(t)}} G(t) \tag{2.60}$$

Then in terms of this variable the equation determining $\lambda_F(t)$ becomes

$$\overset{\circ}{\sigma}_F(t) = \lambda_F(t) K^{t}_{F'(t)F'(t)} \tag{2.61}$$

Hence the constraint merely changes the "normalization" of the source strength, and does not affect our interpretation of $\lambda_F(t)$ as the "normalized" source strength.

Greater complication arises if the system is driven by a set of variables. The λ's are then determined by

$$\overset{\circ}{\sigma}_{F_i}(t) = \sum_{j=1}^{n} K^{t}_{F_i(t)F_j(t)} \lambda_{F_j}(t), \quad i = 1 \dots n \tag{2.62}$$

It will be shown in section (5.1) that the $F_i(t)$ form an inner product space with the inner product $K^{t}_{F_i(t)F_j(t)}$. Therefore it is always possible to find an orthogonal basis $F_i(t)$ for which equation (2.62) becomes

$$\overset{\circ}{\sigma}_{F'_i}(t) = K^{t}_{F'_i(t)F'_i(t)} \lambda_{F'_i}(t) \quad i = 1, \dots, n; \tag{2.63}$$

on this orthogonal basis our interpretation of the λ's is preserved.

The generalization to spatial dependence introduces a new problem. The equation determining $\lambda(x,t)$ for driven $F(x,t)$ is an integral equation in space:

$$\overset{\circ}{\sigma}_F(x,t) \equiv \frac{d}{dt}\langle F(x,t)\rangle - \langle \overset{\circ}{F}(x,t)\rangle \tag{2.64}$$

$$= \int dx' \, K^{t}_{F(x,t)\,F(x',t)} \, \lambda_{F(x',t)} \,, \quad \forall\, x \in R$$

In the linear approximation this integral equation is easily handled by letting R ⟶ P and using Fourier transforms. More generally, note that for gasses and liquids the equal time covariance function is usually very sharply peaked relative to the width of the source term; thus in this approximation,

$$\mathring{\sigma}_{F(x,t)} \,\widehat{=}\, \lambda_{F(x',t)} \int dx' \, K^{t}_{F(x,t)\,F(x',t)} \tag{2.65}$$

CHAPTER III

BEHAVIOR OF THERMALLY DRIVEN SYSTEMS

1. Comparison of Dynamically and Thermally Driven Systems

Driven systems fall in two categories: thermally driven and dynamically driven. Equations (2.48)-(2.54) give our prescription for the time dependent ensemble of a thermally driven system. Now let us compare this formalism with the standard treatment of dynamically driven systems.

By definition an isolated system is dynamically driven if the Hamiltonian for the interacting system is the Hamiltonian of the isolated system plus a known interaction term; $H = H_0 + H_I$ In general the interaction involves scalar and vector coupling of external fields with various physical variables. For simplicity let us take the particular case of a scalar potential field coupling to the density,

$$H_I = \int dx \; \phi(x,t)\, n(x,t) \tag{3.1}$$

At time $t=0$ assume the density matrix to be $\rho(0)$. With H_0, H_I, and $\rho(0)$, known, the ensemble for all later times is determined by the equations of motion. In the interaction representation the time development of the density matrix is given by

$$\rho(t) = V(t)\rho(0)V^{+}(t) \tag{3.2}$$

with

$$V(t) \equiv T\exp\left[-\frac{i}{\hbar}\int_0^t H_{I_{t'}}\,dt'\right] \tag{3.3}$$

In this representation the time development of an operator is

$$F_t = e^{\frac{i}{\hbar}H_0 t} F_0 \, e^{-\frac{i}{\hbar}H_0 t} \tag{3.4}$$

Hence the expectation value of any physical variable at time t is given formally by

$$\langle F_t \rangle_t = \mathrm{Tr}\left[F_t \, \rho(t) \right] \qquad (3.5)$$

The relations above are the analogues of relations (2.48) - (2.54) for the thermally driven system.

The expressions for $\rho(t)$ and ρ_t are of quite different form. As one measure of this difference, note that the information entropy of $\rho(t)$ is constant, since it is obtained by unitary transformation of $\rho(0)$[6], while the information entropy of ρ_t is in general not constant. This indicates that the class of density matrices for thermally driven systems is wider than the class of density matrices for dynamically driven systems. In fact we can prove that for any dynamically driven matrix $\rho(t)$ there corresponds a thermally driven matrix ρ_t such that $\rho_t = \rho(t), \forall t \geq 0$. The converse is not true, as is obvious from the fact that $\rho(t)$ is restricted to unitary transformations of $\rho(0)$, whereas no such restriction applies to ρ_t.

Proof:

In deriving (2.48) - (2.54) it was assumed that F_t was a Heisenberg operator for the isolated system $F_t = e^{\frac{iH_0 t}{\hbar}} F_0 \, e^{-\frac{iH_0 t}{\hbar}}$, since this corresponds to the usual experimental situation where a specific physical variable is driven as a function of time. But this assumption was not necessary; (2.48)-(2.54) hold for any operator defined as a smooth function of time. In particular we can choose

$$\lambda(t) F_t \equiv \frac{d}{dt} \ln \rho(t) \qquad (3.6)$$

Then taking $G \equiv 0$ and $\rho_0 = \rho(0)$, the thermally driven ensemble is

$$\rho_t = \frac{e^{\alpha A + \int_0^t \lambda(t')F_{t'}}}{Z_t} \tag{3.7}$$

$$= \frac{e^{\alpha A + \ln \rho(t) - \ln \rho(0)}}{Z_t}$$

$$= \frac{e^{\ln \rho(t) - \ln Z(0)}}{Z_t}$$

Hence, using

$$Z_t = \mathrm{Tr}\left[e^{\ln \rho(t) - \ln Z(0)}\right]$$

$$= \frac{1}{Z(0)} \mathrm{Tr}\left[\rho(t)\right] = 1 ,$$

we have

$$\rho_t = \rho(t) \tag{3.8}$$

Thus we can always find a thermal driving term producing the same ensemble as a given dynamical driving term. The price we pay is that the physical interpretation of $\lambda(t)$ and F_t is no longer simple. If we represent the variables of the system by Heisenberg operators then in general F_t is a complicated time dependent linear combination of all these operators. That this complexity should arise is quite reasonable; the degree of microscopic control assumed in dynamical driving is much greater than that assumed in thermal driving.

On the other hand, it seems equally reasonable that most of this complexity should not appear in the linear response region. This is indeed the case, as will now be shown. Compare $\mathring{\rho}_t$ and $\mathring{\rho}(t)$:

$$\frac{d}{dt}\rho_t = \rho_t \int dx' \left(\lambda(x',t)\,\overline{F_t(x')} - \lambda(x';t)\langle \overline{F_t(x')}\rangle_{\rho_t}\right) dx' \tag{3.9}$$

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}\int dx'\,\phi(x';t)\left[n_t(x'),\rho(t)\right] \tag{3.10}$$

To lowest order $\mathring{\rho}_t = \mathring{\rho}(t)$ requires

$$\rho_0 \int dx'\,\lambda(x',t)\left(\overline{F_t(x')} - \langle \overline{F_t(x')}\rangle_0\right) = -\frac{i}{\hbar}\int dx'\,\phi(x',t)\left[n_t(x'),\rho_0\right] \tag{3.11}$$

If ρ_0 is the canonical or grand canonical ensemble, $\rho_0 = \exp\left[-\beta(H-\mu N)\right]$, the commutator on the right obeys the Kubo identity.[7]

$$\frac{i}{\hbar}\left[n(x,t),\rho_0\right] = \beta\rho_0\frac{d}{dt}\overline{n(x,t)} \tag{3.12}$$

where

$$\overline{n(x,t)} \equiv \int_0^1 dx\, e^{-x\ln\rho_0}\, n(x,t)\, e^{x\ln\rho_0} = \frac{1}{\beta}\int_0^\beta du\, n(x,t-i\hbar u) \tag{3.13}$$

Hence

$$\int dx'\,\lambda(x';t)\left(\overline{F(x';t)} - \langle F(x',t)\rangle_0\right) = -\int dx'\,\beta\phi(x';t)\,\overline{\mathring{n}(x';t)} \tag{3.14}$$

It is convenient to introduce the force field

$$\vec{E}(x,t) \equiv -\vec{\nabla}\phi(x,t) \tag{3.15}$$

Then using conservation of particles

$$\mathring{n}(x,t) + \vec{\nabla}\cdot\vec{j}(x,t) = 0 \tag{3.16}$$

we can do an integration by parts to find

$$\int dx'\, \lambda(x',t)\, \left(\overline{F_t(x')} - \langle F_t(x') \rangle_0 \right) = + \int dx'\, \beta\, \vec{E}(x',t) \cdot \overline{\vec{j}}(x',t) \tag{3.17}$$

The external potential was assumed to have a finite range so that the surface integral could be neglected.

Hence if we define a thermally driven variable by

$$F_t(x') \equiv \vec{j}_t(x') \tag{3.18}$$

and a corresponding source strength by

$$\lambda(x',t) = \beta\, \vec{E}(x',t) \tag{3.19}$$

then to first order the resulting thermally driven ensemble is equivalent to the original dynamically driven ensemble. The physical interpretation is that in lowest order a potential coupling to the density produces the same effect as an external momentum source.

The condition (3.11) for the first order equivalence of ρ_t and $\rho(t)$ holds for any choice of external field - physical variable coupling for the interaction Hamiltonian. Hence to first order an external field has the same effect as some source term. Conversely, in first order the source terms of a thermally driven system may always be interpreted, through (3.11), as some interaction Hamiltonian.

This is an important point. It is always possible to treat linear response to thermal driving by introducing some appropriate pseudo Hamiltonian without ever introducing the MEE thermally driven ensemble. This approach has been used extensively[8] in deriving Kubo formulas. It suffers from a severe drawback, however; without equation (3.11) which came from the MEE prescription there is no exact procedure for picking the pseudo Hamiltonian corresponding to given driving terms. In practice the pseudo Hamiltonians are not directly identified as source terms. The connection is made through a hydrodynamic model, using the response to the pseudo Hamiltonian driving to obtain expressions for transport coefficients.

2. Response in the Linear Approximation

The general equations (2.48) - (2.54) are the analogue for thermally driven systems of equations (3.1) - (3.2) for dynamically driven systems. In both cases the general equations are usually much too complicated to be solved exactly. Fortunately most experimental relations reveal a first order dependence on the departure from equilibrium. For this reason, the much simpler linear response theory obtained by expanding (3.1) - (3.2) and (2.48) - (2.54) to first order in the driving terms ϕ , λ, and γ is of primary interest.

In equations (2.73) and (2.74) the covariance functions appear multiplied by λ and γ. Hence for linear response it is sufficient to take the zeroth order expressions

$$K^{\circ}_{G_{l}}(x,t)\,F_{j}(x',t') = \langle \overline{F_{j}(x',t')}\, G_{l}(x,t)\rangle_{0} - \langle F_{j}(x',t')\rangle_{0}\,\langle G_{l}(x,t)\rangle_{0} \tag{3.20}$$

For a homogeneous isotropic medium, the correlations are function only of $\vec{X} - \vec{X}'$ and $t - t'$;

$$K^{\circ}_{G_{l}F_{j}}(x-x',t-t') = \langle \overline{F_{j}(0,0)}\, G_{l}(x-x',t-t')\rangle_{0} - \langle F_{j}(0,0)\rangle_{0}\,\langle G_{l}(0,0)\rangle_{0} \tag{3.21}$$

Hence the basic equations for the linear response of an arbitrary variable J in an homogeneous isotropic medium are

$$\langle J(x,t)\rangle \doteq \langle J(x,t)\rangle_0 + \int_0^t dt' \int_R dx'\, \gamma_\ell(x',t')\, K_{JG_\ell}(x-x';t-t') + \int_0^t dt' \int_R dx'\, \lambda_i(x',t')\, K_{JF_i}(x-x',t-t') \tag{3.22}$$

with

$$\rho_0 = \frac{e^{-\beta H}}{Z_0} \tag{3.23}$$

$$\mathring{\sigma}_{F_i}(x,t) = \int_R dx'\, K_{F_i F_j}(x-x',0)\, \lambda_j(x',t) + \int_R dx'\, K_{F_i G_\ell}(x-x',0)\, \gamma_\ell(x',t) \tag{3.24}$$

and

$$0 = \int_R dx'\, K_{G_\ell F_j}(x-x',0)\, \lambda_j(x',t) + \int_R dx'\, K_{G_\ell G_k}(x-x',0)\, \gamma_k(x',t) \tag{3.25}$$

Note for physical interpretation that the simultaneous correlation $\langle F_i(x,t)\, F_j(x',t)\rangle$ will usually be of very short range; thus the source terms at (x,t) are essentially proportional to a linear combination of the λ's and γ's at (x,t).

The basic linear response equations are much simplified by considering the region R to be infinite. Then taking Fourier transforms,

$$\langle J(k,t)\rangle \doteq \langle J(k,0)\rangle_0 + \int_0^t dt'\, \gamma_\ell(k,t')\, K_{JG_\ell}(k,t-t') + \int_0^t dt\, \lambda_i(k,t')\, K_{JF_i}(k,t-t') \tag{3.26}$$

with

$$\rho_0 = \frac{e^{-\beta H}}{Z_0} \tag{3.27}$$

$$\mathring{\sigma}_{F_i}(k,t) = K_{F_iF_j}(k,0)\,\lambda_j(k,t) + K_{F_iG_\ell}(k,0)\,\gamma_\ell(k,t) \tag{3.28}$$

and

$$0 = K_{G_\ell F_j}(k,0)\,\lambda_j(k,t) + K_{G_\ell G_k}(k,0)\,\gamma_k(k,t) \tag{3.29}$$

Since the form of these relations is identical to the dynamical response form, the linear MEE thermal response is conveniently expressed in the familiar dynamical response notation.

Consider the electrical conductivity. First order expansion of $\rho(t)$ leads to the Kubo expression for current at (x,t):

$$\langle j(x,t)\rangle \doteq \beta\int_0^t dt'\,dx'\, K_{\vec{j}\vec{j}}(x-x',t-t')\cdot\vec{E}(x',t') \tag{3.30}$$

where

$$K_{\vec{j}_\alpha\vec{j}_\beta}(x-x',t-t') \equiv \langle j_\beta(0,0)\, j_\alpha(x-x',t-t')\rangle_0 \tag{3.31}$$

It is customary to turn on the interaction adiabatically from an initial equilibrium ensemble at $-\infty$. This simply changes the lower limit of the time integration to $-\infty$. Fourier transform in space and time:

$$\langle \vec{j}(\vec{k},t)\rangle \doteq \beta \int_{-\infty}^{\infty} \int_{-\infty}^{t} dt' \, e^{i\omega t} K_{\vec{j}\vec{j}}(\vec{k},t-t')\cdot\vec{E}(k,t') \tag{3.32}$$

$$\doteq \beta \int_0^{\infty} d\tau \, e^{i\omega t} K_{\vec{j}\vec{j}}(\vec{k},\tau)\cdot\vec{E}(k,\omega)$$

where the Fourier convention used is

$$f(k,t) = \int d\vec{x} \, e^{-i\vec{k}\cdot\vec{x}} \int dt \, e^{i\omega t} f(x,t) \tag{3.33}$$

Define the full Fourier time transform and the imaginary Laplace time transforms of the covariance functions by

$$K_{jj}(k,\omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t} K_{jj}(k,t) \tag{3.34}$$

and

$$K^{+}_{jj}(k,\omega) = \int_0^{\infty} dt \, e^{i\omega t} K_{jj}(k,t) \tag{3.35}$$

Then the conductivity tensor is

$$\sigma_{\alpha\beta}(k,\omega) \equiv \frac{\langle j_\alpha(k,\omega)\rangle}{E_\beta(k,\omega)} = \beta K^{+}_{j_\alpha j_\beta}(k,\omega) \tag{3.36}$$

The relation between Laplace and Fourier transforms is

$$K^{+}_{jj}(k,\omega) = \lim_{\epsilon\to 0} \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega' \, \frac{K_{jj}(k,\omega')}{\omega'-\omega-i\epsilon} \tag{3.37}$$

$$= \frac{1}{2} K_{jj}(k,\omega) + \frac{1}{2\pi i} P\int_{-\infty}^{\infty} d\omega' \, \frac{K_{jj}(k,\omega')}{\omega' - \omega}$$

Since $Kjj\ (k,t)$ is a symmetric function of time, $Kjj\ (k,w)$ is real.

Hence

$$\mathrm{Re}\, K^{+}_{jj}(k,\omega) = \frac{1}{2} K_{jj}(k,\omega) \tag{3.38}$$

and

$$\mathrm{Im}\, K^{+}_{jj}(k,\omega) = \frac{1}{2\pi i} P\int_{-\infty}^{\infty} d\omega' \, \frac{K_{jj}(k,\omega)}{\omega' - \omega} \tag{3.39}$$

The importance of these relations is that $\mathrm{Re}\, K^{+}(k,\omega)$ measures the dissipation of power in the system while $\mathrm{Im}\, K^{+}(k,\omega)$ is a reactive term. To be more precise, from the theory of conductivity the definitions are admittance,

$$\sigma_{\alpha\beta}(k,\omega) = \beta K^{+}_{j_\alpha j_\beta}(k,\omega) \tag{3.40}$$

conductance,

$$\mathrm{Re}\, \sigma_{\alpha\beta}(k,\omega) = \beta\, \mathrm{Re}\, K^{+}_{j_\alpha j_\beta}(k,\omega) \tag{3.41}$$

and susceptance,

$$-\mathrm{Im}\, \sigma_{\alpha\beta}(k,\omega) = -\beta\, \mathrm{Im}\, K^{+}_{j_\alpha j_\beta}(k,\omega) \tag{3.42}$$

To illustrate, consider the behavior of $j(k,t)$ as a function of the past behavior of $E(k,t')$. If we assume $E(k,t') = E(k,w)e^{-iwt'}$, then the rate of energy addition to the medium is

$$P_\omega(k,t) = \mathrm{Re}\langle j(k,t)\rangle \cdot \mathrm{Re}\, E(k,t) \tag{3.43}$$

$$= \beta\, \mathrm{Re}\left(K_{j_\alpha j_\beta}(k,\omega) E_\beta(k,\omega) e^{-i\omega t}\right) \mathrm{Re}\left(E_\alpha(k,\omega) e^{-i\omega t}\right)$$

$$= \frac{\beta}{2} E_\alpha(k,\omega) E_\beta(k,\omega) \left[\left| K^+_{j_\alpha j_\beta} \right| \cos(2\omega t + \phi) + \mathrm{Re}\, K^+_{j_\alpha j_\beta} \right]$$

where

$$\phi = \tan^{-1}\left(\frac{-\mathrm{Im}\, K^+(\omega)}{\mathrm{Re}\, K^+(\omega} \right) \tag{3.44}$$

As asserted, the time independent rate of power loss in a system driven at frequency ω is proportional to $\mathrm{Re}\, K^+_{\alpha\beta}(\omega)$:

$$P_\omega\ \mathrm{avg} = \frac{\beta}{2} E_\alpha(k,\omega) E_\beta(k,\omega)\, \mathrm{Re}\, K^+_{j_\alpha j_\beta}(k,\omega) \tag{3.45}$$

But the general form for linear response of thermally driven systems is the same as (3.30), with the driven variable F replacing j and the source term λ (x,t) replacing E (x,t). The linear prediction for F at (x,t) is

$$\langle F(x,t)\rangle \doteq \langle F(x,t)\rangle_0 + \int dx' \int_0^t dt'\, dx'\, K_{FF}(x-x', t-t')\, \lambda_F(x',t') \tag{3.46}$$

with
$$K_{FF}(k, t=0)\,\lambda(k,t') \doteq \mathring{\sigma}_{F_{t'}}(k)$$

$\mathring{\sigma}_{F_t}$ is assumed to be the experimental information. Taking Fourier transforms,

$$\langle F(k,\omega)\rangle = K^{+}_{FF}(k,\omega)\,\lambda(k,\omega) \qquad (3.47)$$

In order to speak meaningfully of "resistive" and "reactive" parts of K^+ it is necessary to have an analogue of the energy added to the system. This is furnished nicely by the information entropy, defined

$$S_{I_t} = -\mathrm{Tr}\left[\rho_t \ln \rho_t\right] \qquad (3.48)$$

It will be shown in the section on entropy that if the interaction transfering F_t to the system does not couple to the Hamiltonian (i.e. $K^{t}_{HF_t} = 0$) then by (4.12) and (3.46),

$$\mathring{S}_{I_t} \doteq -\lambda(t)\left(\langle F_t\rangle_t - \langle F_t\rangle_0\right) . \qquad (3.49)$$

This has the same form as the power dissipation(3.43), so for a source term $\lambda(k,t) = \lambda(k,\omega)\,e^{-i\omega t}$,

$${}_{\omega}\mathring{S}_{I_t} = -\tfrac{1}{2}\,\lambda^2(k,\omega)\left[\left|K^{+}_{FF}(k,\omega)\right|\cos(2\omega t+\phi) + \mathrm{Re}\,K^{+}_{FF}(k,\omega)\right]$$

(3.50)

with

$$\phi = \tan^{-1}\left(-\frac{\mathrm{Im}\,K^{+}(k,\omega)}{\mathrm{Re}\,K^{+}(k,\omega)}\right)$$

$-\mathring{S}_{It\,\text{constant}} = \frac{1}{2}\lambda^2(k,\omega)\,\mathrm{Re}\,K^{+}_{FF}(k,\omega)$ is interpreted as the minimum time independent rate of entropy increase of the driving reservoirs necessary to maintain the sinusoidal variation in F.

3. Kubo Formulas for Hydrodynamic Coefficients

If we drive a system in some fashion and measure the behavior of some set of variables, we are directly measuring the experimental Green's function of the response. In the hydrodynamic region this is also the Green's function of the differential equations obtained from conservation laws and ad hoc constitutive equations. Thus experiments indirectly determine the parameters in the constitutive equations. But the fundamental quantity is the Green's function rather than the transport coefficients; the Green's functions are perfectly well defined and experimentally accessible quantities even when the ad hoc constitutive equations are invalid.

This is certainly well recognized for dynamically driven systems. Dynamical perturbation theory automatically yields response functions relating applied force and resultant flows; these response functions are accepted as the fundamental physical quantities. Our approach to thermally driven systems yields expressions of exactly the same form relating source strength and resultant flows. It is the covariance functions appearing in these relations which should be considered the fundamental quantities, rather than transport coefficients, since it is these covariance functions which are the experimental Green's functions.

Nevertheless, for historical purposes it seems worth-while to encode the correlation function information in generalized hydrodynamic coefficients. From the expressions for the generalized hydrodynamic coefficients in terms of the correlation functions it is easy to pull out the so-called Kubo Formulas.

Consider first the expression for thermal conductivity. The conservation equation is

$$\vec{\nabla} \cdot \vec{J}_{\varepsilon} + \dot{\varepsilon} = \mathring{\sigma}_{\varepsilon} \tag{3.51}$$

and the constitutive equation defining the thermal conductivity is taken as

$$\vec{J}_{\varepsilon} = -\Lambda \nabla \varepsilon \tag{3.52}$$

If we generalize Λ to non-local space and time dependence. then this becomes

$$\vec{J}_{\varepsilon}(x,t) = -\int dx' \int_{-\infty}^{t} dt' \Lambda(x-x', t-t') \vec{\nabla} \varepsilon(x',t') \tag{3.53}$$

Taking Fourier and Laplace transforms, the solution of (3.51) and (3.53) is

$$\varepsilon(k,\omega) = \frac{\mathring{\sigma}_{\varepsilon}(k,\omega)}{-i\omega + \Lambda(k,\omega)k^2} \tag{3.54}$$

On the other hand, first order MEE for thermally driven systems gives

$$\varepsilon(x,t) = \int dx' \int_{-\infty}^{t} dt' K_{\varepsilon\varepsilon}(x-x', t-t') \lambda(x',t') \tag{3.55}$$

or

$$\varepsilon(k,\omega) = K^{+}_{\varepsilon\varepsilon}(k,\omega) \lambda(k,\omega) \tag{3.56}$$

with the source term

$$\overset{\circ}{\sigma}(k,\omega) = K_{\varepsilon\varepsilon}(k,t=0)\,\lambda(k,\omega) \qquad (3.57)$$

Comparing (3.54) and (3.56),

$$\frac{K^{+}_{\varepsilon\varepsilon}(k,\omega)}{K_{\varepsilon\varepsilon}(k,t=0)} = \frac{1}{-i\omega + \Lambda(k,\omega)k^{2}}$$

or

(3.58)

$$\Lambda(k,\omega) = \frac{K_{\varepsilon\varepsilon}(k,t=0)}{k^{2}K^{+}_{\varepsilon\varepsilon}(k,\omega)} + \frac{i\omega}{k^{2}}$$

This can be put in a little neater form by using the identity

(3.59)

$$\vec{k}\,\vec{k} : K_{\vec{J}_\varepsilon\vec{J}_\varepsilon}(\vec{k},\omega) = \omega^{2}K^{+}_{\varepsilon\varepsilon}(k,\omega) + i\omega K_{\varepsilon\varepsilon}(k,t=0)$$

which follows from the conservation law (3.51). Take $\vec{k}$ in the 1_z direction:

(3.60)

$$\vec{k}\,\vec{k} : K_{\vec{J}_\varepsilon\vec{J}_\varepsilon}(\vec{k},\omega) = k^{2}K_{J_{\varepsilon z}J_{\varepsilon z}}(k,\omega)$$

so

$$K^{+}_{\varepsilon\varepsilon}(k,\omega) = \frac{k^{2}}{\omega^{2}}K^{+}_{J_z J_z}(k,\omega) + \frac{i}{\omega}K_{\varepsilon\varepsilon}(k,t=0)$$

Using these, (3.58) becomes

(3.61)

$$\Lambda(k,\omega) = \frac{K^{+}_{J_z J_z}(k,\omega)}{\frac{k^{2}}{i\omega}K^{+}_{J_z J_z}(k,\omega) + K_{\varepsilon\varepsilon}(k,t=0)}$$

For the limit $k \rightarrow 0$ this becomes the usual frequency dependent Kubo formula

$$\Lambda(k\to 0,\omega) = \frac{K^{+}_{J_z J_z}(k\to 0,\omega)}{K_{\mathcal{E}\mathcal{E}}(k\to 0,t=0)} \qquad (3.62)$$

This may be cast in more familiar form by evaluating $K_{\mathcal{E}\mathcal{E}}(k\to 0, t=0)$ through equilibrium thermodynamic derivatives. Letting H be the total energy of the system,

$$\begin{aligned} K_{\mathcal{E}\mathcal{E}}(k\to 0,t=0) &= \langle H\,\mathcal{E}(x=0,t=0)\rangle_0 - \langle H\rangle_0\langle\mathcal{E}\rangle_0 \\ &= \frac{1}{V}\left(\langle HH\rangle_0 - \langle H\rangle_0\langle H\rangle_0\right) \\ &= -\frac{1}{V}\left(\frac{\partial}{\partial\beta}\langle H\rangle\right)_{\alpha=-\mu\beta} \\ &= \frac{T^2 k_B C_V}{V} \qquad (3.63) \end{aligned}$$

So finally for the frequency dependent conductivity (3.64)

$$\Lambda(k\to 0,\omega) = \frac{V}{k_B T^2 C_V} K^{+}_{J_z J_z}(k\to 0,\omega)$$

and for the static limit, (3.65)

$$\Lambda_{\text{constant}} = \frac{V}{k_B T^2 C_V} \lim_{\omega\to 0}\lim_{k\to 0} K^{+}_{J_z J_z}(k,\omega)$$

(Note: returning to equation (3.58) the static thermal conductivity is also given by (3.66)

$$\frac{1}{\Lambda} = \lim_{k\to 0}\lim_{\omega\to 0} \frac{k^2 K^{+}_{\mathcal{E}\mathcal{E}}(k,\omega)}{K_{\mathcal{E}\mathcal{E}}(k,t=0)}$$

This might be a more convenient starting point for calculating the thermal conductivity of crystals, since it is known that Λ is inversely proportional to the square of anharmonic interaction strength.)

The derivation of generalized viscosity and thermal conductivity for a viscous fluid involves the same principles but is more complicated; there are now five independent variables to consider. The linear hydrodynamic model for a viscous fluid is characterized by three conservation laws and their associated constitutive equations. These are

$$\overset{\circ}{n} + \vec{\nabla}\cdot\vec{j} = \overset{\circ}{\sigma}_n \qquad (3.67)$$

$$\overset{\circ}{\vec{j}} + \vec{\nabla}\cdot\overset{\rightrightarrows}{T} = \overset{\circ}{\vec{\sigma}}_j \qquad (3.68)$$

$$\overset{\circ}{\varepsilon} + \vec{\nabla}\cdot\vec{J}_\varepsilon = \overset{\circ}{\sigma}_\varepsilon \qquad (3.69)$$

with

$$\overset{\rightrightarrows}{T} = \mathbb{1}p - \left(\vec{\nabla}\vec{j} + \vec{j}\vec{\nabla} - \frac{2}{3}\mathbb{1}\vec{\nabla}\cdot\vec{j}\right)\eta - \mathbb{1}\nabla\cdot\vec{j}\,\eta_v \qquad (3.70)$$

and

$$\vec{J}_\varepsilon = \frac{(p_0 + \varepsilon_0)}{n_0}\vec{j} - \lambda\nabla T \qquad (3.71)$$

In order to get a closed set of equations the equilibrium thermodynamic relations must also be used:

$$T - T_0 = \left(\frac{\partial T}{\partial \varepsilon}\right)_n (\varepsilon - \varepsilon_0) + \left(\frac{\partial T}{\partial n}\right)_\varepsilon (n - n_0) \qquad (3.72)$$

$$P - P_0 = \left(\frac{\partial P}{\partial \varepsilon}\right)_n (\varepsilon - \varepsilon_0) + \left(\frac{\partial P}{\partial n}\right)_\varepsilon (n - n_0) \qquad (3.73)$$

The thermodynamic derivatives are

$$A \equiv \left(\frac{\partial T}{\partial \varepsilon}\right)_n = \frac{1}{C_V}$$

$$B \equiv \left(\frac{\partial T}{\partial n}\right)_\varepsilon = -\frac{1}{n_0 C_V}\left(\varepsilon_0 + P_0 - \frac{\alpha T}{K_T}\right)$$

$$C \equiv \left(\frac{\partial P}{\partial \varepsilon}\right)_n = \frac{\alpha}{C_V K_T}$$

$$D \equiv \left(\frac{\partial P}{\partial n}\right)_\varepsilon = \frac{-\alpha}{n_0 C_V K_T}\left(\varepsilon_0 + P_0 - \frac{\alpha T}{K_T} - \frac{C_V}{\alpha}\right)$$

with

$$K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$ (isothermal compressibility)

$$C_V \equiv \left(\frac{\partial \varepsilon}{\partial T}\right)_V$$ (specific heat at constant volume per unit volume)

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$ (coefficient of thermal expansion)

The notation is

$n, \vec{j}$ for the mass and mass current densities

$\vec{j}, \overset{\rightrightarrows}{T}$ for the momentum and momentum current densities

$\varepsilon, \vec{J}_\varepsilon$ for energy and energy current densities

$\mathring{\sigma}_n, \vec{\mathring{\sigma}}_j, \mathring{\sigma}_\varepsilon$ are source terms for mass, momentum, and energy densities,

η for shear viscosity / mass density

η_v for bulk viscosity / mass density

$\xi = \eta + \eta_v$

Λ for thermal conductivity

$P_0, \mathcal{E}_0, n_0$ for equilibrium pressure, energy density, and particle density.

Equations (3.67) to (3.73) form a set of coupled linear driven differential equations in the five physical variables n, $\vec{j}$, and ϵ. The procedure will be to solve these equations for n, $\vec{j}$ and ϵ and compare the result with the linear response predicted by thermally driven MEE. Requiring the two methods to be equivalent determines the generalized transport coefficients.

Substituting (3.70) - (3.73) in (3.67) - (3.69), the five differential equations are

$$\mathring{n} + \nabla \cdot \vec{j} = \mathring{\sigma}_n \tag{3.74}$$

$$\dot{\vec{j}} + c\vec{\nabla}\epsilon + D\vec{\nabla}n - \eta\nabla^2\vec{j} - \frac{1}{3}(\eta + \eta_v)\vec{\nabla}\vec{\nabla}\cdot\vec{j} = \dot{\vec{\sigma}}_j \tag{3.75}$$

$$\mathring{\mathcal{E}} + \frac{(P_0 + \mathcal{E}_0)}{n_0}\vec{\nabla}\cdot\vec{j} - \Lambda(A\nabla^2\epsilon + B\nabla^2 n) = \mathring{\sigma}_\epsilon \tag{3.76}$$

Taking Fourier - Laplace transforms reduces these to coupled algebraic equations,

$$-i\omega n + i\vec{k}\cdot\vec{j} = \mathring{\sigma}_n \tag{3.77}$$

$$- i\omega\mathring{\vec{j}} + i\vec{k}C\epsilon + i\vec{k}Dn + \eta k^2\vec{j} + \left(\frac{1}{3}\eta + \eta_v\right)\vec{k}(\vec{k}\cdot\vec{j}) = \dot{\vec{\sigma}}_j \tag{3.78}$$

$$-i\omega\varepsilon + \frac{(P_0+\varepsilon_0)}{n_0}\, i\vec{k}\cdot j + \Lambda\left(Ak^2\varepsilon + Bk^2 n\right) = \mathring{\sigma}_\varepsilon \tag{3.79}$$

Define F and $\vec{\sigma}$ as the column vectors,

$$F \equiv \begin{pmatrix} n\,(k,\omega) \\ j_x\,(k,\omega) \\ j_y\,(k,\omega) \\ j_z\,(k,\omega) \\ \varepsilon\,(k,\omega) \end{pmatrix} \qquad \mathring{\sigma} \equiv \begin{pmatrix} \mathring{\sigma}_n\,(k,\omega) \\ \mathring{\sigma}_{j_x}\,(k,\omega) \\ \mathring{\sigma}_{j_y}\,(k,\omega) \\ \mathring{\sigma}_{j_z}\,(k,\omega) \\ \mathring{\sigma}_\varepsilon\,(k,\omega) \end{pmatrix} \tag{3.80}$$

Then equations (3.77), (3.78), and (3.79) determine a 5 x 5 matrix $\mathcal{M}$ such that

$$\mathcal{M}\cdot F = \mathring{\sigma} \tag{3.81}$$

The response of the system to thermal driving is then given by

$$\mathcal{M}^{-1}\,\mathring{\sigma} = F \tag{3.82}$$

where $\mathcal{M}^{-1}$ is seen to be the Green's function for the hydrodynamic equation. This has now the same form as the linear MEE result which is

$$K^{+}\lambda = F \tag{3.83}$$

where

$$K^{+}_{\alpha\gamma} = K^{+}_{F_\alpha F_\gamma}(k,\omega) \tag{3.84}$$

and

$$\mathring{\sigma}_\alpha(k,t) = K_{F_\alpha F_\alpha}(k,t=0)\,\lambda_\gamma(k,t) \tag{3.85}$$

The matrix $K_{F_\alpha F_\alpha}(k, t=0)$ has non-diagonal elements only at $K_{\varepsilon n}(k, t=0)$ and $K_{n\varepsilon}(k, t=0)$, since in the equilibrium ensemble for a homogeneous isotropic medium the equal time covariance functions of vector and scalar quantities are zero. We can make the matrix completely diagonal by defining a new energy variable

$$\begin{aligned} \varepsilon'(k,t) &= \varepsilon(k,t) - \frac{K_{\varepsilon n}(k,t=0)}{K_{nn}(k,t=0)}\, n(k,t) \\ &= \varepsilon(k,t) - \frac{d}{a}\, n(k,t) \end{aligned} \tag{3.86}$$

and its associated source strength

$$\overset{\circ}{\sigma}_{\varepsilon'} = \overset{\circ}{\sigma}_{\varepsilon} - \frac{d}{a}\,\overset{\circ}{\sigma}_{n} \tag{3.87}$$

It is also convenient to absorb the normalization of $\overset{\circ}{\sigma}$ given by the $K_{F_\alpha F_\alpha}(k, t=0)$ matrix, in a new $\mathcal{K}$ matrix:

$$\mathcal{K}^{+}\,\overset{\circ}{\sigma} = F$$

where

$$\mathcal{K}^{+}_{\alpha\gamma} = \frac{K^{+}_{F_\alpha F_\gamma}(k,\omega)}{K_{F_\alpha F_\gamma}(k,t=0)} \tag{3.88}$$

and the F and $\overset{\circ}{\sigma}$ matrix are now

$$F = \begin{pmatrix} n \\ j_x \\ j_y \\ j_z \\ \overset{\circ}{\varepsilon}' \end{pmatrix} \qquad \overset{\circ}{\sigma} = \begin{pmatrix} \overset{\circ}{\sigma}_n \\ \overset{\circ}{\sigma}_{j_x} \\ \overset{\circ}{\sigma}_{j_y} \\ \overset{\circ}{\sigma}_{j_z} \\ \overset{\circ}{\sigma}_{\varepsilon'} \end{pmatrix} \tag{3.89}$$

The $\mathcal{U}$ matrix is modified by the addition of the extra terms $-\frac{d}{a}\, i\vec{k}\cdot\vec{j}$ and $\Lambda A k^2 \frac{d}{a}\, n$ on the left hand side of equation (3.79), and the replacement of $\mathring{\sigma}_{\varepsilon}$ by $\mathring{\sigma}_{\varepsilon'}$ on the right. Also, equation (3.78) has an extra term $i\vec{k}c\,\frac{d}{a}\, n$ on the left.

Now we have

$$\mathcal{U}^{-1}\,\mathring{\sigma} = F$$

and

$$\mathcal{K}^{+}\,\mathring{\sigma} = F \tag{3.90}$$

Requiring these to give identical results for any choice of driving terms determines the relation between the covariance functions and the transport coefficients.

Since there are only three variables in $\mathcal{U}$ to determine, we can solve for them in terms of three $\mathcal{K}$'s.

$$\begin{aligned} \mathcal{K}^{+}_{mm} &= (\mathcal{U}^{-1})_{mm} \\ \mathcal{K}^{+}_{m\varepsilon'} &= (\mathcal{U}^{-1})_{m\varepsilon'} \\ \mathcal{K}^{+}_{j_x j_x} &= (\mathcal{U}^{-1})_{j_x j_x} \end{aligned} \tag{3.91}$$

It is convenient to introduce $\mathcal{K}^{+}_{j_z j_z}$ and $\mathcal{K}^{+}_{\varepsilon'\varepsilon'}$ as well although they can be expressed in terms of the first three.

For the particular choice $\vec{k} = \vec{I}_z\, k$, the $\mathcal{U}$ matrix is:

$$\mathcal{U} = \begin{pmatrix} -i\omega & 0 & 0 & ik & 0 \\ 0 & \begin{matrix}-i\omega \\ +\eta k^2\end{matrix} & 0 & 0 & 0 \\ 0 & 0 & \begin{matrix}-i\omega \\ +\eta k^2\end{matrix} & 0 & 0 \\ ik(D+C\frac{d}{a}) & 0 & 0 & \begin{matrix}-i\omega \\ +\xi k^2\end{matrix} & ikc \\ 0 & 0 & 0 & \left(\frac{P_0+\mathcal{E}_0}{n_0}-\frac{d}{a}\right)ik & \begin{matrix}-i\omega \\ +\Lambda Ak^2\end{matrix} \end{pmatrix} \tag{3.92}$$

So the necessary relations are

$$\mathcal{U} = (-i\omega)(-i\omega+\eta k^2)^2\left[(-i\omega+\xi k^2)(-i\omega+\Lambda A k^2) + Ck^2\left(\frac{P_0+\mathcal{E}_0}{n_0}-\frac{d}{a}\right)\right]_1 \tag{3.93}$$

$$+ k^2(-i\omega+\eta k^2)^2\left[(D+C\frac{d}{a})(-i\omega+\Lambda Ak^2)\right]_2$$

$$\mathcal{K}^+_{nn} = \frac{\text{codet } U_{nn}}{\text{Det } \mathcal{U}} = \frac{[\ \ ]_1}{\text{Det } \mathcal{U}/(-i\omega+\eta k^2)^2} \tag{3.94}$$

$$\mathcal{K}^+_{n\varepsilon'} = \frac{\text{codet } U_{\varepsilon' n}}{\text{Det } \mathcal{U}} = \frac{-Ck^2}{\text{Det } \mathcal{U} \;/\; (-i\omega+\eta k^2)^2} \tag{3.95}$$

$$\mathcal{K}^{+}_{\varepsilon'\varepsilon'} = \frac{\text{codet}\,\mathcal{U}_{\varepsilon'\varepsilon'}}{\text{Det}\,\mathcal{U}} = \frac{(-i\omega)(-i\omega+\xi k^{2})+k^{2}(D+C\frac{d}{a})}{\text{Det}\,\mathcal{U}/(-i\omega+\eta k^{2})^{2}} \tag{3.96}$$

$$\mathcal{K}^{+}_{j_z j_z} = \frac{\text{Codet}\,\mathcal{U}_{j_z j_z}}{\text{Det}\,\mathcal{U}} = \frac{(-i\omega)(-i\omega+\Lambda A k^{2})}{(\text{Det}\,\mathcal{U}/(-i\omega+\eta k^{2})^{2}} \tag{3.97}$$

$$\mathcal{K}^{+}_{j_x j_x} = \frac{\text{codet}\,\mathcal{U}_{j_x j_x}}{\text{Det}\,\mathcal{U}} = \frac{1}{-i\omega+\eta k^{2}} \tag{3.98}$$

The last equation determines shear viscosity directly in terms of the transverse velocity covariance function, as is reasonable. Expressions for bulk viscosity and thermal conductivity in terms of covariance functions are

$$(-i\omega+\xi k^{2})\,\mathcal{K}^{+}_{j_z j_z} = (-i\omega)\left(\frac{P_0+\mathcal{E}_0}{n_0} - \frac{d}{a}\right)\mathcal{K}^{+}_{n\varepsilon'} + (-i\omega)\,\mathcal{K}^{+}_{nn} \tag{3.99}$$

and

$$1 = (-i\omega)\,\mathcal{K}^{+}_{nn} - \frac{1}{c}\left[(D+C\frac{d}{a})(-i\omega+\Lambda A k^{2})\right]\mathcal{K}_{n\varepsilon'} \tag{3.100}$$

as may be verified by inspection. By conservation laws and symmetry arguments it can be shown that the parallel velocity covariance function $K_{j_z j_z}$ is essentially K_{nn}. Hence η, ξ and Λ are determined by the three covariance functions $\mathcal{K}^{+}_{nn}$; $K^{+}_{n\varepsilon'}$ and $\mathcal{K}^{+}_{j_x j_x}$.

To obtain an explicit expression for Λ it is more convenient to introduce $\mathcal{K}_{\varepsilon'\varepsilon'}$ and find (3.101)

$$(-i\omega + \Lambda k^2)\,\mathcal{K}^{+}_{\varepsilon'\varepsilon'} = (-i\omega)\left(\frac{P_0+\mathcal{E}_0}{n_0} - \frac{d}{a}\right)\mathcal{K}_{n\varepsilon'} + 1$$

so that equations (3.98), (3.99) and (3.100) have essentially the same form in the long wavelength limit:

$$\lim_{k\to 0} K_{n\varepsilon'}(k,t)\,,\ K_{nn}(k,t) \longrightarrow \text{constants}$$

$$\therefore \lim_{k\to 0} K^{+}_{n\varepsilon'}(k,\omega)\,,\ K^{+}_{nn}(k,\omega) \longrightarrow \frac{\text{constants}}{-i\omega}$$

It is customary to give expressions for the generalized (frequency dependent) transport coefficients in the long wavelength limit. The passage to this limit is facilitated by the identities

$$\mathcal{K}^{+}_{n\varepsilon'}(k,\omega) = \frac{k^2}{\omega^2 b}\,K^{+}_{j_z J_{\varepsilon'_z}}(k,\omega) \tag{3.102}$$

$$\mathcal{K}^{+}_{nn}(k,\omega) = \frac{k^2}{\omega^2 a}\,K^{+}_{j_z j_z}(k,\omega) + \frac{i}{\omega} \tag{3.103}$$

$$\mathcal{K}^{+}_{j_x j_x}(k,\omega) = \frac{k^2}{\omega^2 c}\,K^{+}_{T_{zx} T_{xz}}(k,\omega) + \frac{i}{\omega} \tag{3.104}$$

$$\mathcal{K}^{+}_{j_z j_z}(k,\omega) = \frac{k^2}{\omega^2 c}\,K^{+}_{T_{zz} T_{zz}}(k,\omega) + \frac{i}{\omega} \tag{3.105}$$

and

$$\mathcal{K}^{+}_{\varepsilon'\varepsilon'}(k,\omega) = \frac{k^{2}}{\omega^{2} b} K^{+}_{J_{\varepsilon'_z} J_{\varepsilon'_z}}(k,\omega) + \frac{i}{\omega} \tag{3.106}$$

which follow from the conservation laws. The $\vec{k}$ vector is taken in the $\vec{1}_z$ direction. The small a, b, c, d are the normalizing coefficients introduced earlier; they are time independent and in the k→0 limit may be evaluated thermodynamically:

$$a \equiv K_{nn}(k, t=0) = \frac{n_0^{2} K_T}{\beta} \tag{3.107}$$

$$b \equiv K_{\varepsilon'\varepsilon'}(k, t=0) \underset{k\to 0}{=} \frac{T C_v}{\beta}$$

$$c \equiv K_{j_x j_x}(k, t=0) \underset{k\to 0}{=} \frac{n_0}{\beta}$$

$$d \equiv K_{n\varepsilon}(k, t=0) \underset{k\to 0}{=} \frac{n_0}{\beta} K_T\left(\varepsilon_0 + P_0 - \frac{\alpha T}{K_T}\right)$$

With these identities (3.100), (3.101), and (3.103) yield the exact expressions

$$\eta = \frac{\frac{1}{c} K^{+}_{T_{zx} T_{xz}}(k,\omega)}{1 - i\frac{k^{2}}{\omega c} K^{+}_{T_{zx} T_{xz}}(k,\omega)} \tag{3.108}$$

$$\xi = \frac{\frac{1}{c} K^{+}_{T_{zz} T_{zz}} - \frac{1}{b}\left(\frac{P_0 + \varepsilon_0}{n_0} - \frac{d}{a}\right) K^{+}_{j_z J_{\varepsilon'_z}} - \frac{1}{a} K_{j_z J_{\varepsilon'_z}}}{1 - \frac{i k^{2}}{\omega c} K^{+}_{T_{zz} T_{zz}}(k,\omega)} \tag{3.109}$$

and

$$\Lambda = \frac{\frac{1}{b} K^{+}_{J_{\varepsilon'_z} J_{\varepsilon'_z}} - \frac{1}{b}\left(\frac{P_0 + \varepsilon_0}{n_0} - \frac{d}{a}\right) K^{+}_{j_z J_{\varepsilon'_z}}}{1 - \frac{ik^2}{\omega b} K^{+}_{J_{\varepsilon'_z} J_{\varepsilon'_z}}} \qquad (3.110)$$

In the long wavelength limit these become

$$\eta^{+}(k \rightarrow 0, \omega) = \frac{1}{c} K^{+}_{T_{zx} T_{xz}} (k \longrightarrow 0, \omega) \qquad (3.111)$$

$$\xi^{+}(k \longrightarrow 0, \omega) = \frac{1}{c} K^{+}_{T_{zz} T_{zz}} (k \longrightarrow 0, \omega) - \frac{\alpha^2}{n_0 C_V K_T} K^{+}_{j_z J_{\varepsilon'_z}}{}^{(k \rightarrow 0, \omega)}$$

$$- \frac{\beta}{n_0^2 K_T} K^{+}_{j_z j_z} (k \longrightarrow 0, \omega) \qquad (3.112)$$

and

$$\Lambda^{+}(k \rightarrow 0, \omega) = \frac{\alpha}{T c_V} K^{+}_{J_{\varepsilon'_z} J_{\varepsilon'_z}} (k \rightarrow 0, \omega) - \frac{\alpha^2}{n_0 C_V K_T} K^{+}_{j_z J_{\varepsilon'_z}}{}^{(k \rightarrow 0, \omega)} \qquad (3.113)$$

The notation has been changed to $\eta^{+}(k,\omega)$, $\xi^{+}(k,\omega)$ and $\Lambda^{+}(k,\omega)$ since we have actually been calculating the imaginary Laplace transform of these generalized transport coefficients. The constant transport coefficients of hydrodynamics are

$$\eta \text{ constant} = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \eta^{+}(k,\omega)$$

$$\xi \text{ constant} = \lim_{\omega \rightarrow 0} \lim_{k \rightarrow 0} \xi^{+}(k,\omega)$$

and

$$\Lambda_{\text{constant}} = \lim_{\omega \to 0} \lim_{k \to 0} \Lambda^{+}(k,\omega)$$

These transport coefficients have been calculated by half a dozen other methods.[9] The method closest to ours is the pseudo Hamiltonian method discussed earlier. Actually the hydrodynamic coefficients may all be calculated by solving the hydrodynamic equations for various physically meaningful Hamiltonians.[10] The novelty of our particular derivation is its generality; the relations are obtained by comparing response matrices rather than by solving particular cases.

The fundamental difference between the MEE approach and the six categorized by Zwanzig does not appear in the calculation of hydrodynamic coefficients. The advantage of the MEE formalism is that its validity is independent of the existence of hydrodynamics. In particular note that in order to put the hydrodynamic equations in closed form it was necessary to assume local equilibrium. This assumption is not necessary in the MEE approach.

CHAPTER IV

ENTROPY

1. Time Dependent Information Entropy

The information theory approach to statistical mechanics is based on the fact that there is a unique measure of the information contained in an ensemble. By minimizing this information measure (maximizing the information entropy) subject to macroscopic constraints one selects the least biased ensemble consistent with the constraints. The question naturally arises as to the connection between information entropy and experimental entropy.

For equilibrium ensembles the information entropy is the same as the Gibbs entropy.

For non-equilibrium ensembles it does not correspond with our ideas of entropy. In particular, it is possible to change the temperature of a system by driving it with an external potential - but since the density matrix at time t is a unitary transformation of the density matrix at t=0 the information entropy is constant. Although inconsistent with experimental entropy this is certainly the proper behavior for an information measure; no new information on the ensemble is given, only the time development for any given ensemble. Alternatively, one could construct an initial non-equilibrium ensemble at t=0 and let it decay. For all practical purposes it eventually decays to equilibrium - yet here too the information entropy is constant, befitting an information measure, but not an experimental entropy. From these considerations one is led to the conclusion that experimental entropy is related not to the total information but to the "relevant" part of that information.[11] Although information is not lost, it is "degraded". We will return to this point later, offering a definition of experimental entropy along these lines; but first we shall see that the information entropy for a thermally driven system has itself a physical interpretation.

Let us examine the time development of information entropy for thermally driven systems. The definition of information entropy is

$$S_{I_t} \equiv -\mathrm{Tr}\left[\rho_t \ln \rho_t\right] \tag{4.1}$$

For simplicity consider the ensemble

$$\rho_t = e^{-\beta H + \int_0^t \lambda(t') F(t')\, dt'} \tag{4.2}$$

with

$$\overset{\circ}{\sigma}_F(t) = K^{t}_{F_t F_t}\, \lambda(t) \tag{4.3}$$

Then

$$S_{I_t} = \beta \langle H \rangle_t - \int_0^t \lambda(t') \langle F(t') \rangle_t\, dt' + \ln Z_t \tag{4.4}$$

The time rate of change of information entropy is

$$\overset{\circ}{S}_{I_t} = \beta\, \lambda(t)\, K^{t}_{H F_t} - \lambda(t) \int_0^t \lambda(t')\, K^{t}_{F(t') F(t)} \tag{4.5}$$

This is an exact relation obtained by straightforward differentiation. $-\overset{\circ}{S}_{I_t}$ is interpreted as the rate of increase in information content of the ensemble. Notice that if the driving source is turned off at τ, then $\overset{\circ}{S}_{I_t} = 0$, $t > \tau$; since the system will in general continue to decay, this shows that the time dependence introduced by thermal driving is unrelated to the internal relaxation of the system.

Now expand $\dot{S}_{I_t}$ to second order in the normalized source terms $\lambda(t)$:

$$\int_0^t \lambda(t')\, K^{t}_{F(t)F(t)}\, dt' \doteq \langle F(t) \rangle_t \tag{4.6}$$

$$K^{t}_{H\,F(t)} = K^{t}_{F(t)H} = -\frac{\partial}{\partial \beta} \langle F(t) \rangle_t \tag{4.7}$$

so

$$\mathring{S}_{I_t} \overset{2}{=} \beta\, \lambda(t)\, \mathring{K}_{HF} - \lambda(t)\left(1 + \beta \frac{\partial}{\partial \beta}\right) \int_0^t \lambda(t')\, K^{\circ}_{FF}(t-t') \tag{4.8}$$

where we assumed $\langle F(t) \rangle_0 = 0$

To interpret the term linear in the source strength, note that the first order change in total energy is

$$\begin{aligned} \Delta \langle H \rangle_t = \langle H \rangle_t - \langle H \rangle_0 &\doteq \int_0^t \mathring{K}_{H\,F(t')}\, \lambda(t')\, dt' \\ &= \mathring{K}_{HF} \int_0^t \lambda(t')\, dt' \end{aligned} \tag{4.9}$$

so

$$\frac{d}{dt} \Delta \langle H \rangle_t \doteq K_{HF}\, \lambda(t) \tag{4.10}$$

Thus the first order change in entropy comes from energy carried in directly by the driven variable;

$$\mathring{S}_{I_t} \overset{1}{=} \beta \frac{d}{dt} \langle H \rangle_t \tag{4.11}$$

(In the extreme $F(t) = H$, the exact relation is

$\dot{S}_{I_t} = \beta(t) \frac{d}{dt} \langle H \rangle t$, where $\beta(t) = \beta - \int_0^t \lambda(t')\, dt'.)$

Hence the first order term can be interpreted as the usual $\frac{dQ}{T}$

entropy of quasi-static thermodynamics.

We could remove this first term by considering driving processes which do not couple to the total energy, i.e. by defining F so $K^{t}_{H F_t} = 0$.

Then

$$\dot{S}_{I_t} = -\lambda(t)\int_0^t \lambda(t')\, K^{t}_{F(t')F(t)} \tag{4.12}$$

and the entropy change is of second order in the normalized source strength, $\lambda(t)$. We want to put this in a form similar to (4.11). In order to do this it is necessary to introduce generalized equilibrium parameters corresponding to β .

2. Equilibrium Criteria

Consider a system characterized by physical variables A and B in the usual sense. The MEE ensemble is

$$\rho = \frac{e^{\alpha A + \beta B}}{Z} \tag{4.13}$$

Suppose now this system (1) is allowed to exchange some physical quantity G with a reservoir (2). What is the condition that there be no net transfer of G even though such transfer is dynamically possible?

The problem is not well formulated. From a microscopic point of view the statement "G is exchanged" provides far too little information. As before, in lieu of explicit detailed information on the nature of the transfer mechanism, we shall assume the transfer of G to occur by a "thermally driven" process. Viewed macroscopically this is a very weak condition; any constraints imposed by the real physical mechanism can be included in our definition of thermally driven.

If we assume the transfer of G to be thermally driven then we can associate an ensemble with every possible distribution of G between the two systems. Thus the problem reduces to finding a criterion for picking the "best" of the possible ensembles. But this is precisely the problem handled by information theory - the best ensemble (in the sense of being free of arbitrary assumptions) is that which maximizes the information entropy. These arguments lead to

$$\delta S_{1,2}\Big|_{\substack{\text{thermal transfer}\\ \text{of G}}} = 0 \tag{4.14}$$

as the condition for equilibrium between (1) and (2) under allowed thermal transfer of G. Since the entropy of the composite system is the sum of its parts, and since the total value of G is assumed conserved during the transfer, this becomes

$$0 = \delta S_1 + \delta S_2 \tag{4.15}$$

$$= \left(\frac{\partial S_1}{\partial \langle G\rangle_1}\right)_{\substack{\text{Thermal}\\ \text{Transfer}}} (\Delta G) + \left(\frac{\partial S_2}{\partial \langle G\rangle_2}\right)_{\substack{\text{Thermal}\\ \text{Transfer}}} (-\Delta G)$$

or

$$\left(\frac{\partial S_1}{\partial \langle G\rangle_1}\right)_{\substack{\text{Thermally}\\ \text{Driven}}} = \left(\frac{\partial S_2}{\partial \langle G_2\rangle}\right)_{\substack{\text{Thermally}\\ \text{Driven}}}$$

It should be mentioned here that this "best" result is usually overwhelmingly the most probable. For if we expand the entropy about the equilibrium value of G to second order, then

$$\Delta S = \delta S_1 + \delta S_2$$

$$\cong \left(\frac{\partial^2 S_1}{\partial \langle G_1\rangle^2}\right)\frac{(\Delta G)^2}{2} + \left(\frac{\partial^2 S_2}{\partial \langle G_2\rangle^2}\right)\frac{(\Delta G)^2}{2}$$

$$= -\frac{(\Delta G)^2}{2K_{G_1G_1}} - \frac{(\Delta G)^2}{2K_{G_2G_2}} \tag{4.16}$$

Interpreting $W(\Delta G) = \frac{e^{S(G)}}{e^{S(G_0)}}$

as proportional to the probability of observing a fluctuation in G of magnitude ΔG, we find this probability to be proportional to

$$e^{-\frac{(\Delta G)^2}{2}\left(\frac{1}{K_{G_1G_1}} + \frac{1}{K_{G_2G_2}}\right)}$$

Hence it is extremely unlikely to find the system farther from equilibrium than

$$\sim 4\sqrt{K_{G_1G_1} + K_{G_2G_2}}$$

For the particular case of the Gibbs canonical or the grand canonical ensemble (4.15) reduces to the usual equilibrium conditions simply by using the appropriate constraints; i.e., energy transfered at constant particle number leads to temperature as the equilibrium parameter.

Now consider the case where A is constrained but the change in B is determined by the thermal transfer process. The equilibrium parameter for G transfer is

$$\gamma_G = \left(\frac{\partial S}{\partial\langle G\rangle}\right)_{A,\beta} = \beta\left(\frac{\partial\langle B\rangle}{\partial\langle G\rangle}\right)_{A,\beta} \tag{4.17}$$

This derivative may easily be expressed in terms of covariance functions by introducing

$$G' \equiv G - \frac{K_{AG}}{K_{AA}} A \tag{4.18}$$

and formally rewriting the initial ensemble

$$\rho = \frac{e^{\alpha A + \beta B}}{Z} = \frac{e^{\alpha' A + \beta B + \lambda_{G'} G'}}{Z} \tag{4.19}$$

where

$$\alpha' = \alpha + \frac{K_{AG}}{K_{AA}} \lambda_{G'}$$

and

$$\lambda_{G'} = 0$$

Then

$$\gamma_G = \left(\frac{\partial S}{\partial \langle G \rangle}\right)_{A,\beta} = -\beta \left(\frac{\partial \langle B \rangle}{\partial \langle G' \rangle}\right)_{A,\beta} \tag{4.20}$$

and since the condition A constant is equivalent to α constant,

$$\begin{aligned} \gamma_G &= -\beta \left(\frac{\partial \langle B \rangle}{\partial \langle G' \rangle}\right)_{\alpha,\beta} \\ &= -\beta \left(\frac{\partial \langle B \rangle}{\partial \lambda_{G'}}\right)_{\alpha,\beta} \left(\frac{\partial \lambda_{G'}}{\partial \langle G \rangle}\right)_{\alpha\beta} \\ &= -\beta \frac{K_{BG'}}{K_{G'G'}} \quad . \end{aligned} \tag{4.21}$$

This can be immediately extended to the ensemble

$$\rho_t = \frac{e}{Z}^{\alpha A + \int_0^t \lambda_{F_i}(t') F_i(t')}, \quad i = 1 \cdots n, \tag{4.22}$$

with the result

$$\gamma_{G'}(t) = -\int_0^t dt' \frac{K^t_{F_i(t')G'(t)}}{K^t_{G'(t)G'(t)}} \lambda_{F_i}(t') \tag{4.23}$$

The meaning of the equilibrium parameter $\gamma_{G'}(t)$ is that if a system can exchange the physical variable $G(t)$ with a second system at time t (under constraint A constant) then

$$\gamma_{G'}(t)_1 = \gamma_{G'}(t)_2 \tag{4.24}$$

is the condition that no such net transfer will occur.

These equilibrium parameters will be used to interpret entropy production. Note first another characteristic of thermal exchange equilibrium. The condition for net transfer to occur by a thermally driven mechanism is

$$\delta S_{1,2} \Big|_{\substack{\text{Thermal} \\ \text{Transfer of F}}} > 0 \tag{4.25}$$

or

$$\delta S_2 > -\delta S_1 \tag{4.26}$$

This allows the interpretation of $-\dot{S}_{I_t}$ as the minimum rate of entropy increase necessary in the driving reservoir.

Now let us return to the entropy production equation. In exact form it was

$$\overset{\circ}{S}_t = \lambda(t)\beta K^t_{HF(t)} - \lambda(t)\int_0^t \lambda(t')K^t_{F(t')F(t)} \tag{4.27}$$

But

$$\gamma_{F(t)} = \beta \frac{K^t_{HF(t)}}{K^t_{F(t)F(t)}} - \frac{\int_0^t \lambda(t')K^t_{F(t')F(t)}\,dt'}{K^t_{F(t)F(t)}} \tag{4.28}$$

so

$$\overset{\circ}{S}_t = \lambda(t)\,\gamma_{F(t)}\,K^t_{F(t)F(t)} \tag{4.29}$$

$$= \gamma_{F(t)}\,\overset{\circ}{\sigma}_F(t) \quad ,$$

where $\overset{\circ}{\sigma}_F(t)$ is the source strength for F,

$$\overset{\circ}{\sigma}_{F(t)} = \frac{d}{dt}\langle F(t)\rangle_t - \langle \overset{\circ}{F}(t)\rangle_t \ . \tag{4.30}$$

This has the same form as the first order term

$$\overset{\circ}{S}_t \doteq \beta \frac{d}{dt}\langle H\rangle_t \quad , \tag{4.31}$$

or in the case where H is driven, to the exact form

$$\overset{\circ}{S}_t = \beta(t)\frac{d}{dt}\langle H\rangle_t \quad . \tag{4.32}$$

Hence the equilibrium parameters β and γ_F play corresponding roles with respect to the entropy increase on transfer of H and F. The rate of change of entropy for thermally driven systems is always a product of two terms like this: a source term, measuring the rate of transfer, and an equilibrium parameter regarded as measuring the "potential" at which the transfer occurs.

We conclude that the changes in the information entropy produced by thermally driven processes correspond to generalized $\frac{dQ}{T}$ entropy changes; although information entropy can not in general be identified with the internal experimental entropy, the changes in information entropy can be identified as the experimental entropy of transfer.

3. Internal Entropy Production

In equilibrium thermodynamics, knowledge of the entropy as a function of the physical variables gives us a complete description of the system.

In non-equilibrium statistical mechanics it is the information entropy which has this property. By construction, the information entropy density matrix contains all our knowledge of the physical constraints imposed on the system. If these constraints are sufficient to determine reproducible behavior, then the information entropy density matrix should predict this behavior. Hence in this sense information entropy contains a complete description of the system, and is therefore the logical extension of the Gibbs equilibrium entropy.

We have shown that this relation is even closer: in the thermally driven transfer of F to the system the change in information entropy is given by a generalized $\frac{dQ}{T}$ expression.

On the other hand, internal relaxation is not measured by information entropy. If a system is prepared in a non-equilibrium state, we know that in the absence of further external interaction the non-equilibrium values of physical variables soon relax to equilibrium. The information entropy density matrix should correctly predict this relaxation. But since it is constant, the information entropy itself is obviously not a measure of the extent of relaxation.

It seems desirable to introduce an index of relaxation. This can be done in several ways, depending on what is considered to be the relevant information. In view of their essentially arbitrary nature it is perhaps unfortunate that all these relaxation indices tend to be called entropy.

The commonest procedure[12] is to set up a new density matrix at each instant containing the instantaneous values of some specified set of physical observables. Hence if $[F_i(x,t)]$, $1 \leq i \leq n$ are given (determined, for instance, through the information entropy density matrix ρ_t) then

$$\rho = \frac{e^{-\beta H + \alpha_i(t) F_i(t)}}{Z} \qquad (4.33)$$

with

$$Tr\left(F_i(t)\rho\right) = [F_i(t)], \quad 1 \leq i \leq n$$

The resultant instantaneous "entropy" is

$$\mathcal{S} = -Tr(\rho \ln \rho) \qquad (4.34)$$

For the particular choice of variables

$$\rho = \frac{e^{-\int dx\, \beta(x,t)\left(H(x,t) - \vec{V}(x,t)\cdot\vec{j}(x,t) - \mu(x,t)n(x,t)\right)}}{Z} \qquad (4.35)$$

this is the familiar "local equilibrium" density matrix.

Note that the time development of (4.34) is obtained by specifying the change in the instantaneous values $[F_i(t)]$. In turn, these are determined by the complete density matrix rather than by (4.33). The rate of change of entropy is thus

$$\mathring{\mathcal{S}} = \beta \frac{d\langle H\rangle}{dt} - \alpha_i(t)\frac{d}{dt}\langle F_i(t)\rangle \tag{4.36}$$

where $\frac{d\langle H\rangle}{dt}$ and $\frac{d}{dt}\langle F_i(t)\rangle$ are presumed known, and β and $\alpha_i(t)$ are determined by [H] and [$F_i(t)$] through equations (4.33).

There is no question that this entropy is a useful relaxation index. However, it should be noted that only in first order can β and $\alpha_i(t)$ themselves be interpreted physically. In this limit, they turn out to be equilibrium parameters such as those appearing in the external entropy transfer equation, (4.29). It seems reasonable, therefore, to look for an "entropy" production with the same form as (4.36), but with the "exact" equilibrium parameters (i.e., with the equilibrium parameters determined by the information theory entropy). Such an entropy is presented below.

In equation (4.29) we found the rate of addition of entropy by external means to be given by

$$\mathring{S}_t = \lambda_{F(t)}\,\gamma_{F(t)}\,K^{t}_{F(t)F(t)} \tag{4.37}$$

$$= \gamma_{F(t)}\,\mathring{\sigma}_{F(t)} \tag{4.38}$$

where $\gamma_{F(t)}$ is the equilibrium parameter,

$$\gamma_{F(t)} \equiv \left(\frac{\partial S_I}{\partial\langle F(t)\rangle}\right)_{\substack{\text{Thermally}\\ \text{Driven}}} \tag{4.39}$$

and $\mathring{\sigma}_{F(t)}$ is the source strength,

$$\overset{\circ}{\sigma}_{F(t)} \equiv \frac{d}{dt}\langle F(t)\rangle - \langle \overset{\circ}{F}(t)\rangle \tag{4.40}$$

Within the framework of our method these expressions are exact.

Since the external entropy source is the product of an intensive "potential" and an extensive flow, and since the extensive variable separates naturally in two parts, it is tempting to interpret these parts separately. Thus

$$\overset{\circ}{\mathcal{S}}{}^{n}_{t} \equiv \gamma_{F(t)} \frac{d}{dt}\langle F(t)\rangle \tag{4.41}$$

is the "net" rate of entropy change, and

$$\overset{\circ}{\mathcal{S}}{}^{i}_{t} \equiv \gamma_{F(t)} \langle \overset{\circ}{F}(t)\rangle \tag{4.42}$$

is the rate of "internal" entropy change. By (4.37) we have

$$\overset{\circ}{\mathcal{S}}{}^{n}_{t} = \overset{\circ}{S}_{t} + \overset{\circ}{\mathcal{S}}{}^{i}_{t} \tag{4.43}$$

Now consider the system to be driven by two physical variables, F and G. In this case (4.37) becomes

$$\overset{\circ}{S}_{t} = \gamma_{F(t)} K^{t}_{F(t)F(t)} \lambda_{F(t)} + \gamma_{G(t)} K_{G(t)G(t)} \lambda_{G(t)} \tag{4.44}$$

To put this in the form of (4.38) we must solve

$$\overset{\circ}{\sigma}_{F(t)} = \lambda_{F(t)} K^{t}_{F(t)F(t)} + \lambda_{G(t)} K^{t}_{F(t)G(t)} \tag{4.45}$$

and

$$\mathring{\sigma}_{G(t)} = \lambda_{F(t)} K^{t}_{G(t)F(t)} + \lambda_{G(t)} K^{t}_{G(t)G(t)}$$

for λ_F and λ_G. Thus the analogue of (4.38) is not

$$\mathring{S}_t = \gamma_{Ft}\, \mathring{\sigma}_{Ft} + \gamma_{Gt}\, \mathring{\sigma}_{Gt} \tag{4.46}$$

but

$$\mathring{S}_t = a(t)\, \mathring{\sigma}_{F(t)} + b(t)\, \mathring{\sigma}_{G(t)} \tag{4.47}$$

where

$$a(t) = \frac{K^{t}_{G(t)G(t)} K^{t}_{F(t)F(t)} \gamma_{F(t)} - K^{t}_{G(t)F(t)} K^{t}_{G(t)G(t)} \gamma_{Gt}}{K_{GG} K_{FF} - K_{FG} K_{GF}}$$

and (4.48)

$$b(t) = \frac{K_{FF} K_{GG} \gamma_G - K_{FG} K_{FF} \gamma_F}{K_{GG} K_{FF} - K_{FG} K_{GF}}$$

Only if $K^{t}_{G(t)} F(t) = 0$ are these expressions the same.

By resolving the source terms $\mathring{\sigma}_{F(t)}$ and $\mathring{\sigma}_{G(t)}$ into their components, we find the extension of (4.41) and (4.42) to two variables is found:

$$\dot{s}^{n}_{t} = a(t) \frac{d}{dt} \langle F(t) \rangle + b(t) \frac{d}{dt} \langle G(t) \rangle \tag{4.49}$$

$$\dot{s}^{i}_{t} = a(t) \langle \mathring{F}(t) \rangle + b(t) \langle \mathring{G}(t) \rangle \tag{4.50}$$

Now let us suppose that the transfer of G is not given explicitly after all. The condition for this is $\lambda_{G(t)} = 0$. By (4.45) this implies

$$\overset{\circ}{\sigma}_{F(t)} = \lambda_{F(t)} K^{t}_{F(t)F(t)} \tag{4.51}$$

and

$$\overset{\circ}{\sigma}_{G(t)} = \lambda_{F(t)} K^{t}_{G(t)F(t)} \quad , \tag{4.52}$$

so that the external entropy production reduces, as it should, to the original value for F alone. But the $\lambda_{G(t)} = 0$ condition affects only $\overset{\circ}{\sigma}_{F(t)}$ and $\overset{\circ}{\sigma}_{G(t)}$, not their components; therefore (4.49) and (4.50) do not reduce to (4.41) and (4.42).

On reflection, this is a desirable result. It says that the internal entropy production is a function of the set of variables used to describe the system, whether or not the system is driven by them. But that the internal entropy should be a measure of "relevant" information was anticipated. We are now simply defining this "relevant" information as the information necessary to determine the instantaneous equilibrium parameters and relaxation rates of the set of physical variables under consideration.

In order to extend the definition of internal entropy production to n variables, it is convenient to use a vector notation.

Define:

$$\begin{aligned} (\vec{\Gamma})_{F_i} &\equiv \frac{\delta S_I}{\delta \langle F_i \rangle} K_{F_i F_i} = \gamma_{F_i} K_{F_i F_i} \, , \\ (\vec{\lambda})_{F_i} &= \lambda_{F_i} \, , \\ (\vec{\overset{\circ}{\sigma}})_{F_i} &= \overset{\circ}{\sigma}_{F_i} \, , \end{aligned} \tag{4.53}$$

and

$$\left(\vec{\vec{K}}\right)_{F_i F_j} = K_{F_i F_j}$$

Then the external entropy production is

$$\overset{\circ}{S}_I = \vec{\vec{\Gamma}}^{+} \cdot \vec{\lambda} \tag{4.54}$$

where $\vec{\vec{\Gamma}}^{+}$ denotes the adjoint of $\vec{\vec{\Gamma}}$. $\vec{\lambda}$ is determined by

$$\dot{\vec{\sigma}} = \vec{\vec{K}} \cdot \lambda \quad , \tag{4.55}$$

so in terms of the source strengths,

$$\overset{\circ}{S}_I = \vec{\vec{\Gamma}}^{+} \cdot \vec{\vec{K}}^{-1} \cdot \dot{\vec{\sigma}} \tag{4.56}$$

Hence the internal entropy production is

$$\overset{\circ}{\mathcal{S}}^{i} = \vec{\vec{\Gamma}}^{+} \cdot \vec{\vec{K}}^{-1} \cdot \langle \dot{\vec{F}} \rangle \tag{4.57}$$

It can be proved that this internal entropy production is a function only of the space spanned by the physical variables F, and not of the particular linear combination.

Proof: let $\vec{F}'$ be an arbitrary linear combination of the F's spanning the same space; $\vec{F}' = \vec{\vec{A}} \cdot \vec{F}$. Then the new internal relaxation rates will be $\langle \dot{\vec{F}}' \rangle = \vec{\vec{A}} \cdot \vec{F}$. The transformation law for $\vec{\vec{K}}$ following from the definition

$$\left(\vec{\vec{K}}\right)_{F_i F_j} = K_{F_i F_j} = \langle \overline{F_i}\; F_j \rangle - \langle F_i \rangle \langle F_j \rangle \tag{4.58}$$

is

$$\overset{\rightrightarrows}{K}{}' = \overset{\rightrightarrows}{A}\cdot\overset{\rightrightarrows}{K}\cdot\overset{\rightrightarrows}{A}{}^{+}, \quad \overset{\rightrightarrows}{K}{}'^{-1} = \overset{\rightrightarrows}{A}{}^{+}_{-1}\,\overset{\rightrightarrows}{K}{}^{-1}\,\overset{\rightrightarrows}{A}{}^{-1} \tag{4.59}$$

The transformation law for Γ is slightly more difficult to obtain.

By definition,

$$\left(\vec{\Gamma}\right)_{F_i} = K_{F_iF_i}\left(\frac{\partial S_I}{\partial\langle F_i\rangle}\right)_{\substack{\text{Thermally}\\ \text{Driven}}} \tag{4.60}$$

To evaluate this derivative generally, note first that any density matrix under consideration may be written in the form

$$\rho = \frac{e^{X}}{Z} \tag{4.61}$$

The derivative indicated is taken by writing this as

$$\rho(\alpha) = \frac{e^{X+\alpha F}}{Z(\alpha)} \tag{4.62}$$

with entropy

$$S_{\rho(\alpha)} = -\langle X\rangle_{\rho(\alpha)}\ \alpha\langle F\rangle_{\rho(\alpha)} + \ln Z(\alpha) \tag{4.63}$$

Differentiating with respect to α, then setting $\alpha = 0$, we find

$$\left(\frac{\partial S_I}{\partial\langle F_i\rangle}\right)_{\substack{\text{Thermally}\\ \text{Driven}}} = \frac{K_{XF}}{K_{FF}} \tag{4.64}$$

and

$$\left(\vec{\Gamma}\right)_{F_i} = K_{X F_i} \tag{4.65}$$

Since K_{XF_i} is linear in F_i we then have the general relation

$$\vec{\Gamma}' = \vec{\vec{A}} \cdot \vec{\Gamma} \tag{4.66}$$

Putting the three transformations together proves the theorem:

$$\dot{s}^{i'} = \vec{\Gamma}' \cdot \vec{\vec{K}}'^{-1} \cdot \langle \dot{\vec{F}}' \rangle \tag{4.67}$$

$$= \vec{\Gamma} \cdot \vec{\vec{K}} \cdot \langle \dot{\vec{F}} \rangle = \dot{s}^{i}$$

This result allows us to express the internal entropy production in any convenient basis. In particular, an orthogonal basis yields the simple expressions

$$\dot{S}_t = \gamma_{F_i'}(t)\,\dot{\sigma}_{F_i'}(t) \tag{4.68}$$

$$\dot{s}^{i}_t = \gamma_{F_i'}(t)\,\frac{d}{dt}\langle \mathring{F}_{i'}(t) \rangle \tag{4.69}$$

and

$$\mathring{s}^{i}_t = \gamma_{F_i'}(t)\,\langle \mathring{F}_i'(t) \rangle \tag{4.70}$$

Equation (4.69) should be compared to the "local entropy" production, (4.36). Only in first order are $\alpha_i(t)$ and $\gamma_{F_i}(t)$ the same. Yet for most practical purposes this first order equivalence is sufficient to make the distinction a matter of aesthetics rather than physics. On aesthetic grounds it seems better to express internal entropy production in terms of variables with a definite physical interpretation, as in (4.69).

The treatment of spatial dependence introduces further complications. For a single driven variable (4.37) becomes

$$\mathring{S}_t = \int dx \; \gamma_{F(x,t)} K^{t}_{F(x,t)F(x,t)} \lambda_{F(x,t)} \tag{4.71}$$

where

$$\gamma_{F(x,t)} = \left(\frac{\delta S}{\delta \langle F(x,t) \rangle} \right)_{\substack{\text{Thermally} \\ \text{Driven}}} \tag{4.72}$$

and

$$\mathring{\sigma}_{F(x,t)} = \int dx' \, K^{t}_{F(x,t)F(x',t)} \, \lambda_{F(x',t)} \tag{4.73}$$

Defining the integral operator K^{t-1} by

$$\lambda_{F(x,t)} = \int dx' \, K^{t-1}_{F(x,t)F(x',t)} \, \sigma_{F(x',t)} , \tag{4.74}$$

one finds the formal relation

$$\mathring{S}_t = \int dx \int dx' \; \Gamma_{F(x,t)} K^{t-1}_{F(x,t)F(x',t)} \, \mathring{\sigma}_F (x',t) \tag{4.75}$$

Expanding $\mathring{\sigma}$ then leads to

$$\mathring{\mathcal{S}}^{i}_{t} = \int dx \int dx' \, \Gamma_{F(x,t)} K^{t-1}_{F(x,t)F(x',t)} \langle \dot{F}(x',t) \rangle \tag{4.76}$$

for the internal entropy production.

The general form for n variables is correspondingly

$$\mathring{\mathcal{S}}^{i}_{t} = \int dx \int dx' \; \vec{\Gamma}^{+}_{(x,t)} \cdot \overset{\Rightarrow}{K}{}^{t-1}_{(x,t;x',t)} \cdot \langle \dot{\vec{F}}(x',t) \rangle \tag{4.77}$$

where $\overrightarrow{\overrightarrow{K}}^{-1}$ is the inverse operator defined by

$$\vec{\lambda}(x,t) = \int dx' \, \overrightarrow{\overrightarrow{K}}^{t^{-1}}(x,t;x',t) \cdot \vec{\overset{\circ}{\sigma}}(x,t) \tag{4.78}$$

The spatially dependent form is much simplified in the approximation that the spatial variation of the relaxation rate is small compared to the width of the equal time covariance function.

It is convenient in this limit to introduce the integrated variables

$$F_{\Omega}(\vec{x},t) \equiv \int_{\Omega} d\vec{x}' \, F_i(\vec{x}-\vec{x}\,';t) \quad , \tag{4.79}$$

where the region Ω is assumed to be large relative to the width of the equal time covariance function, but small on the scale of the spatial variation of the relaxation rate. The equilibrium parameter for this variable is

$$\gamma_{F_{\Omega}}(x,t) = \left(\frac{\partial S_I}{\partial F_{\Omega}(x,t)} \right)_{\substack{\text{Thermally} \\ \text{Driven}}} \tag{4.80}$$

Within the range of Ω , the value of $\gamma_{F_{\Omega}}(x,t)$ is independent of Ω .

In this approximation the internal entropy production density for n local variables is

$$\overset{\circ}{\Delta}{}^{i}_{t}(x) \simeq \gamma_{F_{j\Omega}}(x,t) \langle \overset{\circ}{F}_j(x,t) \rangle \tag{4.81}$$

where the Fj's have been chosen orthogonal.

This is essentially the internal entropy production assumed in non-equilibrium thermo-hydrodynamics.[13]

CHAPTER V

BEHAVIOR OF THE COVARIANCE FUNCTIONS

Application of the theory of thermally driven systems to specific problems demands knowledge of the covariance functions. In all but the simplest cases the calculation of these space and time dependent covariance functions from first principles is well beyond our present means.

Nevertheless, there are distinct advantages in formulating the behavior of non-equilibrium systems in terms of covariance functions. These functions are well defined physical quantities. Even though we can not calculate them explicitly from their definition as ensemble averages of physical operators, we can still use this definition to derive general properties which have physical significance.

Also, the covariance function formulation brings great uniformity to the treatment of non-equilibrium systems; the general expressions are always the same, only the behavior of the covariance function differs. For example, the response to a density disturbance is given by the density - density covariance function in both the collision dominated hydrodynamic limit and in the collisionless ideal gas limit. Hence one is led to view the covariance functions as the natural vehicle for interpolation between these limits.

In this chapter we will be concerned with the derivation of covariance functions from ideal gas ensembles, hydrodynamics, and experiments.

1. General Properties of the Covariance Functions

Let $F_1 \cdots F_n$ be an arbitrary set of Hermitian operators, and let ρ be a density matrix with all eigenvalues > 0. (Any information theory density matrix has this property). The covariance of F_i and F_j with respect to ρ is defined

$$K_{F_i F_j} \equiv \mathrm{Tr}\left[\int_0^1 dx\, e^{-x\ln\rho} F_i\, e^{+x\ln\rho} F_j\, \rho\right] - \mathrm{Tr}\left[F_i \rho\right] \mathrm{Tr}\left[F_j \rho\right] . \tag{5.1}$$

Three properties may be deduced directly from this definition.

(1) The $K_{F_i F_j}$ are real.

This is of course a necessary condition for thermal response theory to make sense: the source terms and response are real, so the covariance relating them must be real. It follows mathematically from the fact that $e^{x\ln\rho}$ commutes with ρ:

$$\begin{aligned} K^*_{F_i F_j} &= \mathrm{Tr}\left[\left(\int_0^1 dx\, e^{-x\ln\rho} F_i\, e^{x\ln\rho} F_j\, \rho\right)^{\dagger}\right] - \mathrm{Tr}\left[F_i \rho\right] \mathrm{Tr}\left[F_j \rho\right] \\ &= \mathrm{Tr}\left[\rho F_j \int_0^1 dx\, e^{-x\ln\rho} F_i\, e^{x\ln\rho}\right] - \mathrm{Tr}\left[F_i \rho\right] \mathrm{Tr}\left[F_j \rho\right] , \end{aligned} \tag{5.2}$$

and so by rearranging the operators in the trace, $K^*_{F_i F_j} = K_{F_i F_j}$.

(2) The covariance function $K_{F_i F_j}$ is symmetric in F_i and F_j.

It is this symmetry property which leads to the Onsager reciprocity relations.

Define

$$\langle \overline{F_i}\, F_j \rangle \equiv \int_0^1 dx\, \mathrm{Tr}\left[e^{-x\ln\rho} F_i\, e^{x\ln\rho} F_j\, \rho \right] \tag{5.3}$$

With $y \equiv 1 - x$ this becomes

$$\langle \overline{F_i}\, F_j \rangle = \int_0^1 dy\, \mathrm{Tr}\left[e^{y\ln\rho} F_i\, \rho\, e^{-y\ln\rho} F_j \right] \tag{5.4}$$

$$= \langle \overline{F_j}\, F_i \rangle,$$

therefore

$$K_{F_j F_i} = K_{F_i F_j}\,. \tag{5.5}$$

(3) The $F_1 \cdots F_n$ form an inner product space.

As Hermitian operators the F's obviously form a vector space. The conditions that the $K_{F_i F_j}$ must satisfy to be an inner product for the F's are

(a) $K_{F_i + F_j,\, F_k} = K_{F_i F_k} + K_{F_j F_k}$

(b) $K_{xF_i,\, F_j} = x K_{F_i F_j}$

(c) $K_{F_i F_j} = K_{F_j F_i}$

(d) $K_{F_i F_i} > 0,\ F_i \neq 0$

Conditions (a) and (b) follow by inspection of the definition. (c) was proved above. (d) can be shown by writing K in a representation where the density matrix is diagonal. Assume $0 < \rho_{\alpha\alpha} \leq \rho_{\beta\beta} \leq \rho_{\gamma\gamma} \cdots$ is the ordered sequence of eigenvalues of ρ. Then

$$\langle \bar{C} C \rangle = \sum_{\alpha,\beta} \bar{C}_{\alpha\beta}\, C_{\beta\alpha}\, \rho_{\alpha\alpha} \qquad (5.6)$$

$$= \sum_{\alpha,\beta} \int_0^1 dx\, e^{-x(\ln\rho_{\alpha\alpha} - \ln\rho_{\beta\beta})} |C_{\alpha\beta}|^2 e^{\ln\rho_{\alpha\alpha}}$$

$$= \sum_{\alpha,\beta} |C_{\alpha\beta}|^2 \rho_{\alpha\alpha}\, \delta_{\rho_{\alpha\alpha},\rho_{\beta\beta}}$$

$$+ \sum_{\alpha,\beta} \frac{e^{\ln\rho_{\alpha\alpha}} - e^{+\ln\rho_{\beta\beta}}}{\ln\rho_{\alpha\alpha} - \ln\rho_{\beta\beta}} |C_{\alpha\beta}|^2 (1-\delta_{\rho_{\alpha\alpha},\rho_{\beta\beta}})$$

Since the second sum is symmetric under interchange of α and β, it may be rewritten as

$$\frac{1}{2} \sum_{\alpha} \sum_{\substack{\beta \\ \alpha>\beta}} e^{\ln\rho_{\alpha\alpha}} \frac{(1-e^{-(\ln\rho_{\alpha\alpha} - \ln\rho_{\beta\beta})})}{\ln\rho_{\alpha\alpha} - \ln\rho_{\beta\beta}} \qquad (5.7)$$

$$\times |C_{\alpha\beta}|^2 (1-\delta_{\rho_{\alpha\alpha},\rho_{\beta\beta}}).$$

But for $\alpha > \beta$, $\ln\rho_{\alpha\alpha} - \ln\rho_{\beta\beta} > 0$; hence every term in the sum is ≥ 0, with equality only for $C_{\alpha\beta} = 0$. Thus $\langle \bar{C} C \rangle \geq 0$, with equality if and only if $C \equiv 0$. Defining $C \equiv F_i - \langle F_i \rangle$ therefore leads to

$$\langle \bar{C} C \rangle = K_{F_i F_i} \geq 0, \qquad (5.8)$$

with equality if and only if $F_i = \langle F_i \rangle$. Thus with the additional constraint $\sum_{i=1}^{n} a_i F_i \neq 1$, the F_i form an inner product space. Physically this constraint is equivalent to saying that the F_i can not be made linearly dependent merely by changing the constants from which they are measured; i.e. the F_i represent n rather than n - 1 different physical quantities.

Since the $F_1 \cdots F_n$ form an inner product space all the usual inner product theory is applicable; in particular, they can always be represented on an orthogonal basis, and they satisfy the Schwartz inequality, $K_{F_iF_i}K_{F_jF_j} \geqslant K^2_{F_iF_j}$. An interesting consequence of this inequality is obtained by letting $F_i = F(t=0)$,$F_j = F(t)$. Then $K_{F(t=0)F(t=0)} > |K_{F(t)F(t=0)}|$, so the time dependent covariance function is bounded by its equal time value.

To find additional properties of the covariance functions it is necessary to choose a definite ensemble. The covariance functions obtained from the Grand Canonical Ensemble are of great practical importance, for they give the first order effects of departure from equilibrium. For this density matrix the K functions have four additional properties.

(4) Kubo identity.

For operators F_i which commute with the total particle number, equation (5.1) yields the Kubo identity:

$$\overline{F}_i(t) \equiv \int_0^1 dx\, e^{-x\ln\rho} F_i(t)\, e^{x\ln\rho} \qquad (5.9)$$

$$= \frac{1}{\beta}\int_0^\beta du\, F_i(t - i\hbar u),$$

and so by carrying out the differentiation and integration formally,

$$\frac{d}{dt} K_{F_i(t)F_j(t=0)} = -\frac{i}{\hbar\beta}\left\langle \left[F_i(t), F_j(t=0)\right]\right\rangle \qquad (5.10)$$

(5) Time translation invariance.

Since the time development operator commutes with the density matrix,

$$K_{F_i(t)F_j(t')} = K_{F_i(t-t')F_j(t=0)} \equiv K_{F_iF_j}(t-t') \quad . \tag{5.11}$$

(6) Space translation and rotation invariance.

This requires the additional assumptions of spatial homogeneity and isotropy; these assumptions are usually appropriate for gases and liquids.

$$K_{F_i(\vec{x},t)F_j(\vec{x}',t')} = K_{F_i(\vec{x}-\vec{x}',t-t')F_j(\vec{x}=0,t=0)} \equiv K_{F_iF_j}(\vec{x}-\vec{x}',t-t') \quad . \tag{5.12}$$

(7) Symmetry in space - time.

From (2), (5), and (6) it follows that $K_{F_iF_i}(\vec{x},t) = K_{F_iF_i}(-\vec{x},t)$. This has the consequence that the space - time Fourier transform is real.

Further symmetry properties depend on the nature of the space and time dependence of the F's. For instance, if F_i and F_j are scalars then by isotropy $K_{F_iF_j}(\vec{x},t) = K_{F_iF_j}(-\vec{x},t)$

A third class of general properties of the covariance functions are the so - called sum and limit rules. These have the form

$$\int d\omega \; \omega^n K_{FF}(k,\omega) = B(k) \tag{5.13}$$

and

$$\lim_{k\to 0} K_{FF}(k,\omega) = \delta(\omega) A \; . \qquad (5.14)$$

The limit k→0 is equivalent to a spatial integration of the local variable $F(\vec{x})$. The covariance function of this integrated variable is often related to a thermodynamic derivative. For example, if $F(x,t) = n(x,t)$, the density, then

$$\lim_{k\to 0} K_{nn}(k,t) = m\langle N\, n(\vec{x}=0,t)\rangle_0 - m\langle N\rangle\langle n(x=0,t)\rangle$$

$$= \frac{m^2}{\Omega}\left(\frac{\partial\langle N\rangle}{\beta\partial\mu}\right)_{\beta,\Omega} = \frac{n_0^2}{\beta} K_T \; , \qquad (5.15)$$

where n_0 is the equilibrium density and K_T is the isothermal compressibility.

The sum rules over ω are obtained by explicit evaluation of equal time commutators. Again for the case $F(x,t) = n(x,t)$,

$$\int \frac{d\omega}{2\pi}\, \omega^2 K_{nn}(\vec{k},\omega) = i\int d\omega\, \omega\, K_{\dot{n}n}(\vec{k},\omega) \qquad (5.16)$$

$$= \frac{+i}{\hbar\beta}\int d\omega \left\langle\left[\dot{n}(\vec{k},\omega), n(\vec{x}=0,t=0)\right]\right\rangle$$

$$= \frac{i}{\hbar\beta}\left\langle\left[\dot{n}(\vec{k},t=0), n(\vec{x}=0,t=0)\right]\right\rangle$$

where the Kubo identity was used in the second step. Evaluation of the equal time commutator yields $\int d\omega\, \omega^2 K_{nn}(\vec{k},\omega) = \frac{k^2 n_0}{m\beta}$.

In the paper by Puff and Gillis[14] several of these sum and limit rule calculations are tabulated.

2. Ideal Gas Covariance Functions

The density, momentum density, and energy density operators for the ideal gas are

$$n(\vec{x},t) = \sum_{i=1}^{N} m\,\delta(\vec{x}_i(t)-\vec{x}) \tag{5.17}$$

$$\vec{J}(\vec{x},t) = \sum_{i=1}^{N} \vec{P}\,\delta(\vec{x}_i(t)-\vec{x}) \tag{5.18}$$

$$E(\vec{x},t) = \sum_{i=1}^{N} \frac{\vec{P}_i\cdot\vec{P}_i}{2m}\,\delta(\vec{x}_i(t)-\vec{x}) \tag{5.19}$$

The equations of motion are trivially integrated:

$$\begin{aligned} \vec{P}_i(t) &= \vec{P}_i(0) \\ \vec{X}_i(t) &= \vec{X}_i(0) + \frac{\vec{P}}{m}t \end{aligned} \tag{5.20}$$

For the classical ideal gas the trace of $\rho = \frac{1}{Z}e^{-\beta H}$ is replaced by integration of the N particle distribution function,

$$W_N(x_1P_1\cdots x_NP_N) = \prod_{i=1}^{N} w_1(x_1,P_1) \tag{5.21}$$

where

$$w_1(x_1,P_1) = \frac{1}{V}\left(\frac{\beta}{2\pi m}\right)^{\frac{3}{2}} e^{-\frac{\beta P^2}{2m}} \tag{5.22}$$

Hence

$$\langle n(0,0)n(\vec{x},t)\rangle = m^2\int dx_1\,dp_1\cdots dx_N\,dp_N \times W_N \sum_{\substack{i=1\\j=1}}^{N} \delta(x_i)\,\delta(\vec{x}_j + \frac{\vec{P}_j}{m}t - \vec{x}) \tag{5.23}$$

$$= m^2 \frac{N}{V} \left(\frac{\rho}{2\pi m}\right)^{3/2} \left|\frac{m}{t}\right|^3 e^{-\frac{\beta m x^2}{2t^2}} + m^2 \frac{N(N-1)}{V^2}$$

Therefore in the limit of large volume at constant density,

$$K_{nn}(\vec{x},t) = m n_0 \left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} \frac{1}{|t|^3} e^{-\frac{\beta m x^2}{2t^2}} \tag{5.24}$$

Taking Fourier space and time transforms this may also be written

$$K_{nn}(\vec{k},t) = m n_0 e^{-\frac{k^2 t^2}{2\beta m}} \tag{5.25}$$

and

$$K_{nn}(\vec{k},\omega) = m n_0 \left(\frac{2\pi\beta m}{k^2}\right)^{\frac{1}{2}} e^{-\frac{\beta m}{2}\left(\frac{\omega^2}{k^2}\right)} \tag{5.26}$$

Similarly,

$$K_{\vec{j}\vec{j}}(\vec{x},t) = \frac{\vec{x}\vec{x}}{t^2} K_{nn}(\vec{x},t) \tag{5.27}$$

$$K_{\vec{j}\vec{j}}(\vec{k},t) = \frac{1}{\beta m} \left[\frac{\vec{k}\vec{k}}{k^2}\left(1-\frac{t^2}{\beta m}k^2\right)+\left(\mathbb{1}-\frac{\vec{k}\vec{k}}{k^2}\right)\right] K_{nn}(k,t)$$

$$K_{\vec{j}\vec{j}}(\vec{k},\omega) = \left[\frac{\omega^2}{k^2}\frac{\vec{k}\vec{k}}{k^2} + \left(\mathbb{1}-\frac{\vec{k}\vec{k}}{k^2}\right)\frac{1}{\beta m}\right] K_{nn}(k,\omega)$$

,

$$K_{HH}(\vec{x},t) = \frac{x^4}{4t^4} K_{nn}(\vec{x},t)$$

$$K_{HH}(\vec{k},t) = \frac{1}{4(\beta m)^2}\left[15 - \frac{10 k^2 t^2}{(\beta m)} + \frac{k^4 t^4}{(\beta m)^2}\right] K_{nn}(\vec{k},t)$$

$$K_{HH}(\vec{k},\omega) = \left(\frac{2}{(\beta m)^2} + \frac{\omega^2}{k^2}\frac{1}{\beta m} + \frac{1}{4}\frac{\omega^4}{k^4}\right) K_{nn}(\vec{k},\omega)$$

$$K_{nn}(\vec{x},t) = \frac{x^2}{2t^2} K_{nn}(\vec{x},t)$$

$$K_{Hn}(\vec{k},t) = \frac{1}{\beta m}\left[\frac{3}{2} - \frac{k^2 t^2}{2\beta m}\right] K_{nn}(\vec{k},t)$$

$$K_{Hn}(\vec{k},\omega) = \left(\frac{1}{\beta m} + \frac{1}{2}\frac{\omega^2}{k^2}\right) K_{nn}(\vec{k},\omega)$$

The density - density covariance functions for the ideal Bose and Fermi gases may also be found in closed form.[15]

Bose: (5.28)

$$K_{nn}(k,\omega) = \frac{\sqrt{\pi}}{2\Lambda^3 |\omega| p} \ln\left[\frac{1 - z e^{-(q+p)^2}}{1 - z e^{-(q-p)^2}}\right]$$

$$+ \frac{2\pi}{\beta \hbar \omega V}\left(\langle n_0\rangle \delta(\omega - \omega_0) - \langle n_0\rangle \delta(\omega + \omega_0)\right)$$

Fermi: (5.29)

$$K_{nn}(k,\omega) = \frac{\sqrt{\pi}}{2\Lambda^3 |\omega| p} \ln\left[\frac{1 + z e^{-(q+p)^2}}{1 + z e^{-(q-p)^2}}\right]$$

The notation is

$$\Lambda \equiv \left(\frac{2\pi\hbar^2\beta}{m}\right)^{\frac{1}{2}},$$ thermal wavelength

$q \equiv \left(\frac{\beta m}{2}\frac{\omega^2}{k^2}\right)^{1/2}$, ratio of phase velocity to thermal velocity

$p^2 \equiv \left(\frac{\beta\hbar^2 k^2}{8m}\right)$, ratio of quantum state energy of mode k to thermal energy

and $z = e^{\beta\mu}$, μ chemical potential.

Though in closed form, it is still difficult to calculate with these expressions. The most interesting feature is that the Bose covariance function has a peak for $p \sim q$ $\left(\omega \sim \frac{\hbar k^2}{2m}\right)$. But even for extreme degeneracy $(e^{\beta\mu} \sim e^{-50})$ it is of no practical importance, since the area under the peak is negligible. (The condition for sound waves is a peak approximating a delta function.)

It is also interesting that in the "low" frequency approximation, $4pq = \beta\hbar\omega \simeq 7 \times 10^{-12}\,\frac{\omega}{T} < 1$, the Bose covariance function may be written as a sum of products of "classical" and "quantum" terms"

$$K_{nn}(k,\omega) = \frac{\sqrt{\pi m\beta}}{\Lambda^3|\omega||k|}\sum_{n=1}^{\infty} z^n\left(e^{-nq^2}\right)\left(e^{-np^2}\right) \tag{5.30}$$

$$+ \frac{2\pi}{\beta\hbar\omega V}\left[\langle n_0\rangle\delta(\omega-\omega_0) - \langle n_0\rangle\delta(\omega+\omega_0)\right]$$

The expression for the p → 0 limit

$$K_{nn}(k,\omega) = \frac{\sqrt{\pi m\beta}}{\Lambda^3|\omega||k|}\sum_{n=1}^{\infty} z^n e^{-nq^2} \tag{5.31}$$

would have been obtained in our classical calculation by replacing the Boltzman single particle distribution function, $e^{-\alpha - \frac{\beta p^2}{2m}}$, by the Bose single particle distribution function, $\frac{1}{e^{\alpha + \frac{\beta p^2}{2m}} - 1}$.

To illustrate the use of these ideal gas covariance functions, let us find the effect of space and time dependent heating in a classical ideal gas. The fundamental formulas for linear response are

$$\overset{\circ}{\sigma}_H(x,t) = \int dx' K_{HH}(x-x', t=0)\, \lambda_H(x',t)\,, \tag{5.32}$$

which determines $\lambda_H(x,t)$ in terms of the known heat source $\overset{\circ}{\sigma}_H(x,t)$, and

$$\langle F(x,t)\rangle = \langle F(x,t)\rangle_0 + \int_0^t \int dx' K_{FH}(x-x', t-t')\, \lambda_H(x',t') \tag{5.33}$$

which predicts the response of any variable F.

Taking Fourier transforms in space these become

$$\overset{\circ}{\sigma}_H(k,t) = K_{HH}(k, t=0)\, \lambda_H(k,t) \tag{5.34}$$

and

$$\langle F(k,t)\rangle = \langle F(k,t)\rangle_0 + \int_0^t K_{FH}(k, t-t')\, \lambda_H(k,t')$$

If our interest is restricted to the local density and energy density, the relevant covariance functions are

$$K_{HH}(\vec{k},t) = \frac{1}{4(\beta m)^2}\left[15 - \frac{10k^2t^2}{\beta m} + \frac{k^4t^4}{(\beta m)^2}\right] K_{nn}(\vec{k},t) \tag{5.35}$$

$$K_{Hn}(\vec{k},t) = \frac{1}{\beta m}\left[\frac{3}{2} - \frac{k^2t^2}{2\beta n}\right] K_{nn}(\vec{k},t) \tag{5.36}$$

and

$$K_{nn}(\vec{k},t) = mn_0\, e^{-\frac{k^2t^2}{\beta m}} \tag{5.37}$$

These expressions are appropriate for the transfer of energy without explicit constraints. Actually, "heating" usually implies the explicit constraint that no particles are transferred. Hence the driven variable is not H $(\vec{k},t)$ but H' $(\vec{k},t)$, where in the linear approximation

$$H'(k,t) = H(k,t) - \frac{K_{Hn}(k,0)}{K_{nn}(k,0)}\, n(k,t) \tag{5.38}$$

$$= H(k,t) - \frac{3}{2\beta m}\, n(k,t)$$

The equations determining the response of the system are now

$$\dot{\sigma}_{H'(k,t)} = K_{H'H'}(k,t=0)\, \lambda_{H'}(k,t) \tag{5.39}$$

$$\langle H'(k,t)\rangle = \int_0^t K_{H'H'}(k,t-t')\, \lambda_{H'}(k,t') \tag{5.40}$$

and

$$\langle n(k,t)\rangle = \int_0^t K_{nH'}(k.t-t')\, \lambda_{H'}(k,t) \tag{5.41}$$

where we used the fact that in equilibrium $\langle n(k,t)\rangle_0$ and $\langle H(k,t)\rangle_0$ are zero. The new covariance functions are

$$K_{H'H'}(k,t) = K_{HH}(k,t) - 2\,\frac{K_{Hn}(k,0)}{K_{nn}(k,0)}\, K_{Hn}(k,t) \tag{5.42}$$

$$+ \left(\frac{K_{Hn}(k,0)}{K_{nn}(k,0)}\right)^2 K_{nn}(k,t)$$

$$= \frac{1}{4(\beta m)^2}\left[6 - 4\,\frac{k^2t^2}{\beta m} + \frac{k^4t^4}{(\beta m)^2}\right] K_{nn}(k,t)$$

and

$$K_{nH'}(k,t) = K_{nH}(k,t) - \frac{K_{Hn}(k,0)}{K_{nn}(k,0)}\, K_{nn}(k,t) \tag{5.43}$$

$$= -\frac{k^2t^2}{2(\beta m)^2}\, K_{nn}(k,t)$$

Case I. Pulse Heating.

Suppose $\overset{\circ}{\sigma}(k,t) = \delta(t)\,\Delta H(k)$, corresponding to the instantaneous addition of heat energy of amount $\Delta H(k)$ to mode k. The predicted decay of this heat energy is

$$\langle H'(k,t)\rangle = \frac{K_{H'H'}(k,t)}{K_{H'H'}(k,0)}\,\Delta H(k) \tag{5.44}$$

$$= \Delta H(k)\left[1 - \frac{2}{3}\frac{k^2t^2}{\beta m} + \frac{1}{6}\frac{k^4t^4}{(\beta m)^2}\right] e^{-\frac{k^2t^2}{2\beta m}}$$

while the response of the density is

$$\langle n(k,t)\rangle = \frac{K_{nH'}(k,t)}{K_{H'H'}}\,\Delta H(k) \tag{5.45}$$

$$= -\frac{1}{3}\,k^2t^2\,e^{-\frac{k^2t^2}{2\beta m}}\,\Delta H(k)$$

Qualitatively the density behavior corresponds to atoms leaving the heated regions faster than they are replaced, leading to a build-up in density 180° out of phase with the initial heat pulse. The relaxation time $\sqrt{\frac{R^2}{2\beta n}}$ is the order of time required for an atom of average velocity to travel one wavelength.

Case II. Constant Heating.

Suppose we heat mode k continuously from t = 0 at the rate $\overset{\bullet}{\sigma}(k,t) = \Delta H(k)$.

Then

$$\langle H'(k,t)\rangle = \int_0^t \frac{K_{H'H'}(k,t-t')}{K_{H'H'}(k,t=0)}\,\Delta H(k) \tag{5.46}$$

$$= \frac{\Delta H(k)}{6}\left(t - \frac{k^2t^3}{4\beta m}\right) e^{-\frac{k^2t^2}{2\beta m}}$$

$$+ \Delta H(k)\frac{5}{6}\sqrt{\frac{2\beta m}{k^2}}\;\frac{\sqrt{\pi}}{2}\;\mathrm{erf}\left(\sqrt{\frac{k^2t^2}{2\beta m}}\right.$$

and

$$\langle n(k,t)\rangle = \Delta H(k)\,\frac{t}{3}(\beta m)\,e^{-\frac{k^2t^2}{2\beta m}} \tag{5.47}$$

$$-\Delta H(k)\frac{1}{3}(\beta m)\sqrt{\frac{2\beta m}{k^2}}\;\frac{\sqrt{\pi}}{2}\;\mathrm{erf}\left(\sqrt{\frac{k^2t^2}{2\beta m}}\right)$$

The steady state heat energy maintained in the mode k by the source strength Δ H(k) is therefore $\frac{5}{6}\sqrt{\frac{2\beta m}{k^2}}\Delta H(k)$, while the steady state density is 180° out of phase with the heat energy density and differs by a factor $\frac{2}{5}\beta m$.

Case III. Sinusoidal Heating.

Suppose we heat the k mode sinusoidally from $t = -\infty$ with $\mathcal{S}(k,t) = \Delta H(k)\cos\omega t$. Then

$$\langle H'(k,t)\rangle = \int_{-\infty}^{t}\frac{K_{H'H'}(k,t-t')}{K_{H'H'}(k,t=0)}\,\Delta H(k)\cos\omega t' \tag{5.48}$$

$$= \Delta H(k)\int_0^{\infty}\frac{K_{H'H'}(k,t'')}{K_{H'H'}(k,t=0)}\cos\omega(t-t'')$$

$$= \Delta H(k)\,\frac{2}{3mn_0(\beta m)^2}\left|K^{+}_{H'H'}(k,\omega)\right|\cos(\omega t-\phi),$$

with the phase lag ϕ given by

$$\phi = \tan^{-1}\frac{\mathrm{Im}\,K^{+}_{H'H'}(k,\omega)}{\mathrm{Re}\,K^{+}_{H'H'}(k,\omega)} \tag{5.49}$$

Similarly

$$\langle n(k,t)\rangle = -\Delta H(k)\,\frac{2}{3mn_0(\beta m)^2}\,\left|K^+_{nH'}(k,\omega)\right|\cos(\omega t-\theta) \tag{5.50}$$

with

$$\theta = \tan^{-1}\frac{\operatorname{Im} K^+_{nH'}(k,\omega)}{\operatorname{Re} K^+_{nH'}(k,\omega)}$$

The imaginary time Laplace transforms appearing here are

$$K^+_{H'H'}(k,\omega) = \frac{1}{4(\beta m)^2}\Big[(5-4q^2+4q^4)K^+_{nn}(k,\omega) + i\,\frac{4(\frac{1}{2}-q^2)q^2 mn_0}{\omega} \tag{5.51}$$

$$K^+_{nH'}(k,\omega) = -\frac{1}{\beta m}\left[\left(\tfrac{1}{2}-q^2\right)K^+_{nn}(k,\omega) - \frac{iq^2mn_0}{\omega}\right] \tag{5.52}$$

and

$$K^+_{nn}(k,\omega) = mn_0\sqrt{\pi}\,\frac{q}{\omega}\,e^{-q^2}\operatorname{Erfc}(-iq) \tag{5.53}$$

where $q \equiv \sqrt{\frac{\beta m\omega^2}{2k^2}}$ is the ratio of phase velocity to thermal velocity. (For the collision dominated gas, $q = \sqrt{\frac{5}{6}}$). Using these functions, the phase lags are

$$\phi = \tan^{-1}\left(\frac{2}{\sqrt{\pi}}\int_0^q e^{y^2}dy + \frac{2q-4q^3}{(5-4q^2+4q^4)\sqrt{\pi}}e^{q^2}\right) \tag{5.54}$$

$$\theta = \tan^{-1}\left(\frac{2}{\sqrt{\pi}}\int_0^q e^{y^2}dy + \frac{q}{(\frac{1}{2}-q^2)\sqrt{\pi}}e^{q^2}\right) \tag{5.55}$$

In addition to finding the amplitude and phase lag of the density and heat energy, we can also calculate the entropy transfer. To second order, the rate of change of information entropy is

$$\overset{\circ}{S}_{I_t} \overset{2}{=} \beta\,\lambda(t)\,K_{HF} - \lambda(t)\left(1+\beta\frac{\partial}{\partial\beta}\right)\langle F(t)\rangle_t \tag{5.56}$$

Thus if we drive the system at frequency ω , the rate of information entropy change is

$$\overset{\circ}{S}_{I_t} = -\tfrac{1}{2}\,\lambda(k,\omega)\left(1+\beta\frac{\partial}{\partial\beta}\right)\lambda(k,\omega) \tag{5.57}$$
$$\times\left[\,|K^{+}_{H'H'}(k,\omega)|\cos(2\omega t-\phi)+\mathrm{Re}\,K^{+}_{FF}(k,\omega)\right]$$

From this, the minimum average entropy increase of the reservoirs driving the system at frequency ω must be

$$-\overset{\circ}{S}_{I_{t\,avg.}} = \tfrac{1}{4}\,\lambda(k,\omega)\left(1+\beta\frac{\partial}{\partial\beta}\right)\lambda(k,\omega)\,K_{H'H'}(k,\omega) \tag{5.58}$$
$$=(\Delta H(k))^2\frac{(\beta m)^2}{m n_0}\,\frac{\sqrt{\pi}}{q}\left(\frac{15}{2}-17g^2+18g^4-4g^6\right)\frac{g}{\omega}e^{-g}$$

3. Covariance Functions in the Hydrodynamic Limit

The phenomenological theory of linear hydrodynamics affords an excellent description of non-equilibrium behavior in the collision dominated (many collisions per cycle and many collisions per wavelength) region. Therefore, the equations of hydrodynamics determine a limiting form for the covariance functions. The derivation of this form was essentially carried out in Chapter III, in the inverse problem of expressing transport coefficients in terms of covariance functions.

Equations (3.93) - (3.98) give the imaginary time Laplace transforms of the covariance functions in the hydrodynamic limit. The general form is

$$K^{+}_{FG}(k,\omega) = \frac{a\omega^{2} + b\omega + c}{\omega^{3} + d\omega^{2} + e\omega + f} \tag{5.59}$$

The corresponding expression in the wave number - time representation is

$$K_{FG}(k,t) = A\cos(\omega t + \theta)e^{-G|t|} + Be^{-\delta|t|} \tag{5.61}$$

Physically, this covariance function represents the decay of a pulsed spatial wave. To lowest order in the transport coefficients,

$$\omega = V_s k$$

$$V_s^{2} = \frac{C_p}{C_V n_o K_T}$$

$$\epsilon = \frac{k^{2}}{2}\left(\frac{4}{3}\eta + \eta_v + \Lambda\left(\frac{c_p - C_v}{C_p C_\gamma}\right)\right)$$

and

$$\delta = k^{2}\frac{\Lambda}{C_p}$$

Note that these covariance functions have a discontinuity in their first derivative at $t = 0$, whereas the ideal gas covariance functions are analytic. Since discontinuity in a derivative leads to discontinuous prediction of some physical variable it seems probable that the exact form should be analytic, with sharp but slightly rounded peaks.

In the hydrodynamic limit the covariance functions are essentially the Green's functions of the hydrodynamic equations. The expressions for the response of a single variable initially in equilibrium are

$$\langle F(\vec{x},t)\rangle_G = \int_0^{t^+} dt' \int_R d\vec{x}'\, G(\vec{x},t;\vec{x}',t')\, \mathring{\sigma}_F(\vec{x}',t') \tag{5.62}$$

for the Green's function and

$$\langle F(\vec{x},t)\rangle_K = \int_0^{t} dt' \int d\vec{x}'\, K_{F(\vec{x},t)\,F(\vec{x}',t')}\, \lambda_{F(\vec{x}',t')} \tag{5.63}$$

with

$$\mathring{\sigma}_{F(\vec{x},t)} = \int_R d\vec{x}'\, K_{F(\vec{x},t)\,F(\vec{x}',t)}\, \lambda_{F(\vec{x}',t)} \tag{5.64}$$

for the covariance function. While the content is the same, and the form is similar, there are two important differences.

In the first place, it is the usual convention to define Green's functions so that they go to zero at the upper limit of integration. Hence with $G(\vec{x},t;\vec{x}',t') \equiv 0,\ t' > t$

$$\frac{d}{dt}\langle F(x,t)\rangle_G = \int_0^{t^+} dt' \tag{5.65}$$

On the other hand the K functions are continuous symmetric functions of time, with a non-zero value at the upper limit of integration.

Hence

$$\frac{d}{dt}\langle F(x,t)\rangle_G = \int_0^{t^+} dt' \int_R d\vec{x}'\, \dot{G}(\vec{x},t;\vec{x}',t')\, \mathring{\sigma}_F(\vec{x}',t') \tag{5.66}$$

whereas

$$\frac{d}{dt}\langle F(x,t)\rangle = \langle \mathring{F}(x,t)\rangle + \int_R d\vec{x}'\, K_{F(x,t)\,F(x',t)}\, \lambda_{F(x,t)} \tag{5.67}$$

which is conveniently used to determine λ in terms of the source strength $\dot{\sigma}$.

A second difference is that the Green's function itself includes the boundary conditions. The covariance functions could also be derived separately for each new boundary imposed on the system. It seems more consistent formally, however, since the covariance functions represent solutions of the many body problem, to define the covariance functions once and for all for the infinite medium. The boundary conditions are then incorporated by introducing additional source strengths. For instance, suppose the boundaries of a system prevent the flow of F through them. This case may be treated with the infinite medium covariance functions by including the additional variable J_F, with its associated λ determined by the condition $\langle \vec{J}_F(\vec{x},t)\rangle_{\text{normal}} = 0$ along the boundary.

Hence in the covariance function treatment microscopic and geometrical effects are separated: the K's contain the fundamental microscopic nature of the system, while the λ's contain the geometrical effects of boundaries.

4. Covariance Functions From Experimental Information

As one example of a physical system where the covariance function analysis should prove useful, consider the propagation of heat pulses in liquid He^4. At temperatures $\gtrsim 1^\circ K$ the propagation of heat pulses is well described by the phenomenological equations of superfluid hydrodynamics. As the temperature falls below this, the hydrodynamic description becomes inadequate. In fact, for very low temperatures one might expect the response of liquid He^4 to approach that of an ideal gas of quasi particles.

Robert Guernsey, in K. Luszczynski's group at Washington University has been carrying out experiments with heat pulses in liquid He^4 at temperatures down to 0.16° K. His apparatus consists essentially of a small (~ 1 mm.) carbon film heater with a similar carbon film detector at a distance ~ 1 cm. The heater is pulsed with a square pulse of duration $\sim 100\ \mu$ seconds, and the resultant heating observed at the detector.

Our equations for the linear response of the system are

$$\langle H'(\vec{x},t)\rangle = \int_R d\vec{x}' \int_0^t dt'\, K_{H'H'}(\vec{x}-\vec{x}';t-t')\,\lambda_H(\vec{x}',t') \tag{5.68}$$

and

$$\mathring{\sigma}_{H'}(\vec{x},t) = \int_R d\vec{x}'\, K_{H'H'}(\vec{x}-\vec{x}';t-t')\,\lambda_H(\vec{x}';t') \tag{5.69}$$

where the integration is over the space of the heater, and H' is the part of the energy decoupled from the density. In the approximation that spatial variation of the source terms is slow relative to the equal time covariance function, these equations reduce to

$$\langle H'(\vec{x},t)\rangle = \int_R d\vec{x}' \int_0^t dt'\, \frac{K_{H'H'}(\vec{x}-\vec{x}';t-t')}{K_{H'H'}} \times \mathring{\sigma}_{H'}(\vec{x}';t') \tag{5.70}$$

with $K_{H'H'} \equiv \int dx\, K_{HH}(x,t=0)$.

Hence the covariance function may in principle be obtained from knowledge of the source and response terms, and the geometry. Actually, of course, the experimental imprecision in our knowledge of these terms complicates the problem and reduces the obtainable information.

So far only data for temperatures around 1° has been analyzed in terms of the covariance functions; in this region the linear response is described by hydrodynamics to within the precision of the experiment.

An interesting question is the relation between this experiment with a small source and remote walls, and those performed in closed tubes. In the hydrodynamic limit there is a striking qualitative difference. Assume specular reflection from the walls. Then the closed tube system corresponds mathematically to an infinite plane heater. Hence

$$\langle H'(x=0,y=0,z,t)\rangle = \int_0^t dt' \, \frac{K_{H'H'}(k_x=0,k_y=0,z,t-t')}{K_{H'H'}} \times \mathring{\sigma}_H(x,t') \, , \tag{5.71}$$

where

$$K_{H'H'}(k_x=0,\, k_y=0,\, z,\, t) \equiv \int dx \int dy \, K_{H'H'}(x,y,z,t) \, . \tag{5.72}$$

On the other hand the signal from a small disc of radius 'a' with remote walls is

$$\langle H'(x=0,y=0,z,t)\rangle = \int_0^t dt' \, 2\pi \int_0^a q\,dq \, \frac{K_{H'H'}(x=0,y=0,r;t-t')}{K_{H'H'}} \times \mathring{\sigma}_H(t') \tag{5.73}$$

with $r = \sqrt{z^2+q^2}$. Spatial isotropy was used to write the covariance function in this form. Furthermore

$$K_{HH}(x=0,y=0,z;t) = -\frac{1}{2\pi} \, \frac{\frac{\partial}{\partial z} K_{H'H'}(k_x=0,k_y=0,z;t-t')}{z} \, , \tag{5.74}$$

as is easily checked by integration. Thus the response along the axis of the disc is

$$\langle H'(x=0,\ y=0,\ z;\ t)\rangle = -\int_0^t dt' \int_0^a q\,dq\ \frac{\frac{\partial}{\partial r} K_{H'H'}(k_x=0,\ k_y=0,\ r;\ t-t')}{r\,K_{H'H'}} \times \mathring{\sigma}_H(t')$$

$$= \int_0^t dt'\,\mathring{\sigma}_H(t')\Big[K_{H'H'}(k_x=0,\ k_y=0,\ z;\ t-t') - K_{H'H'}(k_x=0,\ k_y=0,\ \sqrt{z^2+a^2};\ t-t')\Big] \tag{5.75}$$

This is almost the same as the response for the closed tube geometry except for the addition of a "cut - off". The effect of the "cut - off" is clearly seen in the hydrodynamic region where

$$\frac{K_{HH}(x=0,\ y=0,\ z;\ t)}{K_{HH}} \simeq \delta(z-ct) \tag{5.76}$$

For a step function pulse of duration τ the response is then

$$\langle H'(x=0,\ y=0,\ z;\ t)\rangle = \mathring{\sigma}_C \left[\left(\theta\left(t-\frac{z}{c}\right)-\theta\left(t-\frac{\sqrt{z^2+a^2}}{c}\right)\right) - \left(\theta\left(t-\tau-\frac{z}{c}\right)-\theta\left(t-\tau-\frac{\sqrt{z^2+a^2}}{c}\right)\right)\right] \tag{5.77}$$

Hence the response is a positive pulse of duration $\frac{1}{2}\,\frac{a^2}{cz}$ followed by a symmetric negative pulse. Though this is merely a geometrical effect easily obtained from the hydrodynamic equations, the production of a negative heat pulse from a positive driving seems at first thought surprising.

The covariance function formulation should find useful application in any system where the combination of low interaction densities and high frequencies and wave numbers results in a breakdown of hydrodynamics.

ACKNOWLEDGEMENTS

I wish to express my gratitude to Professor E. T. Jaynes, whose M.E.E. formalism provided the foundation and inspiration for this research, and whose suggestions and encouragement were of great value in its development.

I am grateful also to my wife, Carole, for the typing and preparation of the manuscript.

Much of this work was carried out during the tenure of National Science Foundation Predoctoral Fellowships, 1963 through 1966.

REFERENCES

1. R. Kubo, M. Yokota, and S. Nakajima, J. Phys. Soc. (Japan) 12, 1203 (1957).

2. R. Zwanzig, Ann. Rev. Of Phys. Chem. 16, (1965).

3. E. T. Jaynes, Phys. Rev. 106, 620 (1957);

   E. T. Jaynes, Phys. Rev. 108, 171 (1957);

   E. T. Jaynes, in *Statistical Physics*, ed. by K. W. Ford, (Benjamin, 1963);

   D. Scalapino, *Statistical Mechanics and the Principle of Maximum Entropy*, Ph.D. dissertation, Stanford University (1961).

4. D. Scalapino dissertation, op. cit.;

   D. Scalapino and E. T. Jaynes, to be published.

5. D. Scalapino and Jaynes, op. cit.;

   E. T. Jaynes, class notes.

6. E. T. Jaynes, Phys. Rev. 108, 171 (1957);

   E. T. Jaynes, Am. J. Phys. 33, 391 (1965).

7. R. Kubo, J. Phys. Soc. (Japan) 12, 570 (1957).

8. L. P. Kadanoff and P. C. Martin, Ann. Phys. 24, 419 (1963);

   J. M. Luttinger, Phys. Rev. 135A, 1505 (1964);

   E. W. Montroll, *Rendiconti Della Scuola Internazional Di Fisica Enrico Fermi*, X, 217 (Societa Italiana Di Fisica, Bologna, 1960).

9. R. Zwanzig, Ann. Rev. Phys. Chem. 16 (1965).

10. R. D. Puff and N. S. Gillis, to be published.

11. E. T. Jaynes, Am. J. Phys. 33, 391 (1965);

    A. Katz, Nuovo Cimento 33, 1544 (1964);

    F. Andreios, Proc. Natl. Acad. Sci. 54, 13 (1965);

    A. Hobson, Am. J. Phys. 34, 411 (1966).

12. D. Scalapino dissertation, op. cit.;

    B. Robertson, Phys. Rev. 144, 151-161 (1966).

13. S. R. de Groot and P. Mazur, Non-Equilibrium Thermodynamics (North - Holland Pub. Co., Amsterdam, 1962);

I. Prigogine, Thermodynamics of Irreversible Processes (Interscience Publishers, New York, 1961).

14. R. D. Puff and N. S. Gillis, to be published.

15. E. T. Jaynes, class notes.