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Contributions to the Theory of Non-Equilibrium Thermodynamics

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CONTRIBUTIONS TO THE THEORY OF
NON-EQUILIBRIUM THERMODYNAMICS

A thesis submitted to the Faculty of The Rockefeller University
in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

by

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II

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Approved for publication
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Professor.

DEDICATION

To my father for showing me the way.

ACKNOWLEDGMENTS

This dissertation is the manifestation of how the ideas of Professors Mark Kac and George Uhlenbeck come together and achieve a joint harmony. I am very deeply indebted to Professor Kac for encouragement at critical moments and for several inspirational ideas. I owe an even greater thanks to Professor Uhlenbeck for guiding my efforts in the direction of rigor and relevance. His contributions conceptually are referenced several times in the notes to the thesis.

To Marie Grossi goes the credit for the beautiful performance on the typewriter.

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INTRODUCTION

The purpose of this dissertation is to present a generalization of the current theory of non-equilibrium thermodynamics. The current theory was presented in 1953 by Onsager and Machlup, its mathematical context goes back to the 1930 paper of Uhlenbeck and Ornstein on Brownian motion, and the physical foundations for that approach go back to the initial theoretical work on Brownian motion done by Einstein in 1905 and by Langevin in 1908. It will be demonstrated how the ideas presented by these men lead in a natural way to a generalization of the current theory. It will then be shown how the generalized theory extends the domain of applicability of non-equilibrium thermodynamics.

Consider, by way of example, a mole of some mono-atomic gas. The precise description of the behavior of the gas requires of the order of 10^{24} variables since it is necessary to give the values of the momenta and coordinates of each gas atom. We call this the microscopic description of the gas. The gas also has a macroscopic description given by thermodynamics. The equilibrium state of the gas, for instance, is given in terms of three thermodynamical variables: temperature, pressure, and volume. For a non-equilibrium state of the gas one may divide the gas volume up into n little cells which have volumes very much smaller than the volume of the gas but which are still large enough to contain very many gas atoms. In each such cell one can take the average kinetic energy which is the local temperature, the average momentum, and the average density as the local thermodynamical variables. Therefore, for each cell there are 5 variables (the momentum counts as 3) and, consequently, the macroscopic description obtained in this way uses $5n$ variables. However, n is much smaller than 10^{24} in general. The essential point of all this is that for thermodynamical systems, the macroscopic description involves far fewer variables than does the

microscopic description. We call the macroscopic description a contracted description of the system.

The microscopic description is, in general, time reversible. This is so from a classical point of view because the momenta and coordinates of each of the gas atoms change in time following Newton's laws of motion which are time reversible. The macroscopic description is, in general, time irreversible. This is so because the dynamical equations of motion for the macroscopic description involve dissipative constants which create the irreversibility. In the case of the gas, the dissipative constants are the viscosity and the heat conductivity, and they have no counterparts in the microscopic description. Therefore, the macroscopic description is said to be dissipative.

That a macroscopic description is both contracted and dissipative implies something deeper. Consider a single macroscopic state of the gas given by prescribing values to all $5n$ thermodynamical variables. Because each cell volume contains very many gas atoms, this single macroscopic state corresponds with many microscopic states of the gas. This follows from the observation that in a given cell a single value of the average density, for example, may be associated with gas atoms arranged in literally infinitely many different ways just so long as the total number of gas atoms in the cell remains fixed. The contracted macroscopic description is insensitive to many of the details of the microscopic description. Once the microscopic state of the gas is completely specified, it is precisely determined by the dynamical equations for all future times. This property is expressed by saying that the microscopic description is causal. Now suppose a macroscopic state of the gas is completely specified. Associated with this state there are many microscopic states of the gas as was just pointed out. Each of these microscopic states causally changes in time into another microscopic state at some time t later. Do all of these new microscopic

states correspond to a single macroscopic state at this later time t ? In general: No! Several different macroscopic states are possible. Which one actually occurs depends on which of the initial microscopic states of the gas was the true initial state of the gas. The initial macroscopic state was, of course, too insensitive to tell the precise microscopic state and, therefore, any of the initially associated microscopic states could have been the true initial state of the gas. All that can be given is a certain probability that a given macroscopic state will become another macroscopic state at a later time t . The contracted macroscopic description has one more property by virtue of the one macroscopic-to-many microscopic states association which has just been discussed. At any fixed moment in time the values of the macroscopic variables cannot be given precisely. These can only have a certain probability of being a precise number. This is because in a given cell volume, the gas atoms are moving about very rapidly compared with the rate of change in the values of the thermodynamical variables. The local density, for example, fluctuates as a consequence of this microscopic motion. One can observe such fluctuations experimentally even when the gas is in equilibrium. The macroscopic description, therefore, is probabilistic on two counts: a) in terms of specifying a given macroscopic state, and b) in terms of predicting how one state changes into another at a later time. The macroscopic description is, therefore, not causal. The macroscopic description is said to be stochastic. In the theory to be presented it will be shown that the fluctuations just mentioned are intimately connected with the dissipative constants which appear in the dynamical equations. This connection is the central point of the theory. One may now say that because a macroscopic description is contracted, it is necessarily stochastic which, because of the connection just alluded to, means it is also dissipative, and thereby irreversible.

The generality of the theory results from its very general mathematical form. Consequently, it is applicable to hydrodynamics, kinetic theory, and reaction kinetics equally well. The chapters that follow cover these and related topics as is indicated below.

In Chapter I, the Langevin equation for Brownian motion of a particle in a fluid, and the Onsager and Machlup theory of non-equilibrium thermodynamics are presented and shown to be examples of stationary Gaussian Markov processes. In the Onsager and Machlup theory the thermodynamical variables are assumed to be even functions of the time. This suggests that a more general theory would result by dropping this limitation and investigating the most general stationary Gaussian Markov processes possible. The structure of such processes is derived including a general fluctuation-dissipation theorem.

In Chapter II an application to linearized Navier-Stokes hydrodynamics is made. The theory obtained is the linearized form of a theory proposed by Landau and Lifshitz. The justification given by Landau and Lifshitz for their theory is based on an argument using the Onsager and Machlup theory which is in fact not applicable to hydrodynamics. The derivation given here clears up the ambiguities. Applications of this fluctuating hydrodynamical theory are discussed. The fluctuation of the flow around a slowly moving particle is considered in detail. For the average flow this leads to the Stokes' law of friction, while the fluctuations around the average flow give rise to a fluctuating force on the particle. This justifies the Langevin equation for the motion of a Brownian particle in a fluid.

In Chapter III the linearized Boltzmann's equation describing the change in time of the distribution in μ -space for an ideal gas is shown to be of the form of the average regression equations for a stationary Gaussian Markov process. Consequently, a fluctuating force term is implied and its properties are derived and discussed. The question of

how the fluctuating hydrodynamical theory of Chapter II may be contracted out of the fluctuating Boltzmann's equation is raised. The mathematical procedure for such a contraction is presented through explicit application to the Kramer's equation for the Brownian motion of a harmonic oscillator from which the contraction procedure produces the Smoluchovsky equation.

In Chapter IV the procedure for contraction outlined at the end of Chapter III is applied to the fluctuating Boltzmann's equation from which the fluctuating hydrodynamical theory of Chapter II is derived. To a higher order approximation in the contraction procedure fluctuating Burnett hydrodynamics is also derived. This illuminates a symmetry relation for the Burnett dissipation coefficients which is a kind of higher order reciprocity relation of the Onsager type.

In Chapter V a number of problems are discussed which need further investigation. The primary emphasis is on entropy production in open systems. After discussing entropy production and the second law of thermodynamics for closed systems, open systems are defined and entropy production for them is discussed. An interesting entropy reduction theorem is established for open systems. One simple example of an open system is worked out. It suggests that for open systems the inputs and outputs can be replaced by boundary conditions asymptotically in time, if a steady state develops asymptotically in time. The details are still not clear. Finally, the theory of chemical reaction kinetics is shown also to be an example of the general theory.

From the contents of Chapters II and IV the theory presented is seen to possess a remarkable degree of internal consistency. In Chapter II the Langevin equation is derived from the fluctuating hydrodynamical theory of Landau and Lifshitz. Since the theory of fluctuating hydrodynamics follows from a generalization of the principal mathematical features of the Langevin equation, the derivation of the Langevin

equation from fluctuating hydrodynamics can be considered a check of internal consistency of the theory.

A still better check of internal consistency is contained in Chapter IV. There, the theory of fluctuating hydrodynamics is derived from the fluctuating Boltzmann equation using the Enskog contraction procedure which is presented in Chapter III. Both fluctuating hydrodynamics and the fluctuating Boltzmann equation are examples of general stationary Gaussian Markov processes. General stationary Gaussian Markov processes are shown in Chapter I to be the mathematical characterization of the generalized theory of non-equilibrium thermodynamics. In one of the notes at the end of Chapter IV it is proved that Enskog contraction of a stationary Gaussian Markov process always yields another stationary Gaussian Markov process. This feature permits levels of description of a physical system such that each level is a stationary Gaussian Markov process and such that a given level is derived from the one above it by Enskog contraction. This is the sense in which the general theory is said to be internally consistent.

CHAPTER I

General Theory of Stationary Gaussian Markov Processes¹⁾A. Characterization of Random Processes

Let $a(t)$ denote a time dependent random process. $a(t)$ may represent a single random process or may be thought of as a shorthand for a vector of n random processes. In the latter case, constant functions appearing in some places in the following discussion must be thought of as matrices. Instances of this will be made explicit. $a(t)$ is a random process because at time t the value of $a(t)$ is not definitely known but is given instead by a probability distribution function $W_1(a;t)$ where a is the value $a(t)$ can have at time t with probability determined by $W_1(a;t)$. $W_1(a;t)$ is the first of an infinite collection of distribution functions describing the process $a(t)$. The first two are defined by:

$W_1(a;t)da$ = probability at time t that the value of $a(t)$ is between a and $a + da$.

$W_2(a_1t_1; a_2t_2)da_1da_2$ = probability that at time t_1 the value of $a(t)$ is between a_1 and $a_1 + da_1$ and that at time t_2 the value of $a(t)$ is between a_2 and $a_2 + da_2$.

The higher distributions are defined analogously. W_2 contains W_1 through the identity:

$$W_1(a_1t_1) = \int W_2(a_1t_1; a_2t_2)da_2.$$

Similar relations hold among the other distributions.

The condition that the process $a(t)$ is a stationary process

is equivalent to the requirement that all the distribution functions for $a(t)$ are invariant under time translations. This has as a consequence that $W_1(a;t)$ is independent of t and that $W_2(a_1t_1; a_2t_2)$ depends only on $(t_2 - t_1)$. An even stationary process has the additional requirement that its distribution functions are invariant under time reflection. For W_2 this implies: $W_2(a_1; a_2t) = W_2(a_2; a_1t)$. In the literature, even stationary processes are denoted by $\alpha(t)$. The analogous odd stationary processes are denoted by $\beta(t)$. The general stationary process is not necessarily even or odd.

Stationary processes $a(t)$ are also Gaussian if all of their distribution functions have Gaussian form. For W_1 and W_2 this amounts to

$$W_1(a) \sim \exp\left[-\frac{1}{2} a E a\right]$$

$$W_2(a_1; a_2t) \sim \exp\left[-\frac{1}{2} a_1 A(t) a_1 - a_1 B(t) a_2 - \frac{1}{2} a_2 C(t) a_2\right] . \quad (1)$$

In case $a(t)$ represents a vector of n random processes E , A , B and C are matrices and a , a_1 and a_2 are vectors. The proportionality factors are gotten from the normalization conditions

$$\int W_1(a) da = 1 \quad \text{and} \quad \int W_2(a_1; a_2t) da_1 da_2 = 1 . \quad (2)$$

Before defining a Markovian process $a(t)$, it is necessary to introduce conditional probability functions $P_2(a_1t_1 | a_2t_2)$ and $P_3(a_1t_1; a_2t_2 | a_3t_3)$ defined by

$$P_2(a_1t_1 | a_2t_2) da_2 = \text{probability at time } t_2 \text{ that the value of } a(t) \text{ is between } a_2 \text{ and } a_2 + da_2$$

given that at time $t_1 < t_2$ $a(t)$ had the value a_1 .

$P_3(a_1 t_1; a_2 t_2 | a_3 t_3) da_3$ = probability at time t_3 that the value of $a(t)$ is between a_3 and $a_3 + da_3$ given that at time $t_2 < t_3$ $a(t)$ had the value a_2 and at time $t_1 < t_2$ $a(t)$ had the value a_1 .

These condition distributions are related to the W_n 's by

$$W_2(a_1 t_1; a_2 t_2) = W_1(a_1 t_1) P_2(a_1 t_1 | a_2 t_2)$$

and

$$W_3(a_1 t_1; a_2 t_2; a_3 t_3) = W_2(a_1 t_1; a_2 t_2) P_3(a_1 t_1; a_2 t_2 | a_3 t_3)$$

and so forth for the higher order distributions. The Markov property of $a(t)$ is defined by

$$P_2(a_2 t_2 | a_3 t_3) = P_3(a_1 t_1; a_2 t_2 | a_3 t_3) \quad (3)$$

which means that knowledge of the value of $a(t)$ at time t_1 does not influence the distribution of values of $a(t)$ at time $t_3 > t_1$ if there is also information giving the value of $a(t)$ at the intermediate time t_2 . Therefore, a Markov process $a(t)$ is completely characterized by its W_1 and P_2 or equivalently by only W_2 . A stationary Markov process has distributions satisfying the Smoluchovsky equation

$$W_2(a_1; a_2 t) = \int W_2(a_1; a t-s) P_2(a | a_2 s) da \text{ for all } s \in [0, t] . \quad (4)$$

Proof of (4): For $t_1 < t_3 < t_2$ and using (3),

$$\begin{aligned} W_2(a_1 t_1; a_2 t_2) &= \int W_3(a_1 t_1; a_3 t_3; a_2 t_2) da_3 = \int W_2(a_1 t_1; a_3 t_3) P_3(a_1 t_1; a_3 t_3 | a_2 t_2) da_3 = \\ &= \int W_2(a_1 t_1; a_3 t_3) P_2(a_3 t_3 | a_2 t_2) da_3 \end{aligned}$$

Letting $s = t_2 - t_3$ and $t = t_2 - t_1$ and $a_3 = a$ gives (4) for a stationary process $a(t)$. Q. E. D.

B. The Langevin Equation

The prototype for all physical applications of stationary Gaussian Markov processes is the treatment of Brownian motion using the Langevin equation. The Langevin equation describes the time change of the velocity of a slowly moving collidal particle in a fluid. The effect of interactions between the particle and the fluid molecules may be separated into two parts. One part gives an average effect which produces a frictional drag on the particle proportional to its velocity. The other part is the remaining fluctuating force $\tilde{F}(t)$ which has mean value zero. Therefore, a particle of mass M satisfies the Langevin equation

$$M \frac{du(t)}{dt} = -\alpha u(t) + \tilde{F}(t) \quad (5)$$

where α is the frictional drag coefficient and $u(t)$ is the particle velocity at time t . It is the fluctuating force $\tilde{F}(t)$ which makes $u(t)$ a random process. To characterize this process it is necessary to make assumptions giving the precise character of $\tilde{F}(t)$. Therefore, $\tilde{F}(t)$ will be assumed to be a stationary Gaussian process which is purely random. This last condition is defined by the correlation

formula

$$\langle \tilde{F}(t) \tilde{F}(s) \rangle = 2D\delta(t-s) \quad (6)$$

where D is a constant and the Dirac delta function in time expresses the quality of pure randomness. The linearity of (5) is sufficient to guarantee that $u(t)$ is also a stationary Gaussian process.

Equation (5) must be solved with respect to some initial value $u(o)$. In the conditional distribution for the process $u(t)$ the initial value $u(o)$ will be denoted by u_o giving $P_2(u_o | u(t))$. Because $u(t)$ is a Gaussian process $P_2(u_o | u(t))$ is determined by the mean value of $u(t)$ and its mean square value. Using (6) and recalling that $\langle \tilde{F}(t) \rangle = 0$ it can be proved that

$$\langle u(t) \rangle^{u(o)} = u(o) e^{-\frac{\alpha}{M}t} \quad (7)$$

and

$$\langle u^2(t) \rangle^{u(o)} = u^2(o) e^{-\frac{2\alpha}{M}t} + \frac{D}{\alpha M} (1 - e^{-\frac{2\alpha}{M}t})$$

where the superscript $u(o)$ denotes taking the averages with respect to initial condition $u(o)$.

Proof of (7): The solution to (5) may be written as

$$u(t) = u(o) e^{-\frac{\alpha}{M}t} + e^{-\frac{\alpha}{M}t} \int_o^t e^{\frac{\alpha}{M}s} \frac{1}{M} \tilde{F}(s) ds.$$

Therefore,

$$\langle u(t) \rangle^{u(o)} = u(o) e^{-\frac{\alpha}{M}t}.$$

Squaring and averaging gives

$$\langle u^2(t) \rangle u(o) = u^2(o) e^{-\frac{2\alpha}{M}t} + \frac{1}{M^2} e^{-\frac{2\alpha}{M}t} \int_0^t \int_0^t e^{\frac{\alpha}{M}(s+s')} \langle \tilde{F}(s) \tilde{F}(s') \rangle ds ds' .$$

Using (6) in the integral and substituting $x = s + s'$ and $y = s - s'$ gives the identity

$$\int_0^t \int_0^t e^{\frac{\alpha}{M}(s+s')} \langle \tilde{F}(s) \tilde{F}(s') \rangle ds ds' = \frac{1}{2} \int_0^{2t} \int_{-t}^t e^{\frac{\alpha}{M}x} 2D\delta(y) dy dx = D \frac{M}{\alpha} (e^{\frac{2\alpha}{M}t} - 1) .$$

Therefore

$$\langle u^2(t) \rangle u(o) = u^2(o) e^{-\frac{2\alpha}{M}t} + \frac{D}{\alpha M} (1 - e^{-\frac{2\alpha}{M}t}) . \quad \underline{\text{Q. E. D.}}$$

Using the abbreviations $\sigma^2 = \frac{D}{\alpha M}$ and $\rho(t) = e^{-\frac{\alpha}{M}t}$, $P_2(u_o | ut)$ is

given by

$$P_2(u_o | ut) = [2\pi\sigma^2(1-\rho^2(t))]^{-1/2} \exp\left[-\frac{(u-u_o\rho(t))^2}{2\sigma^2(1-\rho^2(t))}\right] \quad (8)$$

which is checked by seeing if it gives back (7). The check follows from the integrals

$$\langle u \rangle^{u_o} = \int u P_2(u_o | ut) du = u_o \rho(t)$$

and

$$\langle u^2 \rangle^{u_0} = \int u^2 P_2(u_0 | ut) du = u_0^2 \rho^2(t) + \frac{D}{\alpha M} (1 - \rho^2(t)) .$$

From (8) it is easily seen that the limit $t \rightarrow \infty$ eliminates any influence of the initial value u_0 . Therefore

$$\lim_{t \rightarrow \infty} P_2(u_0 | ut) = W_1(u)$$

which gives

$$W_1(u) = \left[2\pi \frac{D}{\alpha M} \right]^{-1/2} \exp \left[- \frac{\alpha M u^2}{2D} \right] .$$

However, it will be assumed that $W_1(u)$ should also be given by the Maxwell distribution

$$W_1(u) = \left[2\pi \frac{K_B T}{M} \right]^{-1/2} \exp \left[- \frac{M u^2}{2K_B T} \right]$$

where K_B is Boltzmann's constant and T is the constant temperature of the fluid. These two expressions for $W_1(u)$ result in the Einstein relation

$$D = K_B T \alpha . \quad (9)$$

Putting (9) into (6) gives the prototype example of what is called in the

literature a fluctuation-dissipation theorem

$$\langle \tilde{F}(t)\tilde{F}(s) \rangle = 2K_B T \alpha \delta(t-s) \quad . \quad (10)$$

The name follows from the connection expressed in (10) between the correlation of the fluctuating force and the dissipative constant α the frictional drag coefficient.

Finally, from (8) and $W_1(u)$, $W_2(u_0; ut)$ is given by $W_2 = W_1 P_2$.

These distributions satisfy the Smoluchosvky equation (4) as is seen by performing the integral and thereby guarantees that $u(t)$ is also Markovian²⁾. Consequently, $u(t)$ is an example of a stationary Gaussian Markov process. Written in the form (5) the equation for $u(t)$ describes what is called in the literature an Ornstein-Uhlenbeck process or more simply an O-U process.

As a final point in this discussion of the Langevin equation it is possible to consider an ensemble of particles in Brownian motion. The approach of P_2 to W_1 as $t \rightarrow \infty$ represents a kind of diffusion process in velocity space. The description in these terms is known in the literature as the Fokker-Planck or diffusion equation method for Brownian motion. This point of view will be used only occasionally in the subsequent chapters. Therefore, it will suffice merely to state the result which is that for O-U processes the Fokker-Planck equation is

$$\frac{\partial}{\partial t} P(u, t) = \frac{\alpha}{M} \frac{\partial}{\partial u} (u P(u, t)) + D \frac{\partial^2 P(u, t)}{\partial u^2} \quad (11)$$

subject to the initial condition that $P(u, 0) = \delta(u - u_0)$. The solution to (11) with this initial condition gives precisely $P_2(u_0 | ut)$ given in (8).

C. Theory of Irreversible Thermodynamics following Onsager

The theory of irreversible thermodynamics presented by Onsager and Machlup generalizes the application of the ideas of stationary Gaussian Markov processes. For a system which is close to equilibrium, it is assumed that its state is described by a set of extensive thermodynamical variables $\alpha_1(t) \dots \alpha_n(t)$. In equilibrium the α_i 's are all taken to have value zero so that near equilibrium the entropy is given by

$$S = S_0 - \frac{1}{2} K_B \alpha_i E_{ij} \alpha_j \quad (12)$$

where S_0 is the equilibrium value of the entropy and E_{ij} is a symmetric positive definite time independent matrix³⁾. Thermodynamical forces are defined by

$$X_i = \frac{\partial S}{\partial \alpha_i} = - K_B E_{ij} \alpha_j \quad (13)$$

It is at this point assumed that the phenomenological equations for irreversible processes are given by

$$R_{ij} \dot{\alpha}_j = X_i = - K_B E_{ij} \alpha_j \quad (14)$$

which is a natural generalization of linear phenomenological laws such as Fourier's law of heat conduction, Newton's law of internal friction, etc. The matrix R_{ij} is real and of positive type⁴⁾ in order to ensure that (14) describes regression equations whose solutions approach equilibrium asymptotically in time.

Since the α_i 's are thermodynamical quantities, their values fluctuate in time. Therefore, (14) is properly interpreted as the

average regression equations for a random process which is actually driven by random thermodynamical forces $\tilde{e}_i(t)$. The completed equations are

$$R_{ij} \dot{\alpha}_j = -K_B E_{ij} \alpha_j + \tilde{e}_i \quad . \quad (15)$$

The mean values of the \tilde{e}_i 's are all zero and they are each assumed to be purely random stationary Gaussian processes. The linearity of (15) guarantees that the random process described by the α_i 's is also a stationary Gaussian process. Denoting the inverse of R_{ij} by L_{ij} and using the definition

$$\tilde{F}_i = L_{ij} \tilde{e}_j$$

(15) may be written as

$$\dot{\alpha}_i = -K_B L_{ij} E_{jk} \alpha_k + \tilde{F}_i \quad . \quad (16)$$

Since \tilde{F}_i is linearly related to the \tilde{e}_j 's it is also a purely random stationary Gaussian process. This property is explicitly expressed by

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2Q_{ij} \delta(t - s) \quad (17)$$

where Q_{ij} is necessarily a symmetric positive definite time independent matrix.

Equation (16) has its solution

$$\alpha_i(t) = [e^{-Gt}]_{ij} \alpha_j(o) + [e^{-Gt}]_{ij} \int_0^t [e^{Gs}]_{jk} \tilde{F}_k(s) ds \quad (18)$$

where $G_{ij} = K_B L_{ik} E_{kj}$ and the notation $[e^{-Gt}]_{ij}$ means $\sum_{n=0}^{\infty} \frac{(-t)^n}{n!} (G^n)_{ij}$.

The $\alpha_j(o)$'s are the initial values. From (18) it follows that

$$\langle \alpha_i(t) \rangle^{\alpha(o)} = [e^{-Gt}]_{ij} \alpha_j(o)$$

and

(19)

$$\begin{aligned} \langle \alpha_i(t) \alpha_j(t) \rangle^{\alpha(o)} &= [e^{-Gt}]_{im} [e^{-Gt}]_{jn} \alpha_m(o) \alpha_n(o) \\ &+ M_{ij}^{-1} - [e^{-Gt}]_{im} M_{mn}^{-1} [e^{-G^+t}]_{nj} \end{aligned}$$

where M_{ij}^{-1} is defined by

$$2Q_{ij} = G_{ik} M_{kj}^{-1} + M_{ik}^{-1} G_{kj}^+$$

and G^+ signifies the transpose of G . The superscript $\alpha(o)$ denotes the initial values of the α_i 's in vector notation.

Proof of (19)

$$\langle \alpha_i(t) \rangle^{\alpha(o)} = [e^{-Gt}]_{ij} \alpha_j(o)$$

follows from (18)

$$\begin{aligned} \langle \alpha_i(t) \alpha_j(t) \rangle^{\alpha(o)} &= [e^{-Gt}]_{im} [e^{-Gt}]_{jn} \alpha_m(o) \alpha_n(o) \\ &+ [e^{-Gt}]_{im} [e^{-Gt}]_{jn} \int_0^t \int_0^t [e^{Gs}]_{mp} [e^{Gs'}]_{nq} \langle \tilde{F}_p(s) \tilde{F}_q(s') \rangle ds ds' . \end{aligned}$$

Using (17) the integrals become

$$\int_0^t \int_0^t [e^{Gs}]_{mp} [e^{Gs'}]_{nq} {}^2Q_{pq} \delta(s-s') ds ds' .$$

Changing variable to $x = s + s'$ and $y = s - s'$ gives the equivalent integrals

$$\frac{1}{2} \int_0^{2t} \int_{-t}^t [e^{\frac{1}{2}G(x+y)}]_{mp} [e^{\frac{1}{2}G(x-y)}]_{nq} {}^2Q_{pq} \delta(y) dy dx = \int_0^{2t} [e^{\frac{1}{2}Gx}]_{mp} Q_{pq} [e^{\frac{1}{2}G^+x}]_{qn} dx .$$

Changing variable again to $x = 2s$ gives the equivalent integral

$$2 \int_0^t [e^{Gs}]_{mp} Q_{pq} [e^{G^+s}]_{qn} ds .$$

Therefore

$$\begin{aligned} \langle \alpha_i(t) \alpha_j(t) \rangle &= [e^{-Gt}]_{im} [e^{-Gt}]_{jn} \alpha_m(o) \alpha_n(o) \\ &+ 2 \int_0^t [e^{-G(t-s)}]_{ip} Q_{pq} [e^{-G^+(t-s)}]_{qj} ds . \end{aligned}$$

Defining M_{ij}^{-1} as in (19) permits writing the last integral as

$$\int_0^t \frac{d}{ds} \left\{ [e^{-G(t-s)}]_{ip} M_{pq}^{-1} [e^{-G^+(t-s)}]_{qj} \right\} ds = M_{ij}^{-1} [e^{-Gt}]_{ip} M_{pq}^{-1} [e^{-G^+t}]_{qj} .$$

Putting this into the last expression for $\langle \alpha_i(t) \alpha_j(t) \rangle^{\alpha(o)}$ yields the remainder of (19). Q. E. D.

Equations (19) are sufficient to determine $P_2(\alpha_o | \alpha t)$ since it is Gaussian. The α_o vector corresponds to the vector of initial values $\alpha(o)$. With the definition

$$V_{ij}^{-1} = M_{ij}^{-1} - [e^{-Gt}]_{im} M_{mn}^{-1} [e^{-G^+t}]_{nj} \quad ,$$

$P_2(\alpha_o | \alpha t)$ may be written as

$$P_2(\alpha_o | \alpha t) = \left[\frac{\|V\|}{(2\pi)^n} \right]^{1/2} \exp \left[-\frac{1}{2} V_{\ell k} (\alpha_\ell - [e^{-Gt}]_{\ell m} \alpha_m^o) (\alpha_k - [e^{-G^+t}]_{kn} \alpha_n^o) \right] \quad (20)$$

where the α_m^o 's are the components of α_o and $\|V\|$ is the determinant of V_{ij} . Expression (20) is checked by seeing if it gives back (19) using the integrals

$$\langle \alpha_i \rangle^{\alpha_o} = \int \alpha_i P_2(\alpha_o | \alpha t) d\alpha \quad \text{and} \quad \langle \alpha_i \alpha_j \rangle^{\alpha_o} = \int \alpha_i \alpha_j P_2(\alpha_o | \alpha t) d\alpha \quad .$$

From (20) it follows that the limit $t \rightarrow \infty$ eliminates any influence of the initial state α_o . Also $\lim_{t \rightarrow \infty} V_{ij}^{-1} = M_{ij}^{-1}$. Therefore, $\lim_{t \rightarrow \infty} P_2 = W_1$ which gives for W_1 the expression

$$W_1(\alpha) = \left[\frac{\|M\|}{(2\pi)^n} \right]^{1/2} \exp \left[-\frac{1}{2} \alpha_\ell M_{\ell k} \alpha_k \right] \quad .$$

However, from the expression for the entropy given in (12) and the Boltzmann-Planck relation connecting entropy and probability, W_1

should also be given by

$$W_1(\alpha) = \left[\frac{\|E\|}{(2\pi)^n} \right]^{1/2} \exp\left[-\frac{1}{2} \alpha^T E \alpha\right] .$$

These two expressions result in the identity

$$E_{ij} = M_{ij} \quad (21)$$

which is the generalization of Einstein's relation (9). Putting (21) into the definition of M_{ij} and putting that into (17) gives the fluctuation-dissipation theorem

$$\left\langle \tilde{F}_i(t) \tilde{F}_j(s) \right\rangle = [G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{kj}^+] \delta(t-s) . \quad (22)$$

The α notation has been used throughout this discussion because Onsager and Machlup make the additional assumption that the process is even in time. It will now be shown that this assumption leads to the celebrated Onsager reciprocity relation⁵⁾. Recall from section A that evenness implies that

$$W_2(\alpha_1, \alpha_2, t) = W_2(\alpha_2, \alpha_1, t) .$$

From

$$\begin{aligned} \int \alpha_{1i} \alpha_{2j} W_2(\alpha_1, \alpha_2, t) d\alpha_1 d\alpha_2 &= \int \alpha_{1i} W_1(\alpha_1) \alpha_{2j} P_2(\alpha_1 | \alpha_2, t) d\alpha_1 d\alpha_2 = \\ &= \int \alpha_{1i} W_1(\alpha_1) [e^{-Gt}]_{jk} \alpha_{1k} d\alpha_1 = \int \alpha_{1i} W_1(\alpha_1) \alpha_{1k} [e^{-G^+t}]_{kj} d\alpha_1 = E_{ik}^{-1} [e^{-G^+t}]_{kj} \end{aligned}$$

and similarly from

$$\int \alpha_1 \alpha_2 W_2(\alpha_2, \alpha_1 t) d\alpha_1 d\alpha_2 = E_{jk}^{-1} [e^{-G^+ t}]_{ki}$$

the evenness, therefore, requires the identity

$$E_{ik}^{-1} [e^{-G^+ t}]_{kj} = E_{jk}^{-1} [e^{-G^+ t}]_{ki} \quad .$$

Taking the time derivative of this identity at $t = 0$ gives

$$E_{ik}^{-1} G_{kj}^+ = E_{jk}^{-1} G_{ki}^+$$

which may be rewritten as

$$E_{ik}^{-1} G_{kj}^+ = G_{ik} E_{kj}^{-1}$$

wherein the symmetry of E_{ij}^{-1} was used. Recalling the definition of G_{ij} this leads to the Onsager reciprocity relation

$$L_{ij} = L_{ji} \quad . \quad (23)$$

In this case the fluctuation-dissipation theorem (22) takes on the elegant form

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2L_{ij} \delta(t-s) \quad . \quad (24)$$

The symmetry of L_{ij} implies that of R_{ij} since $L_{ij} = R_{ij}^{-1}$.

Since R_{ij} was assumed to be of positive type, in this case R_{ij} is positive which implies that it has positive real eigenvalues. The matrix $R_{ij}^{1/2}$ therefore, can be defined and it is also symmetric. Defining $\alpha_i' = R_{ij}^{1/2} \alpha_j$ permits writing for (15)

$$\dot{\alpha}_i' = -K_B R_{ij}^{-1/2} E_{jk} R_{kl}^{-1/2} \alpha_l' + R_{ij}^{-1/2} \tilde{e}_j \quad . \quad (25)$$

Since $\tilde{e}_i = R_{ji} \tilde{F}_i$, (24) implies that

$$\left\langle R_{il}^{-1/2} \tilde{e}_l(t) R_{jk}^{-1/2} \tilde{e}_k(s) \right\rangle = 2 \delta_{ij} \delta(t-s) \quad , \quad (26)$$

The matrix $R_{ij}^{-1/2} E_{jk} R_{kl}^{-1/2}$ is real, symmetric, and positive definite.

Therefore, it may be diagonalized by an orthogonal matrix O_{ij} .

Denote the eigenvalues of $R_{ij}^{-1/2} E_{jk} R_{kl}^{-1/2}$ by λ_i and define α_i''

by $\alpha_i'' = O_{ij} \alpha_j'$ where

$$O_{ij} R_{jk}^{-1/2} E_{kl} R_{lm}^{-1/2} O_{mn}^+ = \lambda_i \delta_{in} \quad .$$

This converts (25) into

$$\dot{\alpha}_i'' = -K_B \lambda_i \alpha_i'' + O_{ij} R_{jk}^{-1/2} \tilde{e}_k \quad . \quad (27)$$

Defining $\tilde{\theta}_i$ by

$$\tilde{\theta}_i = O_{ij} R_{jk}^{-1/2} \tilde{e}_k$$

it follows from (26) that

$$\langle \tilde{\theta}_i(t) \tilde{\theta}_j(s) \rangle = 2 O_{il} O_{jk} \delta_{lk} \delta(t-s) = 2 \delta_{ij} \delta(t-s) \quad (28)$$

since O_{ij} is an orthogonal matrix. Therefore, the Onsager and Machlup theory of irreversible thermodynamics may always be written in the form of n independent O-U processes

$$\ddot{\alpha}_i'' = -K_B \lambda_i \alpha_i'' + \tilde{\theta}_i \quad . \quad (29)$$

Consequently, the theory is also Markovian, a conclusion which could have been drawn earlier from (20) and the Smoluchovsky equation.

D. General Stationary Gaussian Markov Processes

Motivated by the preceding treatment of the Langevin equation and of the Onsager and Machlup theory of irreversible thermodynamics, it is natural to ask two questions. What is the most general stationary Gaussian Markov process? What is the associated fluctuation-dissipation theorem? This section is devoted to answering these two questions.

The state of a system will be described by a set of variables $a_1(t) \dots a_n(t)$. Nothing is assumed concerning their time reflection properties as was done in the Onsager and Machlup theory. All that is assumed is that the process is a stationary Gaussian Markov process whose regression equations describe an approach to equilibrium asymptotically in time. The equilibrium values of the a_i 's are taken to be zero.

The Gaussian assumption and the assumption of stationarity require that the first and second probability distributions have the form⁶⁾

$$W_1(a) = W_o \exp\left[-\frac{1}{2} a_i E_{ij} a_j\right]$$

$$P_2(a | a't) = C \exp\left[-\frac{1}{2} a_i A_{ij} a_j - a_i B_{ij} a'_j - \frac{1}{2} a'_i C_{ij} a'_j\right] \quad (30)$$

where E_{ij} is a time independent symmetric positive definite matrix,

$$W_o = \left[\frac{\|E\|}{(2\pi)^n}\right]^{1/2}, \quad A_{ij} \text{ and } C_{ij} \text{ are symmetric positive definite}$$

matrices depending on t and B_{ij} is a matrix depending on t but with no other special properties. C is a constant which will be determined below. Because P_2 must satisfy the normalization condition

$\int P_2(a | a't) da' = 1$ it must be of the form

$$P_2(a | a't) = C \exp\left[-\frac{1}{2} (a'_i - D_{i\ell} a_\ell) C_{ij} (a'_j - D_{jk} a_k)\right] \quad (31)$$

where the constant C is given by $C = \left[\frac{\|C\|}{(2\pi)^n}\right]^{1/2}$. The equality of (30) and (31) determines A_{ij} and B_{ij} in terms of C_{ij} and D_{ij} by

$$A_{ij} = D_{ik}^+ C_{k\ell} D_{\ell j} \quad \text{and} \quad B_{ij} = -D_{ik}^+ C_{kj} \quad (32)$$

Proof of (32): Equality of (30) and (31) implies

$$\begin{aligned} -\frac{1}{2} a_i A_{ij} a_j - a_i B_{ij} a'_j - \frac{1}{2} a'_i C_{ij} a'_j &= -\frac{1}{2} D_{i\ell} a_\ell C_{ij} D_{jk} a_k + \frac{1}{2} D_{i\ell} a_\ell C_{ij} a'_j \\ &+ \frac{1}{2} a'_i C_{ij} D_{jk} a_k - \frac{1}{2} a'_i C_{ij} a'_j \end{aligned}$$

Therefore,

$$A_{ij} = D_{li} C_{lk} D_{kj} \quad \text{and} \quad B_{ij} = -\frac{1}{2} D_{li} C_{lj} - \frac{1}{2} C_{jk} D_{ki} \quad .$$

From these identities (32) follows: Q. E. D.

From the condition

$$\int W_1(a) P_2(a|a't) da = W_1(a')$$

it follows that

$$C_{ij}^{-1} = E_{ij}^{-1} - D_{ik} E_{kl}^{-1} D_{lj}^+ \quad . \quad (33)$$

Therefore P_2 is completely determined by the two matrices E_{ij} and D_{ij} .

Proof of (33): The integral to do in order to obtain (33) is

$$W_0 C \int \exp\left[-\frac{1}{2} a_i (E_{ij} + A_{ij}) a_j - a_i B_{ij} a'_j - \frac{1}{2} a'_i C_{ij} a'_j\right] da$$

using (30). The exponent may be written as

$$-\frac{1}{2} (a_i - K_{il} a'_l) (E_{ij} + A_{ij}) (a_j - K_{jk} a'_k) + \frac{1}{2} K_{il} a'_l (E_{ij} + A_{ij}) K_{jk} a'_k - \frac{1}{2} a'_i C_{ij} a'_j$$

where K_{ij} is given by

$$B_{ij} = - (E_{ik} + A_{ik}) K_{kj} \quad .$$

With the exponent in this form the a integration is easily done and

produces a constant factor of $[\frac{\|E+A\|}{(2\pi)^n}]^{-1/2}$. Therefore, the identity becomes

$$W_o C [\frac{\|E+A\|}{(2\pi)^n}]^{-1/2} \exp[\frac{1}{2} K_{i\ell} a'_\ell (E_{ij} + A_{ij}) K_{jk} a'_k - \frac{1}{2} a'_i C_{ij} a'_j] = W_o \exp[-\frac{1}{2} a'_i E_{ij} a'_j] .$$

From this expression it follows that

$$E_{ij} = C_{ij} - K_{i\ell}^+ (E_{\ell k} + A_{\ell k}) K_{kj}$$

if

$$C = [\frac{\|E+A\|}{(2\pi)^n}]^{1/2} .$$

It is convenient to prove this last identity later and for the time being to assume that it is true. Using (32) the defining relation for K_{ij} becomes

$$D^+ C = (E + D^+ C D) K .$$

The expression

$$E = C - K^+ (E + A) K$$

becomes

$$E = C + K^+ B = C - K^+ D^+ C .$$

Taking the transpose of this equation gives

$$E = C - C D K$$

from which multiplication by D^+ gives

$$D^+C = D^+E + D^+CDK \quad .$$

From the earlier expression above for D^+C it follows that

$$EK = D^+E \quad .$$

Finally, this gives for K the convenient expression

$$K = E^{-1}D^+E \quad .$$

From $E = C - CDK$ this new expression for K gives

$$E = C - CDE^{-1}D^+E \quad .$$

Multiplying from the left with C^{-1} and from the right with E^{-1} gives

$$C^{-1} = E^{-1} - DE^{-1}D^+$$

which is (33). Now to prove

$$C = \left[\frac{\|E+A\|}{(2\pi)^n} \right]^{1/2}$$

recall that

$$C = \left[\frac{\|C\|}{(2\pi)^n} \right]^{1/2}$$

so that it becomes necessary to show that $\|C\| = \|E+A\|$. From

$K = E^{-1}D^+E$ it follows that $\|K\| = \|D\|$. However, the defining relation for K using the expression (32) for B gives $\|D\| \|C\| = \|E+A\| \|K\|$ which with $\|K\| = \|D\|$ implies $\|C\| = \|E+A\|$. Q. E. D.

The form of P_2 in (31) implies the relation

$$\langle a_i^! \rangle^a = \int a_i^! P_2(a | a^!t) da^! = D_{ij}(t) a_j \quad (34)$$

wherein the time dependence of D_{ij} has been made explicit.

At this point the Markov character of the process may be introduced through the Smoluchovsky equation in the form

$$P_2(a | a't) = \int P_2(a | a''t-s) P_2(a'' | a's) da'' \quad \text{for all } s \in [0, t] . \quad (35)$$

Therefore, (34) implies

$$\begin{aligned} D_{ij}(t) a_j &= \int a'_i P_2(a | a''t-s) P_2(a'' | a's) da'' da' = \int P_2(a | a''t-s) D_{ij}(s) a''_j da'' = \\ &= D_{ij}(s) D_{jk}(t-s) a_k . \end{aligned}$$

From this it follows that

$$D_{ij}(t) = D_{ik}(s) D_{kj}(t-s) .$$

The solution to this identity is the Doob formula

$$D_{ij}(t) = [e^{-Gt}]_{ij} \quad (36)$$

where G_{ij} is a time independent matrix with no particular symmetry properties. Putting (36) into (34) and taking the time derivative gives the regression equations for the average behavior

$$\frac{d}{dt} \langle a'_i \rangle^a = - G_{ij} \langle a'_j \rangle^a . \quad (37)$$

In order that (37) actually describes an approach to equilibrium it is necessary to assume that the real parts of the eigenvalues of G_{ij} are positive. G_{ij} may always be written as the sum of an antisymmetric

matrix A_{ij} and a symmetric matrix S_{ij} . It is sufficient to assume that S_{ij} is positive definite in order to guarantee that the real parts of the eigenvalues of G_{ij} are positive. Therefore, the positive-definiteness of S_{ij} will be assumed and G_{ij} will always be written as $G_{ij} = A_{ij} + S_{ij}$.

By introducing purely random stationary Gaussian thermodynamical forces $\tilde{F}_i(t)$, (37) may be completed to a generalized O-U process

$$\frac{d}{dt}a_i + A_{ij}a_j + S_{ij}a_j = \tilde{F}_i \quad . \quad (38)$$

The \tilde{F}_i 's are assumed to satisfy

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2Q_{ij} \delta(t-s) \quad . \quad (39)$$

It is clear that (38) describes a stationary Gaussian process because of its linearity and the character of the \tilde{F}_i 's. It is also Markovian because it produces the expression for P_2 in (31) if

$$2Q_{ij} = G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{kj}^+ \quad . \quad (40)$$

The proof of this last claim goes in a manner identical with the proof of (20) in the previous section. Relation (40) produces the generalized fluctuation-dissipation theorem

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = [G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{kj}^+] \delta(t-s) \quad . \quad (41)$$

Therefore, the most general stationary Gaussian Markov process which converges asymptotically in time is the generalized O-U process (38) wherein the fluctuating forces $\tilde{F}_i(t)$ satisfy the generalized fluctuation-

dissipation theorem (41). In note 3) of Chapter IV a canonical form for equations (38) and (41) is derived. It is given by equations (VI) and (VII) of the note. These equations show that the general case just discussed corresponds to n coupled O-U processes.

E. Brownian Motion of a Harmonic Oscillator as an Example

The Brownian motion of a harmonic oscillator is governed by the equations

$$M \frac{dx}{dt} = p \quad \text{and} \quad \frac{dp}{dt} + \frac{\alpha}{M} p + M\omega^2 x = \tilde{F} \quad (42)$$

where \tilde{F} is a purely random stationary Gaussian process satisfying

$$\langle \tilde{F}(t) \tilde{F}(s) \rangle = 2D\delta(t-s) \quad . \quad (43)$$

Let $y = M\omega x$. Equations (42) become

$$\frac{dy}{dt} - \omega p = 0 \quad \text{and} \quad \frac{dp}{dt} + \omega y + \frac{\alpha}{M} p = \tilde{F} \quad . \quad (44)$$

Letting

$$a_i = \begin{pmatrix} y \\ p \end{pmatrix}, \quad A_{ij} = \begin{pmatrix} 0 & -\omega \\ \omega & 0 \end{pmatrix}, \quad S_{ij} = \begin{pmatrix} 0 & 0 \\ 0 & \frac{\alpha}{M} \end{pmatrix} \quad \text{and} \quad \tilde{F}_i = \begin{pmatrix} 0 \\ \tilde{F} \end{pmatrix}$$

permits writing (44) as

$$\frac{d}{dt} a_i + A_{ij} a_j + S_{ij} a_j = \tilde{F}_i \quad . \quad (45)$$

Since the W_1 for this process is the Maxwell-Boltzmann distribution

$$W_1(y, p) = W_0 \exp \left[-\frac{1}{2} \frac{p^2}{MK_B T} - \frac{1}{2} \frac{y^2}{MK_B T} \right] \quad (46)$$

the E_{ij} matrix is diagonal and is given by $E_{ij} = \frac{1}{MK_B T} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$.

Putting this value of E_{ij} into (41) gives

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2MK_B T S_{ij} \delta(t-s) \quad . \quad (47)$$

Using (43) and the definition of S_{ij} gives $D = K_B T \alpha$. Therefore, the Brownian motion of a harmonic oscillator is an example of the general stationary Gaussian Markov process of form (38). There is, however, one point of difference. The matrix S_{ij} has one zero eigenvalue. This corresponds to the fact that only the p equation in (44) is driven by a fluctuating force. Similar situations with zero eigenvalues for S_{ij} will occur in the following chapters. As an extension of the general stationary Gaussian Markov processes already discussed, those with S_{ij} 's having zero eigenvalues are also permitted. In these cases S_{ij} is only semi-positive definite.

Finally it should be noted for use in a later chapter that for an ensemble of harmonic oscillators undergoing Brownian motion, the corresponding Fokker-Planck equation is

$$\frac{\partial}{\partial t} P(xpt) + \frac{p}{M} \frac{\partial}{\partial x} P(xpt) - M \omega^2 x \frac{\partial}{\partial p} P(xpt) = \frac{\alpha}{M} \left[\frac{\partial}{\partial p} p P(xpt) \right] + MK_B T \frac{\partial^2}{\partial p^2} P(xpt) \quad (43)$$

which has to be solved with the initial condition $P(xp_0) = \delta(x-x_0) \delta(p-p_0)$. In this form, (43) was first derived by Kramers⁷⁾.

NOTES

- 1) Only a short outline of the theory will be presented in order to give the general background for the developments presented in the following chapters. The primary references are: G. E. Uhlenbeck and L. S. Ornstein, *Physical Review*, 36, 823, (1930); M. C. Wang and G. E. Uhlenbeck, *Reviews of Modern Physics*, 17, 323, (1945); L. Onsager and S. Machlup, *Physical Review*, 91, 1505, (1953); and the book by S. R. deGroot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, (1962).
- 2) In general the Smoluchovsky equation does not imply the Markov property. Counterexamples have been presented in the literature. However, they are all non-Gaussian. It appears that the Smoluchovsky equation does imply the Markov property for Gaussian processes which is the case at hand.
- 3) The summation convention for repeated matrix indices will be used often in all chapters.
- 4) A matrix is by definition of positive type if the real parts of all its eigenvalues are positive. R_{ij} is not necessarily symmetric but it cannot be singular so that R_{ij}^{-1} will exist.
- 5) L. Onsager, *Physical Review*, 37, 405, (1931).
- 6) The following argument was suggested by S. R. deGroot. See the book of deGroot and Mazur in 1), p. 470.
- 7) Kramers, *Physica*, 7, 284, (1940).

CHAPTER II

Hydrodynamical Fluctuations

A. The Classical Hydrodynamical Equations

The theory of stationary Gaussian Markov processes developed in Chapter I is shown in this chapter to be applicable to the problem of obtaining a theory of hydrodynamical fluctuations. Such a theory would make possible the computation of correlations of fluctuating hydrodynamical quantities used to describe a fluid in motion. That hydrodynamical quantities fluctuate is a consequence of the fact that they are macroscopic quantities and give a contracted description of the behavior of the fluid. Landau and Lifshitz have proposed a theory for hydrodynamical fluctuations.¹⁾ The linearized form of their theory will be derived in this chapter as an example of a stationary Gaussian Markov process of the most general form.

To begin the derivation, it is first necessary to summarize classical non-fluctuating Navier-Stokes hydrodynamics. The equations are

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial x_\alpha} (\rho u_\alpha) = 0 \quad (1)$$

$$\rho \frac{D}{Dt} u_\alpha = - \frac{\partial}{\partial x_\beta} P_{\alpha\beta} \quad (2)$$

$$\rho \frac{D}{Dt} e = - \frac{\partial}{\partial x_\alpha} q_\alpha - P_{\alpha\beta} D_{\alpha\beta} \quad (3)$$

where ρ is the mass density, u_α is the local velocity, and e is the internal energy density per gram. $\frac{D}{Dt}$ means $\frac{\partial}{\partial t} + u_\alpha \frac{\partial}{\partial x_\alpha}$ and

$$D_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right), \quad P_{\alpha\beta} = p \delta_{\alpha\beta} - 2\eta (D_{\alpha\beta} - \frac{1}{3} D_{\gamma\gamma} \delta_{\alpha\beta}) - \xi D_{\gamma\gamma} \delta_{\alpha\beta}$$

and $q_\alpha = -K \frac{\partial T}{\partial x_\alpha}$ where p is the local pressure and T is the local temperature. η , ξ and K are the transport coefficients: shear viscosity, bulk viscosity, and heat conductivity respectively. Equations (1), (2), and (3) must be completed by giving the equation of state $p = p(\rho, T)$ and the thermal equation of state $e = e(\rho, T)$. These two state equations are not independent and are related through the second law of thermodynamics by

$$\rho^2 \frac{\partial e}{\partial \rho} = p - T \frac{\partial p}{\partial T} \quad . \quad (4)$$

Writing the two laws of thermodynamics as

$$de = T ds + \frac{p}{\rho^2} d\rho \quad (5)$$

and using

$$P_{\alpha\beta} D_{\alpha\beta} = p \frac{\partial}{\partial x_\alpha} u_\alpha - 2\eta D_{\alpha\beta} D_{\alpha\beta} - (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2$$

in (3) and $\frac{\partial}{\partial x_\alpha} u_\alpha = -\frac{1}{\rho} \frac{D}{Dt} \rho$ from (1) gives for the entropy per gram,

s , the equation

$$\rho T \frac{D}{Dt} s = \frac{\partial}{\partial x_\alpha} \left(K \frac{\partial T}{\partial x_\alpha} \right) + 2\eta D_{\alpha\beta} D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma}^2 \quad . \quad (6)$$

Defining the total entropy, S by $S = \int \rho s dV$ gives for \dot{S}

$$\dot{S} = \int \left\{ \frac{K \left(\frac{\partial}{\partial x_\alpha} T \right) \left(\frac{\partial}{\partial x_\alpha} T \right)}{T^2} + \frac{1}{T} \left[2\eta D_{\alpha\beta} D_{\alpha\beta} + \left(\xi - \frac{2}{3}\eta \right) D_{\delta\delta}^2 \right] \right\} dV. \quad (7)$$

Proof of (7):

$$\begin{aligned} \frac{d}{dt} \int \rho s dV &= \int \left[s \frac{\partial}{\partial t} \rho + \rho \frac{\partial}{\partial t} s \right] dV = \int \left\{ -s \frac{\partial}{\partial x_\alpha} (\rho u_\alpha) - \rho u_\alpha \frac{\partial}{\partial x_\alpha} s + \right. \\ &\left. + \frac{1}{T} \frac{\partial}{\partial x_\alpha} \left(K \frac{\partial}{\partial x_\alpha} T \right) + \frac{1}{T} \left(2\eta D_{\alpha\beta} D_{\alpha\beta} + \left(\xi - \frac{2}{3}\eta \right) D_{\delta\delta}^2 \right) \right\} dV \end{aligned}$$

from (1) and (6). The first two terms of the integral are $-\frac{\partial}{\partial x_\alpha} (\rho s u_\alpha)$

which when integrated may be converted to a surface integral of the normal component of $\rho s u_\alpha$ at the surface of the system. This must be zero since no momentum flows across the surface.

$$\frac{1}{T} \frac{\partial}{\partial x_\alpha} \left(K \frac{\partial}{\partial x_\alpha} T \right) = \frac{\partial}{\partial x_\alpha} \left(\frac{K \frac{\partial}{\partial x_\alpha} T}{T} \right) + \frac{K}{T^2} \left(\frac{\partial}{\partial x_\alpha} T \right) \left(\frac{\partial}{\partial x_\alpha} T \right).$$

The first term when integrated may be converted to a surface integral of the normal component of $\frac{K}{T} \frac{\partial}{\partial x_\alpha} T$ at the surface of the system.

This must also be zero since no heat fluxes across the surface.

Therefore, (7) results. Q. E. D.

The form of the integrand in (7) guarantees that $\dot{S} \geq 0$.

B. The Linearized Hydrodynamical Equations

It will now be shown that when linearized, equations (1) through (3) may be put into the form of the average regression equations for a stationary Gaussian Markov process

$$\frac{d}{dt} a_i + A_{ij} a_j = -S_{ij} a_j \quad , \quad (8)$$

Denote the equilibrium density by ρ_{eq} , the equilibrium temperature by T_{eq} , and take the equilibrium velocity to be zero. The deviation of the density from ρ_{eq} is denoted by $\Delta\rho$, the deviation from equilibrium of the temperature is denoted by ΔT , and the velocity deviation is denoted by u_α . Define the constants A , B and C by

$$A = \left(\frac{\partial p}{\partial \rho}\right)_{eq} \quad , \quad B = \left(\frac{\partial p}{\partial T}\right)_{eq} \quad , \quad \text{and} \quad C = \left(\frac{\partial e}{\partial T}\right)_{eq} \quad . \quad (9)$$

The linearized equations may now be written in the form

$$\frac{\partial}{\partial t} \Delta\rho + \rho_{eq} \frac{\partial}{\partial x_\alpha} u_\alpha = 0 \quad (10)$$

$$\rho_{eq} \frac{\partial u_\alpha}{\partial t} + A \frac{\partial}{\partial x_\alpha} \Delta\rho + B \frac{\partial}{\partial x_\alpha} \Delta T = \frac{\partial}{\partial x_\beta} [2\eta D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\delta\delta} \delta_{\alpha\beta}] \quad (11)$$

$$\rho_{eq} C \frac{\partial}{\partial t} \Delta T + T_{eq} B \frac{\partial}{\partial x_\alpha} u_\alpha = K \frac{\partial^2}{\partial x_\alpha \partial x_\alpha} T \quad . \quad (12)$$

To get (11),

$$\frac{\partial p}{\partial x_\alpha} = A \frac{\partial}{\partial x_\alpha} \Delta\rho + B \frac{\partial}{\partial x_\alpha} \Delta T$$

was used. To get (12),

$$\begin{aligned}
\rho_{eq.} \frac{\partial}{\partial t} e &= \rho_{eq.} \left[C \frac{\partial}{\partial t} \Delta T + \left(\frac{\partial e}{\partial \rho} \right)_{eq.} \frac{\partial}{\partial t} \Delta \rho \right] = \rho_{eq.} C \frac{\partial}{\partial t} \Delta T - \rho_{eq.}^2 \left(\frac{\partial e}{\partial \rho} \right)_{eq.} \frac{\partial}{\partial x_\alpha} u_\alpha = \\
&= \rho_{eq.} C \frac{\partial}{\partial t} \Delta T - p \frac{\partial}{\partial x_\alpha} u_\alpha + T_{eq.} B \frac{\partial}{\partial x_\alpha} u_\alpha
\end{aligned}$$

was used. This last set of equalities used (4) and (10). Q. E. D.

Define $a_i(rt)$ for $i = 1, 2, \dots, 5$ by

$$\begin{aligned}
a_1(rt) &= \rho_{eq.}^{-1/2} \Delta \rho(rt), \quad a_\alpha(rt) = \left(\frac{\rho_{eq.}}{A} \right)^{1/2} u_\alpha(rt) \quad \text{for } \alpha = 2, 3, 4 \quad \text{and} \\
a_5(rt) &= \left(\frac{\rho_{eq.} C}{T_{eq.} A} \right)^{1/2} \Delta T(rt) \quad .
\end{aligned} \tag{13}$$

Greek indices α and β will always go from 2 to 4 and will also be used for vector and tensor components, whereas Latin indices i and j are intended for 1, 2, 3, 4 and 5. With this convention two five by five matrices are defined by

$$A_{ij}(rr') = \begin{pmatrix} 0 & A_{1\alpha} & 0 \\ A_{\alpha 1} & 0 & A_{\alpha 5} \\ 0 & A_{5\alpha} & 0 \end{pmatrix} \tag{14}$$

where $A_{1\alpha} = A_{\alpha 1} = A^{1/2} \frac{\partial}{\partial x_\alpha} \delta(r-r')$ and $A_{5\alpha} = A_{\alpha 5} = \frac{B}{\rho_{eq.}} \left(\frac{T_{eq.}}{C} \right)^{1/2} \frac{\partial}{\partial x_\alpha} \delta(r-r')$, and

$$S_{ij}(rr') = \begin{pmatrix} 0 & 0 & 0 \\ 0 & S_{\alpha\beta} & 0 \\ 0 & 0 & S_{55} \end{pmatrix} \tag{15}$$

where

$$S_{\alpha\beta} = S_{\beta\alpha} = \frac{1}{\rho_{eq.}} \frac{\partial^2}{\partial x_{\mu} \partial x'_{\nu}} \delta(r-r') [\eta(\delta_{\alpha\nu} \delta_{\mu\beta} + \delta_{\alpha\beta} \delta_{\mu\nu}) + (\xi - \frac{2}{3}\eta) \delta_{\alpha\mu} \delta_{\beta\nu}]$$

and

$$S_{55} = \frac{K}{\rho_{eq.} C} \frac{\partial^2}{\partial x_{\mu} \partial x'_{\nu}} \delta(r-r') \delta_{\mu\nu} .$$

Note that $A_{ij}(rr') = -A_{ji}(r'r)$ and that $S_{ij}(rr') = +S_{ji}(r'r)$. Equations (10) through (12) may now be written as

$$\frac{\partial}{\partial t} a_i(rt) + \int A_{ij}(rr') a_j(r't) dr' = - \int S_{ij}(rr') a_j(r't) dr' . \quad (16)$$

By considering $a_i(rt)$ as labeled by both i and r , the summation over the labels corresponds to summing over i and integrating over r . In this manner of thinking, (16) corresponds to a specific instance of (8). The antisymmetry of $A_{ij}(rr')$ and the symmetry of $S_{ij}(rr')$ have already been indicated. That $S_{ij}(rr')$ is also semi-positive definite is also easily verified from (15). Note that this is again a case in which the S_{ij} matrix for the process has a zero eigenvalue, as was discussed in section E of Chapter I.

C. Fluctuation Formulae

Equation (16) may be completed to a Langevin type of equation by adding to (16) purely random stationary Gaussian Markov fluctuating hydrodynamical forces, $\tilde{F}_i(rt)$, giving

$$\frac{\partial}{\partial t} a_i(rt) + \int A_{ij}(rr') a_j(r't) dr' = - \int S_{ij}(rr') a_j(r't) dr' + \tilde{F}_i(rt) . \quad (17)$$

The $\tilde{F}_i(\mathbf{r}t)$'s must satisfy a correlation formula

$$\langle \tilde{F}_i(\mathbf{r}t) \tilde{F}_j(\mathbf{r}'t') \rangle = 2Q_{ij}(\mathbf{r}\mathbf{r}') \delta(t-t') \quad . \quad (18)$$

$Q_{ij}(\mathbf{r}\mathbf{r}')$ is explicitly determined from the fluctuation-dissipation theorem once the entropy matrix, $E_{ij}(\mathbf{r}\mathbf{r}')$ has been determined. The entropy matrix may be obtained from the entropy production, (7), as follows: From (7) the entropy production near equilibrium may be written to quadratic order in the hydrodynamical quantities as

$$\dot{S} = \int \left\{ \frac{K}{T_{eq}^2} \left(\frac{\partial}{\partial \mathbf{x}_\alpha} T \right) \left(\frac{\partial}{\partial \mathbf{x}_\alpha} T \right) + \frac{1}{T_{eq}} \left[2\eta D_{\alpha\beta} D_{\alpha\beta} + \left(\xi - \frac{2}{3}\eta \right) D_{\delta\delta}^2 \right] \right\} dV. \quad (19)$$

Substituting (13) and (15) into (19) gives

$$\dot{S} = K_B \left(\frac{A}{K_B T_{eq}} \right) \iint a_i(\mathbf{r}t) S_{ij}(\mathbf{r}\mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r} d\mathbf{r}' \quad . \quad (20)$$

However, from the canonical expression for the entropy

$$S = S_{eq} - \frac{1}{2} K_B \iint a_i(\mathbf{r}t) E_{ij}(\mathbf{r}\mathbf{r}') a_j(\mathbf{r}'t) d\mathbf{r} d\mathbf{r}' \quad (21)$$

it follows from (16) that

$$\dot{S} = \frac{1}{2} K_B \iiint a_i(\mathbf{r}t) [S_{ij}(\mathbf{r}\mathbf{r}'') E_{jk}(\mathbf{r}''\mathbf{r}') + E_{ij}(\mathbf{r}\mathbf{r}'') S_{jk}(\mathbf{r}''\mathbf{r}')] a_k(\mathbf{r}'t) d\mathbf{r} d\mathbf{r}' d\mathbf{r}'' \quad . \quad (22)$$

Comparison of (22) and (20) gives for $E_{ij}(\mathbf{r}\mathbf{r}')$ the value

$$E_{ij}(\mathbf{r}\mathbf{r}') = \frac{A}{K_B T_{eq}} \delta_{ij} \delta(\mathbf{r}-\mathbf{r}') \quad . \quad (23)$$

The fluctuation-dissipation theorem in this context is

$$\langle \tilde{F}_i(\mathbf{r}t) \tilde{F}_j(\mathbf{r}'t') \rangle = \int [G_{ik}(\mathbf{r}\mathbf{r}'') E_{kj}^{-1}(\mathbf{r}''\mathbf{r}') + E_{ik}^{-1}(\mathbf{r}\mathbf{r}'') G_{kj}^+(\mathbf{r}''\mathbf{r}')] d\mathbf{r}'' \delta(t-t') \quad (24)$$

where

$$G_{ij}(\mathbf{r}\mathbf{r}') = A_{ij}(\mathbf{r}\mathbf{r}') + S_{ij}(\mathbf{r}\mathbf{r}') \quad .$$

The integration in (24) may be performed using (23) which gives for

$$Q_{ij}(\mathbf{r}\mathbf{r}') = \frac{K_T T_{eq}}{A} S_{ij}(\mathbf{r}\mathbf{r}') \quad . \quad (25)$$

Since $S_{11}(\mathbf{r}\mathbf{r}') = 0$ it follows that $\tilde{F}_1(\mathbf{r}t) = 0$. Therefore, the continuity equation (10) has no fluctuating force.

The standard hydrodynamical variables may be introduced again giving for the linearized Navier-Stokes hydrodynamical equations with fluctuations the equations

$$\frac{\partial}{\partial t} \Delta \rho + \rho_{eq} \frac{\partial}{\partial \mathbf{x}_\alpha} u_\alpha = 0 \quad (26)$$

$$\rho_{eq} \frac{\partial}{\partial t} u_\alpha + A \frac{\partial}{\partial \mathbf{x}_\alpha} \Delta \rho + B \frac{\partial}{\partial \mathbf{x}_\alpha} \Delta T = \frac{\partial}{\partial \mathbf{x}_\beta} [2\eta D_{\alpha\beta} + (\xi - \frac{2}{3}\eta) D_{\gamma\gamma} \delta_{\alpha\beta}] + \frac{\partial}{\partial \mathbf{x}_\beta} \tilde{S}_{\alpha\beta} \quad (27)$$

$$\rho_{eq} C \frac{\partial}{\partial t} \Delta T + T_{eq} B \frac{\partial}{\partial \mathbf{x}_\alpha} u_\alpha = K \frac{\partial^2}{\partial \mathbf{x}_\alpha \partial \mathbf{x}_\alpha} \Delta T + \frac{\partial}{\partial \mathbf{x}_\alpha} \tilde{g}_\alpha \quad (28)$$

where $\tilde{S}_{\alpha\beta}$ and \tilde{g}_α are defined by

$$\frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(rt) = (\rho_{eq.} A)^{1/2} \tilde{F}_\alpha(rt) \quad \text{and} \quad \frac{\partial}{\partial x_\alpha} \tilde{g}_\alpha = (\rho_{eq.} T_{eq.} AC)^{1/2} \tilde{F}_5(rt). \quad (29)$$

Putting (29) into (18) and then using (25) gives

$$\langle \tilde{S}_{\alpha\beta}(rt) \tilde{S}_{\mu\nu}(r't') \rangle = 2K_B T_{eq.} \delta(r-r') \delta(t-t') [\eta (\delta_{\alpha\mu} \delta_{\beta\nu} + \delta_{\alpha\nu} \delta_{\beta\mu}) + (\xi - \frac{2}{3}\eta) \delta_{\alpha\beta} \delta_{\mu\nu}] \quad (30)$$

$$\langle \tilde{g}_\alpha(rt) \tilde{g}_\beta(r't') \rangle = 2K_B T_{eq.}^2 \delta(r-r') \delta(t-t') K \delta_{\alpha\beta} \quad (31)$$

From (25) it is also seen that $\tilde{S}_{\alpha\beta}(rt)$ and $\tilde{g}_\alpha(r't')$ are uncorrelated. Equations (30) and (31) are identical with the corresponding formulae Landau and Lifshitz obtain. $\tilde{S}_{\alpha\beta}$ may be thought of as the fluctuating stress tensor "force" and \tilde{g}_α may be thought of as the fluctuating heat flux "force".

D. Applications

Applications of equations (26) through (28) requires solving these equations as inhomogeneous equations with given inhomogeneities $\tilde{S}_{\alpha\beta}$ and \tilde{g}_α . The linearity of the equations results in giving $\Delta\rho$, ΔT and u_α as linear functions of the inhomogeneities $\tilde{S}_{\alpha\beta}$ and \tilde{g}_α . The correlations of the quantities $\Delta\rho$, ΔT and u_α are induced through their functional dependence on $\tilde{S}_{\alpha\beta}$ and \tilde{g}_α using equations (30) and (31). Note that for a particular problem the fluctuating stress tensor, for example, is obtained by solving for u_α as a functional of $\tilde{S}_{\alpha\beta}$ and \tilde{g}_α and then putting u_α into the expression

$$-2\eta(D_{\alpha\beta} - \frac{1}{3} D_{\gamma\gamma} \delta_{\alpha\beta}) - \xi D_{\gamma\gamma} \delta_{\alpha\beta} \quad .$$

This is very different from the fluctuating stress tensor "force";

$\tilde{S}_{\alpha\beta}$ and the two should not be confused!

The most simple and straightforward application is the calculation of the fluctuating hydrodynamical quantities around complete equilibrium where $\rho = \rho_{eq.}$, $T = T_{eq.}$, and $u_{\alpha} = 0$ in an infinite medium. This has been done by Rytov²⁾ and it explains both the Rayleigh and the Brillouin scattering of light in a fluctuating fluid.

It seems reasonable that the same methods are applicable to the case of steady state flow solutions which are still near equilibrium. This is a slight generalization, of course, since it has not been argued how a system could give rise to a steady state solution. This would require some kind of input on the system to drive the steady state since otherwise only full equilibrium qualifies as a solution to the equations.

Precisely how inputs effect a system is deferred to Chapter V. Here it will simply be assumed that the Landau and Lifshitz equations (26) through (28) also can be used for the discussion of fluctuations around stationary flows as long as the hydrodynamical equations are linear which implies that the inertial terms must be negligible.

The simplest example of such a flow is the slow, stationary flow of a fluid around a fixed body with boundary condition that infinitely far from the body the fluid has velocity $-U_{\alpha}$. This is mathematically equivalent to flow around a body with velocity U_{α} in a fluid which is at rest infinitely far away from the body. This second point of view is more convenient in the following computations.

For a slowly moving body it is permitted to neglect all inertial terms in equations (26) through (28). Equation (26) becomes

$$\frac{\partial}{\partial x_{\alpha}} u_{\alpha}(rt) = 0 \quad . \quad (32)$$

Equation (27) in conjunction with (32) becomes

$$\frac{\partial}{\partial x_\beta} P_{\alpha\beta}(rt) = - \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta}(rt) \quad (33)$$

where

$$P_{\alpha\beta}(rt) = -p(rt)\delta_{\alpha\beta} + \eta\left(\frac{\partial u_\alpha(rt)}{\partial x_\beta} + \frac{\partial u_\beta(rt)}{\partial x_\alpha}\right)$$

with

$$p(rt) = A\Delta\rho(rt) + B\Delta T(rt) \ .$$

$P_{\alpha\beta}$ does not contain a bulk viscosity term as a result of (32). Equation (28) in conjunction with (32) is independent of u_α altogether. Its solution is a uniform temperature field on the average which fluctuates as a result of the fluctuating heat flux force $\tilde{g}_\alpha(rt)$. However, further consideration of the temperature behavior is omitted since it does not effect $u_\alpha(rt)$. Equations (32) and (33) determine the problem.

The recipe for solving (32) and (33) is first of all to solve the average equations

$$\frac{\partial}{\partial x_\alpha} u_\alpha(rt) = 0 \quad \text{and} \quad \frac{\partial}{\partial x_\beta} P_{\alpha\beta}(rt) = 0 \quad (34)$$

with appropriate boundary conditions on the surface of the body, S , and infinitely far away from S . The boundary conditions are that

$u_\alpha = U_\alpha$ on S and that $u_\alpha = 0$ infinitely far away from S . The solution to (34) with these boundary conditions gives the average velocity field, u_α , everywhere outside the body. This is called the Stokes' problem and for a sphere the solution is well known. Next, the

fluctuating equations (32) and (33) must be solved with appropriate boundary conditions on S and infinitely far away from S . In order to distinguish these two cases, the fluctuating case will use the notation \tilde{u}_α and $\tilde{P}_{\alpha\beta}$ for the fluctuating velocity field and the fluctuating stress tensor. Equations (32) and (33) become

$$\frac{\partial}{\partial x_\alpha} \tilde{u}_\alpha = 0 \quad \text{and} \quad \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} = -\frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta} \quad (35)$$

in this notation. The boundary conditions are that on S , $\tilde{u}_\alpha = 0$ and that $\tilde{u}_\alpha = 0$ infinitely far away from S . The solution to (35) with these boundary conditions gives the fluctuating velocity field everywhere outside of the body. In general both problems given by (34) and (35) with their respective boundary conditions may be solved by the method of Green's functions. This has been extensively discussed by Oseen.³⁾ For the case of a spherical body Oseen has explicitly constructed the appropriate Green's functions.

The complete solutions to (34) and (35) will not be presented here⁴⁾ and a check which is far less involved computationally will be presented. By solving both (34) and (35) the average velocity field and the fluctuating velocity field are obtained. From these the average stress tensor and the fluctuating stress tensor may be computed. From each of these by integrating them over the surface of the body, S , it is possible to obtain the average force on the body as well as the fluctuating force on the body. Call these two forces F_α and \tilde{F}_α respectively. The equation of motion for the body is, therefore, given by

$$M \frac{dU_\alpha}{dt} = F_\alpha + \tilde{F}_\alpha \quad (36)$$

The solution to the Stokes' problem given by (34) will lead to a force

F_α which is proportional to U_α . Therefore, (36) is precisely of the form of the Langevin equation discussed in Chapter I. The check on all of the discussion up to here will be to see if the fluctuating force \tilde{F}_α satisfies the fluctuation-dissipation theorem for the Langevin equation. If so, the Langevin equation has been derived from the fluctuating hydrodynamics.

To begin the proof of the fluctuation-dissipation theorem for (36) the following identity is necessary

$$\int_V (u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta}) dV = \int_S (u_\alpha \tilde{P}_{\alpha\beta} n_\beta - \tilde{u}_\alpha P_{\alpha\beta} n_\beta) d\Omega \quad (37)$$

where the volume integral is over the entire region outside the surface

S . n_β is a unit vector normal to S .

Proof of (37):

$$\frac{\partial}{\partial x_\alpha} u_\alpha = 0 = \frac{\partial}{\partial x_\alpha} \tilde{u}_\alpha$$

gives

$$(\frac{\partial}{\partial x_\beta} u_\alpha) \tilde{P}_{\alpha\beta} = (\frac{\partial}{\partial x_\beta} u_\alpha) \eta (\frac{\partial \tilde{u}_\alpha}{\partial x_\beta} + \frac{\partial \tilde{u}_\beta}{\partial x_\alpha}) = (\frac{\partial}{\partial x_\beta} \tilde{u}_\alpha) \eta (\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha}) = (\frac{\partial}{\partial x_\beta} \tilde{u}_\alpha) P_{\alpha\beta}.$$

Therefore,

$$\begin{aligned} \int_V (u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta}) dV &= \int_V (u_\alpha \frac{\partial}{\partial x_\beta} \tilde{P}_{\alpha\beta} + (\frac{\partial}{\partial x_\beta} u_\alpha) \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha \frac{\partial}{\partial x_\beta} P_{\alpha\beta} - \\ &- (\frac{\partial}{\partial x_\beta} \tilde{u}_\alpha) P_{\alpha\beta}) dV = \int_V \frac{\partial}{\partial x_\beta} (u_\alpha \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha P_{\alpha\beta}) dV = \int_S (u_\alpha \tilde{P}_{\alpha\beta} - \tilde{u}_\alpha P_{\alpha\beta}) n_\beta d\Omega. \end{aligned}$$

Q. E. D.

Into the left hand side of (37), (34) and (35) are substituted while into the right-hand side of (37) the boundary conditions for u_α and \tilde{u}_α on S are substituted. This gives

$$- \int_V u_\alpha \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta} dV = \int_S U_\alpha \tilde{P}_{\alpha\beta} n_\beta d\Omega \quad . \quad (38)$$

U_α is a constant and may be factored out of the integral over S . The fluctuating force, \tilde{F}_α , is by definition given by

$$\tilde{F}_\alpha = \int_S \tilde{P}_{\alpha\beta} n_\beta d\Omega \quad . \quad (39)$$

Therefore, putting (39) into (38) gives

$$U_\alpha \tilde{F}_\alpha = - \int_V u_\alpha \frac{\partial}{\partial x_\beta} \tilde{S}_{\alpha\beta} dV \quad . \quad (40)$$

From (30) it can be shown that

$$U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq} \delta(t-s) \int_S u_\alpha P_{\alpha\beta} n_\beta d\Omega \quad . \quad (41)$$

Proof of (41): Directly from (30),

$$U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle =$$

$$2K_B T_{eq} \delta(t-s) \eta \int_V \int_V u_\alpha(r) u_\beta(r') \frac{\partial^2}{\partial x_\mu \partial x'_\nu} \delta(r-r') (\delta_{\alpha\beta} \delta_{\mu\nu} + \delta_{\alpha\nu} \delta_{\beta\mu} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\nu}) dV_r dV_{r'} =$$

$$= 2K_B T_{eq} \delta(t-s) \eta \int_V \left[\frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\alpha}{\partial x_\beta} - \frac{2}{3} \left(\frac{\partial u_\alpha}{\partial x_\alpha} \right)^2 \right] dV \quad .$$

Using $\frac{\partial u}{\partial x_\alpha} = 0$ gives

$$\frac{\partial^2}{\partial x_\alpha \partial x_\beta} (u_\alpha u_\beta) = \frac{\partial}{\partial x_\alpha} (u_\beta \frac{\partial u_\alpha}{\partial x_\beta}) = \frac{\partial u_\beta}{\partial x_\alpha} \frac{\partial u_\alpha}{\partial x_\beta}$$

and

$$\frac{\partial^2}{\partial x_\beta \partial x_\beta} (u_\alpha u_\alpha) = 2 \frac{\partial u_\alpha}{\partial x_\beta} \frac{\partial u_\alpha}{\partial x_\beta} + 2 u_\alpha \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha \quad .$$

Therefore

$$U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq} \cdot \delta(t-s) \eta \int_V \left\{ \frac{1}{2} \frac{\partial^2}{\partial x_\beta \partial x_\beta} (u_\alpha u_\alpha) - u_\alpha \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha + \frac{\partial^2}{\partial x_\alpha \partial x_\beta} (u_\alpha u_\beta) \right\} dV.$$

The divergence theorem may be applied. Surface terms infinitely far from

S vanish because of the asymptotic behavior of u_α at that distance. Applying the divergence theorem and using (34) in the form

$$\eta \frac{\partial^2}{\partial x_\beta \partial x_\beta} u_\alpha = \frac{\partial}{\partial x_\alpha} p$$

gives

$$U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq} \cdot \delta(t-s) \eta \left\{ \int_S \left[\frac{1}{2} n_\beta \frac{\partial}{\partial x_\beta} (u_\alpha u_\alpha) + n_\alpha \frac{\partial}{\partial x_\beta} (u_\alpha u_\beta) \right] d\Omega - \int_V u_\alpha \frac{1}{\eta} \frac{\partial}{\partial x_\alpha} p dV \right\}.$$

Now,

$$\int_S \frac{1}{2} n_\beta \frac{\partial}{\partial x_\beta} (u_\alpha u_\alpha) d\Omega = \int_S n_\beta u_\alpha \frac{\partial u_\alpha}{\partial x_\beta} d\Omega$$

and

$$-\int_V u_\alpha \frac{1}{\eta} \frac{\partial}{\partial x_\alpha} p dV = -\frac{1}{\eta} \int_V \frac{\partial}{\partial x_\alpha} (u_\alpha p) dV = -\frac{1}{\eta} \int_S n_\beta p \delta_{\alpha\beta} u_\alpha d\Omega$$

and

$$\int_S n_\alpha \frac{\partial}{\partial x_\beta} (u_\alpha u_\beta) d\Omega = \int_S n_\alpha u_\beta \frac{\partial u_\alpha}{\partial x_\beta} d\Omega = \int_S n_\beta u_\alpha \frac{\partial u_\beta}{\partial x_\alpha} d\Omega \quad .$$

Therefore,

$$\begin{aligned} U_\alpha U_\beta \langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle &= 2K_B T_{eq.} \delta(t-s) \eta \int_S [n_\beta u_\alpha \left(\frac{\partial u_\alpha}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\alpha} \right) - n_\beta u_\alpha \frac{1}{\eta} p \delta_{\alpha\beta}] d\Omega = \\ &= 2K_B T_{eq.} \delta(t-s) \int_S u_\alpha P_{\alpha\beta} n_\beta d\Omega \quad . \quad \underline{\text{Q. E. D.}} \end{aligned}$$

On S , $u_\alpha = U_\alpha$ so that

$$\int_S u_\alpha P_{\alpha\beta} n_\beta d\Omega = U_\alpha \int_S P_{\alpha\beta} n_\beta d\Omega \quad .$$

The average frictional force on the body is given by definition by

$$f_{\alpha\beta} U_\beta = \int_S P_{\alpha\beta} n_\beta d\Omega \quad (42)$$

where $f_{\alpha\beta}$ is the friction tensor. Therefore (41) and (42) combine to give

$$\langle \tilde{F}_\alpha(t) \tilde{F}_\beta(s) \rangle = 2K_B T_{eq.} f_{\alpha\beta} \delta(t-s) \quad . \quad (43)$$

This is the fluctuation-dissipation theorem for the Langevin equation in a

form applicable to an arbitrarily shaped body. Note that (43) implies that the friction tensor $f_{\alpha\beta}$ must be symmetric, which can also be shown directly. For a sphere of radius a , $f_{\alpha\beta} = 6\pi\eta a\delta_{\alpha\beta}$ which gives the results in Chapter I. Therefore, fluctuating hydrodynamics permits a derivation of the Langevin equation as is demonstrated by (36) and (43).⁵⁾

NOTES

- 1) Landau and Lifshitz, Fluid Mechanics, Pergamon Press, (1959), Chapter XVII of this book presents the theory. The argument given in the book justifying the theory is based on the Onsager and Machlup theory of irreversible thermodynamics presented in section C of Chapter I of this dissertation. The argument is actually invalid since hydrodynamics uses both α and β type variables simultaneously whereas the Onsager and Machlup theory is only presented for α variables alone. The derivation here clears up the ambiguity.
- 2) S. M. Rytov, Soviet Physics JETP, 6, 401, 513, (1958). A more complete account is given by J. Foch, Physics of Fluids, (in press).
- 3) C. W. Oseen, Neuere Methoden und Ergebnisse in der Hydrodynamik (Akad. Verlag, Leipzig (1927)).
- 4) They would be of interest for the discussion of the effect of the stationary motion on the scattering of light.
- 5) R. Zwanzig, Journal of Research, National Bureau of Standards, Volume 68B, 143, (1964). Zwanzig has attempted a similar proof for the case of a sphere. However, his argument is confused since he does not follow the recipe for solving the fluctuating hydrodynamical equations which was outlined in the beginning of this section. Furthermore, Zwanzig appeals to a theory of Faxen which is not applicable for flows with outside forces as is the case here. Faxen's theorem may be found in an article by R. Berker in Volume VIII/2 of the Encyclopedia of Physics, Springer-Verlag, Berlin, (1963), sections 68 and 76.

CHAPTER III

Fluctuations in μ -SpaceA. The Linearized Boltzmann Equation¹⁾

The state of a dilute gas is described by a distribution function, $f(\mathbf{rpt})$, which gives the number of particles at time t at position \mathbf{r} with momentum \mathbf{p} . The six dimensional domain of $f(\mathbf{rpt})$ is called μ -space. Asymptotically in time $f(\mathbf{rpt})$ approaches, in the case of no outside forces, the Maxwell distribution for equilibrium

$$f_{\text{eq.}}(\mathbf{rp}) = n_{\text{eq.}} (2\pi m K_B T_{\text{eq.}})^{-3/2} \exp\left[-\frac{\mathbf{p}^2}{2m K_B T_{\text{eq.}}}\right] \quad (1)$$

where $n_{\text{eq.}}$ is the equilibrium density and $T_{\text{eq.}}$ is the equilibrium temperature. The gas molecules have mass m and K_B is Boltzmann's constant. When the distribution $f(\mathbf{rpt})$ is near $f_{\text{eq.}}(\mathbf{rp})$ it may be written as

$$f(\mathbf{rpt}) = f_{\text{eq.}}(\mathbf{rp})[1 + h(\mathbf{rpt})] \quad .$$

The linearized Boltzmann equation governs the time development of $h(\mathbf{rpt})$. The equation is

$$\frac{\partial}{\partial t} h(\mathbf{rpt}) + \frac{\mathbf{p}_\alpha}{m} \frac{\partial}{\partial \mathbf{x}_\alpha} h(\mathbf{rpt}) = \int f_{\text{eq.}}(\mathbf{p}_1) g I(g, \theta) [h' + h'_1 - h - h_1] d\Omega d\mathbf{p}_1. \quad (2)$$

The right hand side of (2) gives the effect of binary collisions on the change of distribution function with time. The prime and subscript 1 on the h 's refer to its momentum variable, \mathbf{p} , only. For instance,

h_1^t means $h(rp_1^t)$. The four different momentum variables indicated refer to the binary collision $(p, p_1) \rightleftharpoons (p', p'_1)$. g is the relative velocity which turns over the angle θ in the solid angle $d\Omega$ during the collision. $I(g, \theta)$ is the differential cross-section, which depends on the intermolecular force.

It will be shown that (2) may be rewritten such that it possesses the form of the average regression equations of a stationary Gaussian Markov process

$$\frac{d}{dt} a_i + A_{ij} a_j = -S_{ij} a_j \quad (3)$$

where $A_{ij} = -A_{ji}$, $S_{ij} = S_{ji}$ and S_{ij} is a semi-positive definite. In analogy with the thinking used in section B of Chapter II, the analogue of a_i in (3) for this case will be $h(rpt)$ which must be thought of as labeled by r and p . Therefore, the summations indicated in (3) over the labels of the a_i 's become integrations over r and p for $h(rpt)$. After establishing the form (3), in this sense, for (2), fluctuations will also be introduced transforming the linearized Boltzmann equation into a generalized O-U process.

B. Linearized Boltzmann Equation as a Regression Equation

The right hand side of (2) may be written in the form $-\int f_{eq.}(p')K(p, p')h(rp't)dp'$ where the kernel $K(p, p')$ is symmetric, isotropic, and semi-positive definite. Isotropy means that $K(p, p')$ depends only on $|p|$, $|p'|$ and $p_\alpha p'_\alpha$. Semi-positive definiteness means that except for five zero-eigenvalues corresponding to the five conservation laws for binary collisions, the eigenvalues of $K(pp')$ are positive. All of these properties were proved by Hilbert and Enskog.²⁾ Not very much is known about the eigenvalue spectrum in general. For Maxwell molecules with intermolecular force $\sim \frac{1}{r^5}$, the spectrum is discrete

and goes to infinity.³⁾ For hard spheres the spectrum begins with a discrete series which converges to a continuum which extends to infinity.⁴⁾ In some of the following it will be assumed that a discrete spectrum is being dealt with, so that formally summations are used everywhere. This is merely a formal convenience and the case of a continuum spectrum requires only formal changes in presentation. Moreover, the question of convergence of eigenfunction expansions will not be broached and they too must be considered as formal series.

Define $a(rpt)$, $A(rp, r'p')$ and $S(rp, r'p')$ by

$$a(rpt) = f_{eq.}^{1/2}(p)h(rpt)$$

$$A(rp, r'p') = f_{eq.}^{1/2}(p) \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} \delta(r-r')\delta(p-p') \quad (4)$$

$$S(rp, r'p') = f_{eq.}^{1/2}(p)f_{eq.}^{1/2}(p')K(pp')\delta(r-r') \quad .$$

Putting (4) into (2) and using the $K(pp')$ form of the right hand side of (2) gives

$$\frac{\partial}{\partial t} a(rpt) + \iint A(rp, r'p')a(r'p't)dr'dp' = - \iint S(rp, r'p')a(r'p't)dr'dp' \quad . \quad (5)$$

$A(rp, r'p')$ is antisymmetric because of its $\frac{\partial}{\partial x_\alpha} \delta(r-r')$ factor and

$S(rp, r'p')$ is symmetric and semi-positive definite because of its $K(pp')$ factor. Therefore, thinking of r and p as labels as suggested at the end of section A, the linearized Boltzmann equation, (5), is of the form of the average regression equation for a stationary Gaussian Markov process of general type, (3).

C. Fluctuation Formulae

The linearized Boltzmann equation gives a contracted description of the behavior of a dilute gas. The precise description of the gas requires the Lionville equation which describes the motion of the gas in its phase-space. Consequently, $h(rpt)$ must be considered to fluctuate in time. The form of the linearized Boltzmann equation given in (5) suggests that the fluctuation may be described by adding to the regression equation, (5), a fluctuating force term $f_{eq.}^{1/2}(p) \tilde{C}(rpt)$ so as to make it a generalized O-U process. In terms of $h(rpt)$ the linearized Boltzmann equation with fluctuations then becomes

$$\frac{\partial}{\partial t} h(rpt) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h(rpt) = - \int K(pp') f_{eq.}(p') h(rp't) dp' + \tilde{C}(rpt) . \quad (6)$$

To get (6), a common factor of $f_{eq.}^{1/2}(p)$ has been factored out of (5), as well as replacing $A(rp, r'p')$ and $S(rp, r'p')$ in (5) by their definitions. $\tilde{C}(rpt)$ must satisfy a correlation formula

$$\langle \tilde{C}(rpt) \tilde{C}(r'p't') \rangle = 2Q(rp, r'p') \delta(t-t') . \quad (7)$$

$Q(rp, r'p')$ may be explicitly determined by invoking the fluctuation-dissipation theorem once the entropy "matrix", $E(rp, r'p')$, has been determined.

The entropy "matrix" for a dilute gas obeying Boltzmann's equation follows from the expression for the entropy given by

$$S(t) = - K_B \iint f(rpt) \ln[f(rpt)] dr dp . \quad (8)$$

Near equilibrium, $f(rpt)$ may be replaced by $f_{eq.}(p)[1 + h(rpt)]$.

This converts (8) into

$$S(t) = -K_B \iint \left\{ f_{eq.}(p) \ln[f_{eq.}(p)] + f_{eq.}(p) \ln[1 + h(rpt)] + \right. \\ \left. + f_{eq.}(p) h(rpt) \ln[f_{eq.}(p)] + f_{eq.}(p) h(rpt) \ln[1 + h(rpt)] \right\} dr dp . \quad (9)$$

Define $S_{eq.}$ by

$$S_{eq.} = -K_B \iint f_{eq.}(p) \ln[f_{eq.}(p)] dr dp .$$

Since $h(rpt)$ is small because the gas is near equilibrium, $\ln[1+h(rpt)]$ may be approximated by $h(rpt) - \frac{1}{2} h^2(rpt)$. Therefore, to second order in $h(rpt)$, (9) becomes

$$S(t) = S_{eq.} - K_B \iint \left\{ f_{eq.}(p) h(rpt) - \frac{1}{2} f_{eq.}(p) h^2(rpt) + \right. \\ \left. + f_{eq.}(p) h(rpt) \left[\ln[n_{eq.} (2\pi m K_B T_{eq.})^{-3/2}] - \frac{p^2}{2m K_B T_{eq.}} \right] + f_{eq.}(p) h^2(rpt) \right\} dr dp . \quad (10)$$

The integrals of $f_{eq.}(p) h(rpt)$ and $f_{eq.}(p) h(rpt) \ln[n_{eq.} (2\pi m K_B T_{eq.})^{-3/2}]$ are zero since the total number of gas molecules is constant. Similarly, the integral of $-f_{eq.}(p) h(rpt) \frac{p^2}{2m K_B T_{eq.}}$ is zero since the total kinetic energy of the gas is also a constant of the motion. Therefore, (10) simplifies to

$$S(t) = S_{eq.} - \frac{1}{2} K_B \iint f_{eq.}(p) h^2(rpt) dr dp . \quad (11)$$

Using definition (4) in (11) gives

$$S(t) = S_{\text{eq.}} - \frac{1}{2} K_B \iint a^2(rpt) dr dp$$

from which it follows that $E(rp, r'p')$, the entropy "matrix", must be

$$E(rp, r'p') = \delta(r-r')\delta(p-p') \quad . \quad (12)$$

Putting (12) into the fluctuation-dissipation theorem and using (4) gives the expression which is explicitly the fluctuation-dissipation theorem for this case

$$\langle \tilde{C}(rpt) \tilde{C}(r'p't') \rangle = 2K(pp')\delta(r-r')\delta(t-t') \quad . \quad (13)$$

Equations (6) and (13) completely describe the fluctuating linearized Boltzmann equation.

D. Eigenfunction Expansions

As discussed in section B a discrete spectrum for $K(pp')$ is assumed for formal convenience. The eigenvalues of $K(pp')$ may be denoted by λ_i while the eigenfunctions are denoted by $\phi_i(p)$. The ϕ_i 's are taken to be orthogonal to each other with respect to the weighting function $\frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(p)$. This means that

$$\int \frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(p) \phi_i(p) \phi_j(p) = \delta_{ij} \quad . \quad (14)$$

$K(pp')$ has the expansion

$$K(pp') = \sum_{i=1}^{\infty} \lambda_i \phi_i(p) \phi_i(p')$$

and $\tilde{C}(\mathbf{rpt})$ has the expansion

$$\tilde{C}(\mathbf{rpt}) = \sum_{i=1}^{\infty} \tilde{F}_i(\mathbf{rt}) \phi_i(\mathbf{p}) \quad .$$

Because $K(\mathbf{pp}')$ has five zero eigenvalues, they will be taken to be the first five for $i = 1, \dots, 5$. The two expansions just given then become sums from 6 to ∞ . This is obvious for $K(\mathbf{pp}')$ and for $\tilde{C}(\mathbf{rpt})$ it follows from (13) since this requires that $\tilde{F}_i(\mathbf{rt}) = 0$ for $i = 1, \dots, 5$. Finally $h(\mathbf{rpt})$ may also be expanded as

$$h(\mathbf{rpt}) = \sum_{i=1}^{\infty} a_i(\mathbf{rt}) \phi_i(\mathbf{p}) \quad .$$

Putting all these expansions into (6) gives

$$\frac{\partial}{\partial t} a_{\ell}(\mathbf{rt}) + \int B_{\alpha}^{\ell k} \frac{\partial}{\partial \mathbf{x}_{\alpha}} a_k(\mathbf{r}'t) d\mathbf{r}' = -\lambda_{\ell} a_{\ell}(\mathbf{rt}) + \tilde{F}_{\ell}(\mathbf{rt}) \quad (15)$$

where $B_{\alpha}^{\ell k}$ is defined by

$$B_{\alpha}^{\ell k} = \int \frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(\mathbf{p}) \phi_{\ell}(\mathbf{p}) \frac{p_{\alpha}}{m} \phi_k(\mathbf{p}) d\mathbf{p} \quad . \quad (16)$$

From (13) the \tilde{F}_{ℓ} 's are easily seen to satisfy

$$\langle \tilde{F}_{\ell}(\mathbf{rt}) \tilde{F}_k(\mathbf{r}'t') \rangle = 2 \lambda_{\ell} \delta_{\ell k} \delta(\mathbf{r}-\mathbf{r}') \delta(t-t') \quad . \quad (17)$$

The form of the fluctuating Boltzmann equation in terms of eigenfunction expansions will be used extensively in the next chapter.

E. Consistency with the Landau and Lifshitz Theory

In Chapter II it was shown that the theory of hydrodynamical fluctuations gave rise to the Langevin equation. By analogy, it is of interest in this chapter to see if the theory of μ -space fluctuations just presented can give rise to the theory of hydrodynamical fluctuations. In the case of the linearized Boltzmann equation the $a_\ell(rt)$'s are the variables necessary for a complete description of the system in μ -space. They are very many in number since ℓ goes from 1 to ∞ and r roams over the entire domain of the system. In the Landau and Lifshitz theory for hydrodynamical fluctuations there are many fewer variables since the description is given in terms of the five hydrodynamical variables which correspond to the first five of the coefficients $a_\ell(rt)$ in the eigenfunction expansion of $h(rpt)$. Note that these first five of the $a_\ell(rt)$'s are associated with the five zero eigenvalues and will therefore vary in time much more slowly than the other $a_\ell(rt)$'s. The condition for the possibility of a contracted description is therefore fulfilled and the question arises how to express the contraction idea by an unambiguous mathematical procedure. Such a procedure was first developed by Enskog⁵⁾ for the derivation of the Navier-Stokes equations from the Boltzmann equation, and the Enskog method has been adapted here to derive the Landau and Lifshitz equations from the linearized Boltzmann equation with fluctuations as proposed in the previous section. The details will be presented in Chapter IV since the computations are quite long. To illustrate the Enskog procedure it will be shown in the next section how the Kramer's diffusion equation in phase space for a harmonic oscillation (see Chapter I, section E) can for the case of strong damping be contracted to the so-called Smoluchovski diffusion equation in coordinate space.

F. Contraction Procedure for Brownian Motion of a Harmonic Oscillator

For the case of the Brownian motion of an overdamped harmonic oscillator, the distribution of momenta quickly relaxes to a Maxwell distribution while the distribution in coordinate space takes much longer to relax to its equilibrium distribution. Consequently, it is expected that after a short initial period the description in terms of both momentum and position will contract to a description in terms of position only. The complete distribution function, is governed by the equation given at the end of Chapter I.

$$\frac{\partial}{\partial t}P(xpt) + \frac{p}{M} \frac{\partial}{\partial x}P(xpt) - M\omega^2 x \frac{\partial}{\partial p}P(xpt) = \frac{\alpha}{M} \left[\frac{\partial}{\partial p} (pP(xpt) + MK_B T_{eq.} \frac{\partial^2}{\partial p^2} P(xpt)) \right]. \quad (18)$$

Note that equation (18) is not of the same kind as the Boltzmann equation. Equation (18) is the Fokker-Planck equation for an O-U process describing the Brownian motion of harmonic oscillator while the fluctuating Boltzmann equation is itself an O-U process.⁶⁾ However, formally, either kind of equation may be contracted. Note also that (18) can be looked upon as an average regression equation of the standard type (3), which makes the analogy still closer.

Denote the equilibrium Maxwell distribution in the momenta by:

$$P_{eq.}(p) = (2\pi MK_B T_{eq.})^{-1/2} \exp\left[-\frac{p^2}{2MK_B T_{eq.}}\right]$$

which is, of course, independent of x . Define $Q(xt)$ by

$$Q(xt) = \int P(xpt) dp.$$

Near enough to equilibrium $P(xpt)$ may be expected to behave like

$P_{eq.}(p)Q(xt)$ in the strongly overdamped case, which corresponds to large values of $\frac{\alpha}{M}$. Therefore, the behavior of the oscillator will approximately be described by $Q(xt)$ which is independent of p .

$Q(xt)$ gives a contracted description. The equation $Q(xt)$ must satisfy will now be determined.

Let $\frac{\alpha}{M} = \theta$ and let the rate of relaxation be measured in terms of θ . Expand $P(xpt)$ as

$$P(xpt) = P_{eq.}(p)[R_0(xpt) + \frac{1}{\theta} R_1(xpt) + \frac{1}{\theta^2} R_2(xpt) + \dots] \quad (19)$$

Define $J_n(xt)$ by

$$J_n(xt) = \int P_{eq.}(p) p R_n(xpt) dp \quad .$$

Therefore, integration of (18) over p yields

$$\frac{\partial}{\partial t} Q(xt) = - \frac{1}{M} \frac{\partial}{\partial x} \sum_{n=0}^{\infty} \frac{1}{\theta^n} J_n(xt) \quad . \quad (20)$$

Equation (20) suggests that it is meaningful to introduce a formal expansion of the time derivative by

$$\frac{\partial}{\partial t} \rightarrow \frac{\partial_0}{\partial t} + \frac{1}{\theta} \frac{\partial_1}{\partial t} + \frac{1}{\theta^2} \frac{\partial_2}{\partial t} + \dots \quad . \quad (21)$$

The meaning of each order of the expanded time derivative follows from putting (21) into (20) and equating terms of equal order in $\frac{1}{\theta}$. This gives the definitions

$$\frac{\partial_n}{\partial t} Q(xt) = - \frac{1}{M} \frac{\partial}{\partial x} J_n(xt) \quad . \quad (22)$$

Putting (19) and (21) into (18) and equating terms of equal order in $\frac{1}{\theta}$ gives a series of equations which must be solved successively. The first few are

$$MK_B T_{eq.} \frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} R_o) = 0 \quad (23)$$

$$\frac{\partial_o}{\partial t} P_{eq.} R_o + \frac{p}{M} \frac{\partial}{\partial x} P_{eq.} R_o - M\omega^2 x \frac{\partial}{\partial p} P_{eq.} R_o = MK_B T_{eq.} \frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} R_1) \quad (24)$$

$$\frac{\partial_o}{\partial t} P_{eq.} R_1 + \frac{\partial_1}{\partial t} P_{eq.} R_o + \frac{p}{M} \frac{\partial}{\partial x} P_{eq.} R_1 - M\omega^2 x \frac{\partial}{\partial p} P_{eq.} R_1 = MK_B T_{eq.} \frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} R_2) \quad (25)$$

The operator $\frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} \cdot)$ has one zero-eigenvalue eigenfunction

which in normalized form with respect to the weighting function

$P_{eq.}(p)$ is simply the constant function 1. Therefore, the solution to (23) is

$$R_o(xpt) = Q_o(xt) \quad (26)$$

In order that (24) has a solution it is necessary that the left hand side of (24) does not contain zero-eigenvalue eigenfunctions of the operator

$\frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} \cdot)$. This can be guaranteed by imposing a solubility

condition which requires that the left hand side of (24) is orthogonal

with the zero-eigenvalue eigenfunctions of $\frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} \cdot)$. In the

case at hand this is achieved by multiplying (24) by 1 and integrating over p . Doing this to the left hand side of (24) and setting the result equal to zero gives the solubility condition

$$\frac{\partial}{\partial t} Q_o(xt) = 0 \quad . \quad (27)$$

In general solubility conditions must be imposed to all orders in any problem involving contraction as in this case. A uniqueness condition on the solutions must also be imposed by requiring that the solution for R_1 in (24) does not contain a contribution proportional to the zero-eigenvalue eigenfunctions of $\frac{\partial}{\partial p} (P_{eq} \frac{\partial}{\partial p} \cdot)$. Such an uniqueness condition will also be imposed on all orders of the solutions in any problem involving contraction. Therefore, to solve (24) assume that

$$R_1(xpt) = Q_1(xt)p \quad .$$

Equation (24) becomes

$$\frac{p}{M} \frac{\partial}{\partial x} Q_o + \frac{\omega^2}{K_B T_{eq.}} xp Q_o = -p Q_1 \quad (28)$$

which trivially has the solution

$$Q_1(xt) = - \left[\frac{1}{M} \frac{\partial}{\partial x} Q_o(xt) + \frac{\omega^2}{K_B T_{eq.}} x Q_o(xt) \right] \quad . \quad (29)$$

The computation must go on for one more order at least in order to finish the contraction. The solubility condition for (25) is

$$\frac{\partial}{\partial t} Q_o + \frac{1}{M} \frac{\partial}{\partial x} Q_1 \int p^2 P_{eq.}(p) dp - M \omega^2 x Q_1 \int \frac{\partial}{\partial p} (p P_{eq.}(p)) dp = 0 \quad . \quad (30)$$

The integrals in (30) can be performed and give

$$\frac{\partial}{\partial t} Q_o + \frac{1}{M} \frac{\partial}{\partial x} Q_1 M K_B T_{eq.} = 0 \quad . \quad (31)$$

Putting (29) into (31) gives the equation

$$\frac{\partial}{\partial t} Q_o(xt) = \frac{K_B T_{eq.}}{M} \frac{\partial^2}{\partial x^2} Q_o(xt) + \omega^2 \frac{\partial}{\partial x} (x Q_o(xt)) \quad . \quad (32)$$

Coupled with (27), (32) gives up to order $\frac{1}{\theta}$ a contracted description of the Brownian motion of a harmonic oscillator through the equation

$$\frac{\partial}{\partial t} Q_o(xt) = \frac{1}{\theta} \left[\frac{K_B T_{eq.}}{M} \frac{\partial^2}{\partial x^2} Q_o(xt) + \omega^2 \frac{\partial}{\partial x} (x Q_o(xt)) \right] \quad (33)$$

which is the so-called Smoluchovski equation. To get a contracted description up to order $\frac{1}{\theta}$ the procedure was applied twice; this will be generally true for any equation which is to be contracted. To get a description valid to higher orders in $\frac{1}{\theta}$ it is necessary to apply the procedure an appropriate greater number of times. For this particular example of Brownian motion of a harmonic oscillator it can, in fact, be shown how to solve the equation in this manner to all orders of $\frac{1}{\theta}$.⁷⁾ The solubility conditions turn out to be

$$\frac{\partial_n}{\partial t} Q_o = 0 \quad .$$

for even n and

$$\frac{\partial_n}{\partial t} Q_o = (\omega^2)^{\frac{n-1}{2}} \left[\frac{K_B T_{eq.}}{M} \frac{\partial^2}{\partial x^2} Q_o + \omega^2 \frac{\partial}{\partial x} (x Q_o) \right] \quad (34)$$

for odd n .

Putting all of these equations together with (21) gives

$$\frac{\partial}{\partial t} Q_o(xt) = \frac{1}{\theta} \left(\frac{1}{1-\omega^2/\theta^2} \right) \left[\frac{K_B T_{eq}}{M} \frac{\partial^2}{\partial x^2} Q_o(xt) + \omega^2 \frac{\partial}{\partial x} (x Q_o(xt)) \right] \quad (35)$$

if θ is large enough, which is the case for overdamping as was assumed initially. Note that (35) differs from (33) only by a factor $\left(\frac{1}{1-\omega^2/\theta^2} \right)$ which modifies the friction constant. Generally, the solution of a contraction procedure to higher and higher order of the relaxation parameter, $\frac{1}{\theta}$, will introduce higher and higher order derivatives in x . That this does not occur in this example is fortuitous and is a consequence of the harmonic potential.

The essential features of the contraction procedure in general are the expanded time derivative, the solubility conditions, and the uniqueness conditions. The solubility conditions up to the desired order give the equations which govern the contracted description up to that order.

NOTES

- 1) Uhlenbeck and Ford, Lectures in Statistical Mechanics, American Mathematical Society, (1963). Chapter IV of this book covers the Boltzmann equation in detail.
- 2) D. Hilbert, Theorie des Integralgleichungen, Teubner Verlag, Leipzig, Chapter 22 and; D. Enskog, Kinetische Theorie der Vorgänge in mässig verdünnte Gasen, Dissertation, Upsala, (1917), p. 140. See also: L. Waldmann, Handbuch der Physik, Volume 12, p. 366.
- 3) C. S. Wang Chang and G. E. Uhlenbeck, Report of the Eng. Res. Inst., University of Michigan, (1952) and; L. Waldmann, Handbuch der Physik, Volume 12, §38.
- 4) I. Kuscer and M. M. R. Williams, Physics of Fluids, Volume 10, Number 9, (1967).
- 5) D. Enskog, loc. cit. note 2). This should be compared with the presentation in: S. Chapman and T. G. Cowling, The Mathematical Theory of Non-uniform Gases, Cambridge University Press, (1961).
- 6) It can be asked what the corresponding Fokker-Planck equation for the Boltzmann equation would be. It clearly must be a functional equation for the probability functional: $P[h(\mathbf{rpt})]$ which determines the probability that the distribution function has value $h(\mathbf{rpt})$ at time t . Construction of such an equation has as yet not been attempted.
- 7) To see how the computation proceeds for the higher orders, the next two orders will be explicitly computed here. The rest are very similar. First of all the solution to equation (25) is necessary.

Assuming that

$$R_2(xpt) = Q_2(xt)(p^2 - MK_B T_{eq.})$$

and putting this into (25) results in the identity

$$\begin{aligned} Q_2(xt) = \frac{1}{2} \left[\frac{1}{M^2} \frac{\partial^2}{\partial x^2} Q_o + \frac{\omega^2}{MK_B T_{eq.}} \frac{\partial}{\partial x} (x Q_o) + \frac{\omega^2}{MK_B T_{eq.}} x \frac{\partial}{\partial x} Q_o + \right. \\ \left. + \left(\frac{\omega^2}{K_B T_{eq.}} x \right)^2 Q_o \right] \quad . \end{aligned} \quad (I)$$

Two more equations are necessary to obtain the next two orders of the approximation. To orders $\frac{1}{\theta^2}$ and $\frac{1}{\theta^3}$ the equations are

$$\begin{aligned} \frac{\partial_o}{\partial t} P_{eq.} R_2 + \frac{\partial_1}{\partial t} P_{eq.} R_1 + \frac{\partial_2}{\partial t} P_{eq.} R_o + \frac{p}{M} \frac{\partial}{\partial x} P_{eq.} R_2 - M\omega^2 x \frac{\partial}{\partial p} P_{eq.} R_2 = \\ = MK_B T_{eq.} \frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} R_3) \end{aligned} \quad (II)$$

$$\begin{aligned} \frac{\partial_o}{\partial t} P_{eq.} R_3 + \frac{\partial_1}{\partial t} P_{eq.} R_2 + \frac{\partial_2}{\partial t} P_{eq.} R_1 + \frac{\partial_3}{\partial t} P_{eq.} R_o + \frac{p}{M} \frac{\partial}{\partial x} P_{eq.} R_3 - M\omega^2 x \frac{\partial}{\partial p} P_{eq.} R_3 = \\ = MK_B T_{eq.} \frac{\partial}{\partial p} (P_{eq.} \frac{\partial}{\partial p} R_4) \quad . \end{aligned} \quad (III)$$

The solubility condition for (II) results very simply in

$$\frac{\partial_2}{\partial t} Q_o = 0 \quad . \quad (IV)$$

Assuming that

$$R_3(xpt) = Q_3(xt)(p^3 - 3MK_B T_{eq.} p) + Q'_3(xt)p$$

and putting this into (II) results in the identities

$$Q_3 = \frac{1}{6} \left[\frac{1}{M^2} \frac{\partial^2}{\partial x^2} Q_1 + \frac{\omega^2}{MK_B T_{eq.}} \frac{\partial}{\partial x} (xQ_1) \right] - \frac{1}{3} \frac{\omega^2}{K_B T_{eq.}} xQ_2$$

(V)

and $Q'_3 = \omega^2 Q_1$.

The solubility condition for (III) results in the equation

$$\frac{\partial}{\partial t} Q_o = \omega^2 \left[\frac{K_B T_{eq.}}{M} \frac{\partial}{\partial x} Q_o + \omega^2 xQ_o \right] \quad . \quad \text{(VI)}$$

Equations (IV) and (VI) give (34) for the cases of $n = 2$ and $n = 3$ respectively.

CHAPTER IV

The Application of the Enskog Contraction Procedure to the
Linearized Boltzmann Equation with Fluctuations

A. The Basic Formulae

It is convenient to collect together here some of the results of Chapter III. There, the linearized Boltzmann equation with fluctuations was established in the form

$$\frac{\partial}{\partial t} h(\mathbf{r}|\mathbf{p}|\mathbf{t}) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h(\mathbf{r}|\mathbf{p}|\mathbf{t}) = - \int K(\mathbf{p}|\mathbf{p}') f_{\text{eq.}}(\mathbf{p}') h(\mathbf{r}|\mathbf{p}'|\mathbf{t}) d\mathbf{p}' + \tilde{C}(\mathbf{r}|\mathbf{p}|\mathbf{t}) \quad (1)$$

with $\tilde{C}(\mathbf{r}|\mathbf{p}|\mathbf{t})$ satisfying

$$\langle \tilde{C}(\mathbf{r}|\mathbf{p}|\mathbf{t}) \tilde{C}(\mathbf{r}'|\mathbf{p}'|\mathbf{t}') \rangle = 2K(\mathbf{p}|\mathbf{p}') \delta(\mathbf{r}-\mathbf{r}') \delta(\mathbf{t}-\mathbf{t}') \quad . \quad (2)$$

$$f_{\text{eq.}}(\mathbf{p}) = n_{\text{eq.}} (2\pi m K_B T_{\text{eq.}})^{-3/2} \exp\left[-\frac{p^2}{2m K_B T_{\text{eq.}}}\right] \quad .$$

The kernel $K(\mathbf{p}|\mathbf{p}')$ has orthonormal eigenfunctions $\phi_i(\mathbf{p})$ with eigenvalues λ_i and weighting function $\frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(\mathbf{p})$. For $\ell = 1, \dots, 5$,

$\phi_\ell(\mathbf{p})$ has eigenvalue $\lambda_\ell = 0$ and corresponds to the five conserved quantities in a collision. The explicit values of the $\phi_\ell(\mathbf{p})$'s for $\ell = 1, \dots, 5$ are¹⁾

$$\phi_1(\mathbf{p}) = 1, \quad \phi_\alpha(\mathbf{p}) = (m K_B T_{\text{eq.}})^{-1/2} p_\alpha$$

for $\alpha = 2, 3, 4$ and

$$\phi_5(p) = \left(\frac{2}{3}\right)^{1/2} (K_B T_{eq.})^{-1} \left(\frac{p^2}{2m} - \frac{3}{2} K_B T_{eq.}\right) . \quad (3)$$

Eigenfunction expansions for $K(pp')$, $\tilde{C}(rpt)$ and $h(rpt)$ are possible and are

$$K(pp') = \sum_{\ell=0}^{\infty} \lambda_{\ell} \phi_{\ell}(p) \phi_{\ell}(p') . \quad (4)$$

$$\tilde{C}(rpt) = \sum_{\ell=0}^{\infty} \tilde{F}_{\ell}(rt) \phi_{\ell}(p) \quad (5)$$

$$h(rpt) = \sum_{\ell=1}^{\infty} a_{\ell}(rt) \phi_{\ell}(p) . \quad (6)$$

The $\tilde{F}_{\ell}(rt)$'s using (2) must satisfy

$$\left\langle \tilde{F}_{\ell}(rt) \tilde{F}_k(r't') \right\rangle = 2 \lambda_{\ell} \delta_{\ell k} \delta(r-r') \delta(t-t') . \quad (7)$$

From the usual definition of the hydrodynamical variables: density, local velocity, and local temperature, their values for the linearized case given by

$$f(rpt) = f_{eq.}(p) [1 + h(rpt)]$$

are

$$\Delta n(rt) = n(rt) - n_{eq.} = \int f_{eq.}(p) h(rpt) dp \quad (8)$$

$$n_{eq.} u_{\alpha}(rt) = \int f_{eq.}(p) \frac{p_{\alpha}}{m} h(rpt) dp \quad (9)$$

$$\frac{3}{2} K_B \Delta T(\text{rt}) + \frac{3}{2} \frac{K_B T_{\text{eq.}}}{n_{\text{eq.}}} \Delta n(\text{rt}) = \frac{1}{n_{\text{eq.}}} \int f_{\text{eq.}}(p) \frac{p^2}{2m} h(\text{rpt}) dp \quad (10)$$

where $\Delta T(\text{rt}) = T(\text{rt}) - T_{\text{eq.}}$. Note that the left hand side of (10) is also $\frac{3}{2n_{\text{eq.}}} \Delta p(\text{rt})$ where $\Delta p(\text{rt}) = p(\text{rt}) - p_{\text{eq.}}$.

As in section F of Chapter III a scaling parameter θ is introduced.²⁾ Both $h(\text{rpt})$ and the time derivative $\frac{\partial}{\partial t}$ are expanded.

$$h(\text{rpt}) = h_0(\text{rpt}) + \frac{1}{\theta} h_1(\text{rpt}) + \frac{1}{\theta^2} h_2(\text{rpt}) + \dots \quad (11)$$

$$\frac{\partial}{\partial t} \rightarrow \frac{\partial_0}{\partial t} + \frac{1}{\theta} \frac{\partial_1}{\partial t} + \frac{1}{\theta^2} \frac{\partial_2}{\partial t} + \dots \quad (12)$$

It is further asserted that $K(pp')$ is of order θ so that if $K = \theta \bar{K}$ the \bar{K} is of order zero in θ . Moreover, the eigenvalues of \bar{K} are $\bar{\lambda}_\ell = \frac{1}{\theta} \lambda_\ell$. Finally, $\tilde{C}(\text{rpt})$ is taken to be of order zero in θ . Taking this into account and putting (11) and (12) into (1) gives to equal orders in $\frac{1}{\theta}$ the set of equations

$$\int \bar{K}(pp') f_{\text{eq.}}(p') h_0(\text{rp}'t) dp' = 0 \quad (13)$$

$$\frac{\partial_0}{\partial t} h_0(\text{rpt}) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h_0(\text{rpt}) = - \int \bar{K}(pp') f_{\text{eq.}}(p') h_1(\text{rp}'t) dp' + \tilde{C}(\text{rpt}) \quad (14)$$

$$\frac{\partial_0}{\partial t} h_1(\text{rpt}) + \frac{\partial_1}{\partial t} h_0(\text{rpt}) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h_1(\text{rpt}) = - \int \bar{K}(pp') f_{\text{eq.}}(p') h_2(\text{rp}'t) dp' \quad (15)$$

$$\frac{\partial}{\partial t} h_2(rpt) + \frac{\partial}{\partial t} h_1(rpt) + \frac{\partial}{\partial t} h_0(rpt) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h_2(rpt) = -\sqrt{K}(pp') f_{eq.}(p') h_3(rp't) dp'. \quad (16)$$

This series of equations goes on for higher and higher orders of $\frac{1}{\theta}$. The solution to these equations is obtained successively by invoking, as in Chapter III, solubility conditions and conditions for uniqueness. The uniqueness conditions are expressed by assuming that in the expansions of the successive approximations, $h_n(rpt)$, in terms of the eigenfunctions, $\phi_\ell(p)$, only $h_0(rpt)$ contains the first five eigenfunctions. Therefore, if

$$h_n(rpt) = \sum_\ell a_\ell^{(n)}(rt) \phi_\ell(p) ,$$

then it is assumed that

$$a_\ell^{(n)}(rt) = 0 \quad \text{for } \ell = 1, \dots, 5 \text{ when } n > 0 . \quad (17)$$

That the conditions (17) insure uniqueness will become apparent as the computation proceeds in the following.

B. The Zero and First Order Approximations

Clearly, the solution to (13) is given by the zero-eigenvalue eigenfunctions of $\bar{K}(pp')$. Therefore,

$$h_0(rpt) = \sum_{\ell=1}^5 a_\ell^{(0)}(rt) \phi_\ell(p) . \quad (18)$$

The uniqueness conditions (17) imply that the hydrodynamical quantities given by (8) through (10) are determined exclusively by $h_0(rpt)$. The

following identities are obtained

$$a_1^{(o)}(rt) = n_{eq.}^{-1} \Delta n(rt) \quad (19)$$

$$a_\alpha^{(o)}(rt) = \left(\frac{m}{K_B T_{eq.}} \right)^{1/2} u_\alpha(rt) \quad (20)$$

$$a_5^{(o)}(rt) = \left(\frac{3}{2} \right)^{1/2} \frac{1}{T_{eq.}} \Delta T(rt) \quad . \quad (21)$$

In order to solve (14) it is necessary to impose a solubility condition which requires that all terms in (14) must be orthogonal with the zero-eigenvalue eigenfunctions of $\bar{K}(pp')$. $\tilde{C}(rpt)$ automatically has this property by virtue of (5). The solubility condition is therefore

$$\int \phi_\ell(p) \frac{1}{n_{eq.}} f_{eq.}(p) \left[\frac{\partial}{\partial t} h_o(rpt) + \frac{p_\alpha}{m} \frac{\partial}{\partial x_\alpha} h_o(rpt) \right] dp = 0 \text{ for } \ell = 1, \dots, 5 \quad . \quad (22)$$

Define $B_\alpha^{\ell k}$ by

$$B_\alpha^{\ell k} = \int \frac{1}{n_{eq.}} f_{eq.}(p) \phi_\ell(p) \frac{p_\alpha}{m} \phi_k(p) dp \quad . \quad (23)$$

Putting (23) and (18) into (22) gives

$$\frac{\partial}{\partial t} a_\ell^{(o)}(rt) + \sum_{k=1}^5 B_\alpha^{\ell k} \frac{\partial}{\partial x_\alpha} a_k^{(o)}(rt) = 0 \text{ for } \ell = 1, \dots, 5 \quad . \quad (24)$$

Using (19) through (21) it is easily verified that (24) are the linearized Euler hydrodynamical equations

$$\frac{\partial}{\partial t} \Delta n(\mathbf{r}, t) + n_{\text{eq.}} \frac{\partial}{\partial \mathbf{x}_\alpha} u_\alpha(\mathbf{r}, t) = 0 \quad (25)$$

$$mn_{\text{eq.}} \frac{\partial}{\partial t} u_\alpha(\mathbf{r}, t) = - \frac{\partial}{\partial \mathbf{x}_\alpha} [\Delta n(\mathbf{r}, t) K_B T_{\text{eq.}} + n_{\text{eq.}} K_B \Delta T(\mathbf{r}, t)] \quad (26)$$

$$n_{\text{eq.}} K_B \frac{\partial}{\partial t} \Delta T(\mathbf{r}, t) = - \frac{2}{3} n_{\text{eq.}} K_B T_{\text{eq.}} \frac{\partial}{\partial \mathbf{x}_\alpha} u_\alpha(\mathbf{r}, t) . \quad (27)$$

Equations (25) through (27) may be viewed as defining the zero order time derivative of the hydrodynamical quantities. Note that to this order of approximation the fluctuating force, $\tilde{C}(\mathbf{r}, t)$ has made no contribution.

Finally, if conditions (22) are satisfied then the uniqueness conditions, (17), guarantee that (14) admits of a unique solution for $h_1(\mathbf{r}, t)$. The expansion coefficients, $a_\ell^{(1)}(\mathbf{r}, t)$ are easily verified to be given by

$$a_\ell^{(1)}(\mathbf{r}, t) = \frac{1}{n_{\text{eq.}} \tilde{\lambda}_\ell} [\tilde{F}_\ell(\mathbf{r}, t) - \sum_{k=1}^5 B_\alpha^{\ell k} \frac{\partial}{\partial \mathbf{x}_\alpha} a_k^{(0)}(\mathbf{r}, t)] . \quad (28)$$

C. The Second Order Approximation

The solubility conditions for (15) are

$$\int \phi_\ell(\mathbf{p}) \frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(\mathbf{p}) \left[\frac{\partial}{\partial t} h_0(\mathbf{r}, t) + \frac{p_\alpha}{m} \frac{\partial}{\partial \mathbf{x}_\alpha} h_1(\mathbf{r}, t) \right] d\mathbf{p} = 0 \text{ for } \ell = 1, \dots, 5 . \quad (29)$$

In terms of the expansion coefficients (29) becomes

$$\frac{\partial}{\partial t} a_\ell^{(0)}(\mathbf{r}, t) = - \sum_{k=6}^{\infty} B_\alpha^{\ell k} \frac{\partial}{\partial \mathbf{x}_\alpha} a_k^{(1)}(\mathbf{r}, t) \text{ for } \ell = 1, \dots, 5 . \quad (30)$$

Substituting (28) into (30) gives

$$\frac{\partial}{\partial t} a_{\ell}^{(o)}(rt) = \frac{1}{n_{eq.}} \sum_{k=6}^{\infty} \sum_{j=6}^{\infty} B_{\alpha}^{\ell k} \frac{1}{\bar{\lambda}_k} B_{\beta}^{kj} \frac{\partial^2}{\partial x_{\alpha} \partial x_{\beta}} a_j^{(o)}(rt) - \frac{1}{n_{eq.}} \sum_{k=6}^{\infty} B_{\alpha}^{\ell k} \frac{1}{\bar{\lambda}_k} \frac{\partial}{\partial x_{\alpha}} \tilde{F}_k(rt) . \quad (31)$$

For the case of spherically symmetric intermolecular potentials, which is assumed throughout this discussion, the $\phi_{\ell}(p)$'s are either even or odd under the reflection: $p \longleftrightarrow -p$. Therefore, from (23) it is seen that

$$B_{\alpha}^{\ell k} \frac{1}{\bar{\lambda}_k} B_{\beta}^{kj} = 0$$

unless $\phi_{\ell}(p)$ and $\phi_j(p)$ have the same parity under $p \longleftrightarrow -p$. Keeping this in mind and using the following list of definitions

$$\Pi_{\alpha\beta}^{\mu\nu} = \frac{m}{\theta} \sum_{k=6}^{\infty} B_{\alpha}^{\mu k} \frac{1}{\bar{\lambda}_k} B_{\beta}^{k\nu} \quad \text{and} \quad Q_{\alpha\beta} = \frac{3K_B}{2\theta} \sum_{k=6}^{\infty} B_{\alpha}^{5k} \frac{1}{\bar{\lambda}_k} B_{\beta}^{k5} \quad (32)$$

$$P_{\alpha\beta}^{(1)}(rt) = - \Pi_{\beta\nu}^{\alpha\mu} \frac{\partial}{\partial x_{\nu}} u_{\mu}(rt) \quad \text{and} \quad q_{\alpha}^{(1)}(rt) = - Q_{\alpha\beta} \frac{\partial}{\partial x_{\beta}} \Delta T(rt) \quad (33)$$

$$\tilde{P}_{\alpha\beta}(rt) = (mK_B T_{eq.})^{1/2} \frac{1}{\theta} \sum_{k=6}^{\infty} B_{\beta}^{\alpha k} \frac{1}{\bar{\lambda}_k} \tilde{F}_k(rt) \quad \text{and} \quad \tilde{q}_{\alpha}^{(1)}(rt) = \left(\frac{3}{2}\right)^{1/2} \frac{K_B T_{eq.}}{\theta} \sum_{k=6}^{\infty} B_{\alpha}^{5k} \frac{1}{\bar{\lambda}_k} \tilde{F}_k(rt) \quad (34)$$

equations (31) become upon substitution of (19) through (21)

$$\frac{\partial}{\partial t} \Delta n(rt) = 0 \quad (35)$$

$$m n_{eq.} \frac{\partial}{\partial t} u_{\alpha}(rt) = - \theta \frac{\partial}{\partial x_{\beta}} P_{\alpha\beta}^{(1)}(rt) - \theta \frac{\partial}{\partial x_{\beta}} \tilde{P}_{\alpha\beta}^{(1)}(rt) \quad (36)$$

$$\frac{3}{2} n_{\text{eq.}} K_B \frac{\partial}{\partial t} \Delta T(\mathbf{r}t) = - \theta \frac{\partial}{\partial \mathbf{x}_\alpha} q_\alpha^{(1)}(\mathbf{r}t) - \theta \frac{\partial}{\partial \mathbf{x}_\alpha} \tilde{q}_\alpha^{(1)}(\mathbf{r}t) . \quad (37)$$

Furthermore, from (7) it is easily verified that

$$\left\langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}t) \tilde{P}_{\mu\nu}^{(1)}(\mathbf{r}'t') \right\rangle = 2K_B T_{\text{eq.}} \delta(t-t') \delta(\mathbf{r}-\mathbf{r}') \Pi_{\beta\nu}^{\alpha\mu} \quad (38)$$

$$\left\langle \tilde{q}_\alpha^{(1)}(\mathbf{r}t) \tilde{q}_\beta^{(1)}(\mathbf{r}'t') \right\rangle = 2K_B T_{\text{eq.}}^2 \delta(t-t') \delta(\mathbf{r}-\mathbf{r}') Q_{\alpha\beta} \quad (39)$$

$$\left\langle \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}t) \tilde{q}_\gamma^{(1)}(\mathbf{r}'t') \right\rangle = 0 . \quad (40)$$

Combining equations (35) through (37) with equations (25) through (27)

and taking $\frac{\partial}{\partial t}$ up to order $\frac{1}{\theta}$ so that

$$\frac{\partial}{\partial t} = \frac{\partial_o}{\partial t} + \frac{1}{\theta} \frac{\partial_1}{\partial t}$$

gives

$$\frac{\partial}{\partial t} \Delta n(\mathbf{r}t) + n_{\text{eq.}} \frac{\partial}{\partial \mathbf{x}_\alpha} u_\alpha(\mathbf{r}t) = 0 \quad (41)$$

$$n_{\text{eq.}} \frac{\partial}{\partial t} u_\alpha(\mathbf{r}t) + \frac{\partial}{\partial \mathbf{x}_\alpha} [\Delta n(\mathbf{r}t) K_B T_{\text{eq.}} + n_{\text{eq.}} K_B \Delta T(\mathbf{r}t)] = - \frac{\partial}{\partial \mathbf{x}_\beta} P_{\alpha\beta}^{(1)}(\mathbf{r}t) - \frac{\partial}{\partial \mathbf{x}_\beta} \tilde{P}_{\alpha\beta}^{(1)}(\mathbf{r}t) \quad (42)$$

$$\frac{3}{2} n_{\text{eq.}} K_B \frac{\partial}{\partial t} \Delta T(\text{rt}) + n_{\text{eq.}} K_B T_{\text{eq.}} \frac{\partial}{\partial x_\alpha} u_\alpha(\text{rt}) = - \frac{\partial}{\partial x_\alpha} q_\alpha^{(1)}(\text{rt}) - \frac{\partial}{\partial x_\alpha} \tilde{q}_\alpha^{(1)}(\text{rt}) . \quad (43)$$

Equations (38) through (40) give the correlations of the fluctuating forces. These equations are precisely of the same form as the Landau and Lifshitz equations for fluctuating hydrodynamics. For the case of spherically symmetric intermolecular potentials it will be shown in a subsequent section of this chapter that the tensor form of $\Pi_{\beta\nu}^{\alpha\mu}$ and $Q_{\alpha\beta}$ is that given for the Landau and Lifshitz theory in Chapter II.

It should be noted that since the Landau and Lifshitz theory of fluctuating hydrodynamics is derivable from the contraction of the fluctuating Boltzmann equation, and since each of these theories is of the standard form of a stationary Gaussian Markov process, then the second order approximation of the contraction of a stationary Gaussian Markov process is itself sometimes a stationary Gaussian Markov process. It turns out always to be true for any stationary Gaussian Markov process, and this specific instance is merely an example of a very general situation.³⁾

Finally, if conditions (29) are satisfied, then the uniqueness conditions (17), guarantee that (15) admits of a unique solution for $h_2(\text{rpt})$. The expansion coefficients, $a_\ell^{(2)}(\text{rt})$ are found to be given by

$$\begin{aligned} a_\ell^{(2)}(\text{rt}) = & - \frac{1}{n_{\text{eq.}}^2} \frac{1}{\bar{\lambda}_\ell} \left[\frac{1}{\bar{\lambda}_\ell} \left(\frac{\partial}{\partial t} \tilde{F}_\ell(\text{rt}) - \sum_{k=1}^5 B_\alpha^{\ell k} \frac{\partial}{\partial x_\alpha} \frac{\partial}{\partial t} a_k^{(0)}(\text{rt}) \right) + \right. \\ & \left. + \sum_{k=6}^{\infty} B_\alpha^{\ell k} \frac{\partial}{\partial x_\alpha} \frac{1}{\bar{\lambda}_k} \left(\tilde{F}_k(\text{rt}) - \sum_{j=1}^5 B_\beta^{kj} \frac{\partial}{\partial x_\beta} a_j^{(0)}(\text{rt}) \right) \right] \end{aligned} \quad (44)$$

wherein (28) has been substituted.

D. The Third Order Approximation

It is of interest to carry the contraction procedure further by one more order in $\frac{1}{\theta}$ and thereby obtain the Burnett hydrodynamical fluctuations. The solubility conditions for (16) are

$$\int \phi_{\ell}(p) \frac{1}{n_{\text{eq.}}(p)} f_{\text{eq.}}(p) \left[\frac{\partial}{\partial t} h_o(\text{rpt}) + \frac{p_{\alpha}}{m} \frac{\partial}{\partial x_{\alpha}} h_2(\text{rpt}) \right] dp = 0 \text{ for } \ell = 1, \dots, 5. \quad (45)$$

In terms of the expansion coefficients and using (44) to eliminate the $a_{\ell}^{(2)}$'s equations (45) become

$$\begin{aligned} \frac{\partial}{\partial t} a_{\ell}^{(o)}(\text{rt}) = & -\frac{1}{n_{\text{eq.}}^2} \sum_{k=6}^{\infty} B_{\alpha}^{\ell k} \frac{\partial}{\partial x_{\alpha}} \left[\left(\frac{1}{\bar{\lambda}_k} \right)^2 \sum_{j=1}^5 B_{\beta}^{kj} \frac{\partial}{\partial x_{\beta}} \frac{\partial}{\partial t} a_j^{(o)}(\text{rt}) + \right. \\ & \left. + \frac{1}{\bar{\lambda}_k} \sum_{j=6}^{\infty} B_{\beta}^{kj} \frac{\partial}{\partial x_{\beta}} \frac{1}{\bar{\lambda}_j} \sum_{i=1}^5 B_{\delta}^{ji} \frac{\partial}{\partial x_{\delta}} a_i^{(o)}(\text{rt}) \right] \\ & + \frac{1}{n_{\text{eq.}}^2} \sum_{k=6}^{\infty} B_{\alpha}^{\ell k} \frac{\partial}{\partial x_{\alpha}} \left[\left(\frac{1}{\bar{\lambda}_k} \right)^2 \frac{\partial}{\partial t} \tilde{F}_k(\text{rt}) + \frac{1}{\bar{\lambda}_k} \sum_{j=6}^{\infty} B_{\beta}^{kj} \frac{\partial}{\partial x_{\beta}} \frac{1}{\bar{\lambda}_j} \tilde{F}_j(\text{rt}) \right] \end{aligned} \quad (46)$$

for $\ell = 1, \dots, 5$.

Again using (23), note that

$$B_{\alpha}^{\ell k} \frac{1}{\bar{\lambda}_k} B_{\beta}^{kj} \frac{1}{\bar{\lambda}_j} B_{\delta}^{ji} = 0$$

unless $\phi_{\ell}(p)$ and $\phi_i(p)$ have opposite parity under $p \longleftrightarrow -p$. Keeping

End

this in mind and using the following list of definitions

$$D_{\alpha\beta}^{\mu\nu} = \frac{m}{n_{eq.}} \frac{1}{\theta^2} \sum_{k=6}^{\infty} B_{\alpha}^{\mu k} \left(\frac{1}{\bar{\lambda}_k} \right)^2 B_{\beta}^{k\nu} ; D'_{\alpha\beta} = \frac{3K_B}{2n_{eq.}} \frac{1}{\theta^2} \sum_{k=6}^{\infty} B_{\alpha}^{5k} \left(\frac{1}{\bar{\lambda}_k} \right)^2 B_{\beta}^{k5} \quad (47)$$

and

$$Q_{\alpha\beta\gamma}^{\mu} = \frac{1}{n_{eq.}} \frac{1}{\theta^2} \left(\frac{3}{2} mK_B T_{eq.} \right)^{1/2} \sum_{k=6}^{\infty} B_{\alpha}^{\mu k} \frac{1}{\bar{\lambda}_k} \sum_{j=6}^{\infty} B_{\beta}^{kj} \frac{1}{\bar{\lambda}_j} B_{\gamma}^{j5}$$

$$P_{\alpha\beta}^{(2)}(rt) = \frac{1}{T_{eq.}} Q_{\mu\beta\nu}^{\alpha} \frac{\partial^2}{\partial x_{\mu} \partial x_{\nu}} \Delta T(rt) + D_{\beta\nu}^{\alpha\mu} \frac{\partial}{\partial x_{\nu}} \frac{\partial}{\partial t} u_{\mu}(rt) \quad (48)$$

and

$$q_{\alpha}^{(2)}(rt) = Q_{\nu\alpha\beta}^{\mu} \frac{\partial^2}{\partial x_{\nu} \partial x_{\beta}} u_{\mu}(rt) + D'_{\alpha\beta} \frac{\partial}{\partial x_{\beta}} \frac{\partial}{\partial t} \Delta T(rt)$$

$$\tilde{P}_{\alpha\beta}^{(2)}(rt) = - \frac{(mK_B T_{eq.})^{1/2}}{n_{eq.} \theta^2} \sum_{k=6}^{\infty} B_{\beta}^{\alpha k} \left[\left(\frac{1}{\bar{\lambda}_k} \right)^2 \frac{\partial}{\partial t} \tilde{F}_k(rt) + \frac{1}{\bar{\lambda}_k} \sum_{j=6}^{\infty} B_{\gamma}^{kj} \frac{\partial}{\partial x_{\gamma}} \frac{1}{\bar{\lambda}_j} \tilde{F}_j(rt) \right] \quad (49)$$

and

$$\tilde{q}_{\alpha}^{(2)}(rt) = - \left(\frac{3}{2} \right)^{1/2} \frac{K_B T_{eq.}}{n_{eq.} \theta^2} \sum_{k=6}^{\infty} B_{\alpha}^{5k} \left[\left(\frac{1}{\bar{\lambda}_k} \right)^2 \frac{\partial}{\partial t} \tilde{F}_k(rt) + \frac{1}{\bar{\lambda}_k} \sum_{j=6}^{\infty} B_{\gamma}^{kj} \frac{\partial}{\partial x_{\gamma}} \frac{1}{\bar{\lambda}_j} \tilde{F}_j(rt) \right]$$

equations (46) become upon substitution of (19) through (21)⁴⁾

$$\frac{\partial}{\partial t} \Delta n(rt) = 0 \quad (50)$$

$$mn_{eq.} \frac{\partial}{\partial t} u_{\alpha}(rt) = - \theta^2 \frac{\partial}{\partial x_{\beta}} P_{\alpha\beta}^{(2)}(rt) - \theta^2 \frac{\partial}{\partial x_{\beta}} \tilde{P}_{\alpha\beta}^{(2)}(rt) \quad (51)$$

$$\frac{3}{2} n_{eq.} K_B \frac{\partial}{\partial t} \Delta T(rt) = - \theta^2 \frac{\partial}{\partial x_{\alpha}} q_{\alpha}^{(2)}(rt) - \theta^2 \frac{\partial}{\partial x_{\alpha}} \tilde{q}_{\alpha}^{(2)}(rt) . \quad (52)$$

Furthermore from (7) it is easily verified that

$$\left\langle \tilde{P}_{\alpha\beta}^{(2)}(rt) \tilde{q}_{\gamma}^{(1)}(r't') \right\rangle = - 2K_B T_{eq.} \delta(t-t') Q_{\beta\gamma}^{\alpha} \frac{\partial}{\partial x_{\gamma}} \delta(r-r') \quad (53)$$

$$\left\langle \tilde{P}_{\alpha\beta}^{(1)}(rt) \tilde{q}_{\gamma}^{(2)}(r't') \right\rangle = - 2K_B T_{eq.} \delta(t-t') Q_{\beta\gamma}^{\alpha} \frac{\partial}{\partial x'_{\gamma}} \delta(r-r') \quad (54)$$

$$\left\langle \tilde{P}_{\alpha\beta}^{(1)}(rt) \tilde{P}_{\mu\nu}^{(2)}(r't') \right\rangle = - 2K_B T_{eq.} \delta(r-r') D_{\beta\nu}^{\alpha\mu} \frac{\partial}{\partial t'} \delta(t-t') \quad (55)$$

$$\left\langle \tilde{q}_{\alpha}^{(1)}(rt) \tilde{q}_{\beta}^{(2)}(r't') \right\rangle = - 2K_B T_{eq.}^2 \delta(r-r') D_{\alpha\beta}^{\gamma} \frac{\partial}{\partial t'} \delta(t-t') . \quad (56)$$

In the last several equations the derivative $\frac{\partial}{\partial t}$ appears. It is to be applied only when manipulations finally result in its application on a hydrodynamical quantity. In such cases it is defined by equations (25) through (27). When equations (50) through (52) are combined with equations (41) through (43) and $\frac{\partial}{\partial t}$ is taken to mean $\frac{\partial}{\partial t} + \frac{1}{\theta} \frac{\partial}{\partial t} + \frac{1}{\theta^2} \frac{\partial}{\partial t}$

up to order $\frac{1}{\theta^2}$ then the Burnett hydrodynamical equations in linearized form with fluctuations are obtained. For the case of spherically symmetric intermolecular potentials the tensor form of $D_{\beta\nu}^{\alpha\mu}$, $D'_{\alpha\beta}$ and $Q_{\beta\mu}^{\alpha}$ may be determined. This will be done in the next section.

Note that while the contraction procedure produced a stationary Gaussian Markov process to order $\frac{1}{\theta}$ of the approximation, it did not do so to order $\frac{1}{\theta^2}$. This is most easily seen by noting that, for instance, $\langle \tilde{q}_{\alpha}^{(2)}(rt) \tilde{q}_{\beta}^{(2)}(r't') \rangle$ does not correspond to any dissipative coefficient of the average Burnett equations since it must contribute to the next order in $\frac{1}{\theta}$.

E. Spherically Symmetric Intermolecular Potentials

For spherically symmetric intermolecular potentials the $\phi_k(p)$'s may always be written in manifestly spherically symmetric form as products of scalar functions of p with spherical tensors in p

$$\phi_k(p) \rightarrow \psi_{\ell_k}^{r_k}(p) p^{-\ell_k} \langle p_{\mu_1} \dots p_{\mu_{\ell_k}} \rangle \quad (57)$$

where r_k and ℓ_k manifestly depend on k , $\psi_{\ell_k}^{r_k}(p)$ is a scalar function of p , and $\langle p_{\mu_1} \dots p_{\mu_{\ell_k}} \rangle$ is a totally symmetric form in the

p_{μ_i} 's with all possible traces equal to zero. Examples are

$$\begin{aligned} \langle p_{\mu} p_{\nu} \rangle &= p_{\mu} p_{\nu} - \frac{1}{3} p^2 \delta_{\mu\nu} \\ \langle p_{\alpha} p_{\beta} p_{\gamma} \rangle &= p_{\alpha} p_{\beta} p_{\gamma} - \frac{1}{5} p^2 (p_{\alpha} \delta_{\beta\gamma} + p_{\beta} \delta_{\alpha\gamma} + p_{\gamma} \delta_{\alpha\beta}) . \end{aligned} \quad (58)$$

In the notation of (57) the five zero-eigenvalue eigenfunctions are given by

$$\phi_1(p) = 1 = \psi_0^o(p)$$

$$\phi_\mu(p) = (mK_B T_{eq.})^{-1/2} p_\mu = \psi_1^o(p) p^{-1} p_\mu \rightarrow \psi_1^o(p) = p (mK_B T_{eq.})^{-1/2} \quad (59)$$

$$\phi_5(p) = \left(\frac{2}{3}\right)^{1/2} (K_B T_{eq.})^{-1} \left(\frac{p^2}{2m} - \frac{3}{2} K_B T_{eq.}\right) = \psi_0^1(p).$$

It is desired to compute the precise tensor form of $\Pi_{\alpha\beta}^{\mu\nu}$,

$Q_{\alpha\beta}$, $D_{\alpha\beta}^{\mu\nu}$, $D'_{\alpha\beta}$ and $Q_{\alpha\beta}^\mu$. To do so it is necessary to compute

$B_\alpha^{\mu j}$, B_α^{5j} and B_α^{kj} for $j, k \geq 6$ first. Using (23) and (59) with (58)

gives

$$B_\alpha^{\mu j} = \frac{(mK_B T_{eq.})^{-1/2}}{mn_{eq.}} \int f_{eq.}(p) [\langle p_\mu p_\alpha \rangle + \frac{1}{3} p^2 \delta_{\mu\alpha}] \phi_j(p) dp \quad (60)$$

$$B_\alpha^{5j} = \left(\frac{2}{3}\right)^{1/2} \frac{1}{mn_{eq.} K_B T_{eq.}} \int f_{eq.}(p) \left(\frac{p^2}{2m} - \frac{3}{2} K_B T_{eq.}\right) p_\alpha \phi_j(p) dp \quad (61)$$

$$B_\alpha^{jk} = \frac{1}{mn_{eq.}} \int f_{eq.}(p) p_\alpha \phi_j(p) \phi_k(p) dp \quad (62)$$

In (60) the $\frac{1}{3} p^2 \delta_{\mu\alpha}$ term may be written as a linear combination of $\phi_1(p)$ and $\phi_5(p)$ and therefore makes no contribution to the integral for $j \geq 6$.

Similarly, the $-\frac{3}{2} K_B T_{eq.} p_\alpha$ term of (61) is proportional to $\phi_\alpha(p)$ and

therefore makes no contribution to the integral for $j \geq 6$. Because the $\langle p_\mu p_\alpha \rangle$ term of (60) corresponds to $\ell = 2$, only $\phi_j(p)$'s with $\ell_j = 2$ will give non-zero integrals. Therefore, using (57), (60) becomes

$$B_\alpha^{\mu j} = \frac{(mK_{B \text{ eq.}})^{-1/2}}{mn_{\text{eq.}}} \int f_{\text{eq.}}(p) \psi_2^j(p) p^{-2} \langle p_\mu p_\alpha \rangle \langle p_{\mu_1} p_{\mu_2} \rangle. \quad (63)$$

In (61) the $\frac{p^2}{2m} p_\alpha$ term corresponds to $\ell = 1$ so that $\phi_j(p)$'s with $\ell_j = 1$ only will produce non-zero integrals. Therefore, using (57), (61) becomes

$$B_\alpha^{5j} = \left(\frac{2}{3}\right)^{1/2} \frac{1}{2m^2 n_{\text{eq.}} K_{B \text{ eq.}} T_{\text{eq.}}} \int f_{\text{eq.}}(p) \psi_1^j(p) p p_\alpha p_\mu dp. \quad (64)$$

The B_α^{jk} terms are necessary only for computation of $Q_{\alpha\beta}^\mu$ which it may be seen from (47) requires that $\ell_j = 2$ and $\ell_k = 1$ because of (63) and (64). Therefore, B_α^{jk} will be evaluated only for the $\ell_j = 2$ and $\ell_k = 1$ case. Therefore, (62) becomes

$$B_\alpha^{jk} = \frac{1}{mn_{\text{eq.}}} \int f_{\text{eq.}}(p) p_\alpha \psi_2^j(p) p^{-2} \langle p_{\mu_1} p_{\mu_2} \rangle p^{-1} p_\nu dp. \quad (65)$$

Using some well known integral theorems for spherical tensors multiplied by scalar functions⁵⁾ as in (63) through (65) these integrals become

$$B_\alpha^{\mu j} = \frac{(mK_{B \text{ eq.}})^{-1/2}}{15 mn_{\text{eq.}}} \int f_{\text{eq.}}(p) p^2 \psi_2^j(p) dp (\delta_{\mu\mu_1} \delta_{\alpha\mu_2} + \delta_{\mu\mu_2} \delta_{\alpha\mu_1} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\mu_1\mu_2}) \quad (66)$$

$$B_{\alpha}^{5j} = \left(\frac{2}{3}\right)^{1/2} \frac{1}{6m_{eq}^2 K_B T_{eq.}} \int f_{eq.}(p) p^3 \psi_1^{rj}(p) dp \delta_{\alpha\mu} \quad (67)$$

$$B_{\alpha}^{jk} = \frac{1}{15mn_{eq.}} \int f_{eq.}(p) p \psi_2^{rj}(p) \psi_1^{rk}(p) dp (\delta_{\alpha\mu_1} \delta_{\nu\mu_2} + \delta_{\alpha\mu_2} \delta_{\nu\mu_1} - \frac{2}{3} \delta_{\alpha\nu} \delta_{\mu_1\mu_2}) . \quad (68)$$

In order to simplify these expressions further the following definitions are useful

$$N_2^j = \frac{(mK_B T_{eq.})^{-1/2}}{15mn_{eq.}} \int f_{eq.}(p) p^2 \psi_2^{rj}(p) dp$$

$$N_1^j = \left(\frac{2}{3}\right)^{1/2} \frac{1}{6m_{eq}^2 K_B T_{eq.}} \int f_{eq.}(p) p^3 \psi_1^{rj}(p) dp \quad (69)$$

$$N_{21}^{jk} = \frac{1}{15mn_{eq.}} \int f_{eq.}(p) p \psi_2^{rj}(p) \psi_1^{rk}(p) dp .$$

Putting (69) into (66) through (68) and using (32) and (47) gives

$$\Pi_{\alpha\beta}^{\mu\nu} = 2m \sum_{j=6}^{\infty} \frac{1}{\lambda_j} (N_2^j)^2 (\delta_{\alpha\beta} \delta_{\mu\nu} + \delta_{\alpha\nu} \delta_{\mu\beta} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\nu}) \quad (70)$$

$$Q_{\alpha\beta} = \frac{3}{2} K_B \sum_{j=6}^{\infty} \frac{1}{\lambda_j} (N_1^j)^2 \delta_{\alpha\beta} \quad (71)$$

$$D_{\alpha\beta}^{\mu\nu} = 2 \frac{m}{n_{eq.}} \sum_{j=6}^{\prime} \left(\frac{1}{\lambda_j} N_2^j \right)^2 (\delta_{\alpha\beta} \delta_{\mu\nu} + \delta_{\alpha\nu} \delta_{\mu\beta} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\nu}) \quad (72)$$

$$D'_{\alpha\beta} = \frac{3K_B}{2n_{eq.}} \sum_{j=6}^{\prime} \left(\frac{1}{\lambda_j} N_1^j \right)^2 \delta_{\alpha\beta} \quad (73)$$

$$Q_{\alpha\beta\gamma}^{\mu} = \frac{2}{n_{eq.}} \left(\frac{3}{2} m K_B T_{eq.} \right)^{1/2} \sum_{j=6}^{\prime} \sum_{k=6}^{\prime} \frac{1}{\lambda_j \lambda_k} N_2^j N_{21}^{jk} N_1^k (\delta_{\alpha\beta} \delta_{\mu\gamma} + \delta_{\alpha\gamma} \delta_{\mu\beta} - \frac{2}{3} \delta_{\alpha\mu} \delta_{\beta\gamma}) \quad (74)$$

The primes on the Σ 's is to indicate that the sums are to be taken over only those values of j or k which correspond with the allowed values of ℓ_j or ℓ_k which are either 1 or 2 in the cases above. For instance, in (70), $\ell_j = 2$ must hold so that only those j for which $\ell_j = 2$ are summed over by $\sum_{j=6}^{\prime}$. Similarly, for the others the proper value of ℓ is given by the subscript of the N term.

Note that from (70) and (71) the tensor form of the Landau and Lifshitz theory is obtained.

F. Maxwell Molecules⁶⁾

The assumption of Maxwell molecules means that the inter-molecular potential is assumed to be $\frac{K}{r^4}$ where K is a constant. This results in explicit values for the λ_j 's and for the $\psi_{\ell_j}^{rj}(p)$'s. The eigenvalues for Maxwell molecules will be denoted by $\lambda_{rj\ell_j}$. The eigenfunctions will have their scalar factor, $\psi_{\ell_j}^{rj}(p)$, denoted by

$M_{\ell_j}^{rj}(p)$. A few M_{ℓ}^r 's in explicit form are

$$\begin{aligned}
M_1^1(p) &= \left(\frac{4}{5}\right)^{1/2} (2mK_B T_{eq.})^{-3/2} p(p^2 - 5mK_B T_{eq.}), \quad M_1^0(p) = (mK_B T_{eq.})^{-1/2} p \\
M_2^0(p) &= (2)^{1/2} (2mK_B T_{eq.})^{-1} p^2, \quad M_0^1(p) = \left(\frac{2}{3}\right)^{1/2} (K_B T_{eq.})^{-1} \left(\frac{p^2}{2m} - \frac{3}{2} K_B T_{eq.}\right).
\end{aligned}
\tag{75}$$

For the same value of ℓ two M_ℓ^r 's are orthogonal if their r 's are different. Using this property and remembering that $j_1 k \geq 6$, gives for N_2^j , N_1^j and N_{21}^{jk}

$$N_2^j = \left(\frac{K_B T_{eq.}}{2m}\right)^{1/2} \delta_{r_j 0}, \quad N_1^j = \left(\frac{5}{3}\right)^{1/2} \left(\frac{K_B T_{eq.}}{m}\right)^{1/2} \delta_{r_j 1}, \quad N_{21}^{jk} = \left(\frac{K_B T_{eq.}}{5m}\right)^{1/2} \delta_{r_j 0} \delta_{r_k 1}.
\tag{76}$$

For Maxwell molecules, the numerical value of the eigenvalues is given by the substitution $\lambda_j \rightarrow \left(\frac{2k}{m}\right)^{1/2} \lambda_{r_j \ell_j}$ where k is the strength of the potential. Using this substitution with (76), the numerical coefficients for the tensors given in (70) through (74), which will be denoted by η , K , D , D' , and Q are given by

$$\begin{aligned}
\eta &= K_B T_{eq.} \left(\frac{m}{2k}\right)^{1/2} \frac{1}{\lambda_{02}}, \quad K = \frac{5}{2} \frac{K_B^2 T_{eq.}^2}{m} \left(\frac{m}{2k}\right)^{1/2} \frac{1}{\lambda_{11}}, \quad D = \frac{K_B T_{eq.}}{n_{eq.}} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{02}^2} \\
D' &= \frac{5}{2} \frac{K_B^2 T_{eq.}^2}{mn_{eq.}} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{11}^2} \quad \text{and} \quad Q = \frac{1}{n_{eq.}} \frac{(K_B T_{eq.})^2}{m} \left(\frac{m}{2k}\right) \frac{1}{\lambda_{02} \lambda_{11}}.
\end{aligned}
\tag{77}$$

These values check with the values given in the literature.⁷⁾

NOTES

- 1) The following integrals are useful for checking the orthonormality conditions for (3):

$$\int \frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(p) p_{\alpha} p_{\beta} dp = m K_B T_{\text{eq.}} \delta_{\alpha\beta}$$

and

$$\int \frac{1}{n_{\text{eq.}}} f_{\text{eq.}}(p) \frac{p^2}{2m} p_{\alpha} p_{\beta} dp = \frac{5}{2} m (K_B T_{\text{eq.}})^2 \delta_{\alpha\beta} .$$

- 2) In contrast with the problem of Brownian motion of a harmonic oscillator treated in Chapter III, the parameter θ here does not have a direct physical interpretation. It is desired to develop a scaling parameter which measures how slowly the hydrodynamical variables vary in time, and it will turn out afterwards that $\frac{1}{\theta}$ is of the order of the relative change of the hydrodynamical variables over a mean free time.
- 3) In order to prove that the second order approximation for the contraction of a stationary Gaussian Markov process is again a stationary Gaussian Markov process it is very useful to establish a canonical representation for general stationary Gaussian Markov processes. This will be done first and then the contraction procedure will be applied to the canonical representation.

In general an arbitrary stationary Gaussian Markov process has the following properties: The dynamical laws are

$$\dot{a}_i + A_{ij} a_j = - S_{ij} a_j + \tilde{F}_i \quad (I)$$

where A_{ij} is antisymmetric, S_{ij} is symmetric and semi-positive definite and the \tilde{F}_i 's satisfy

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = [G_{i\ell} E_{\ell j}^{-1} + E_{i\ell}^{-1} G_{\ell j}^+] \delta(t-s) \quad (\text{II})$$

wherein $G_{ij} = A_{ij} + S_{ij}$ and E_{ij} is a real positive definite matrix.

E_{ij} is determined by the first probability distribution function for the process, $W_1(a)$, by

$$W_1(a) = W_0 \exp\left[-\frac{1}{2} a_i E_{ij} a_j\right] . \quad (\text{III})$$

The properties of E_{ij} allow it to be diagonalized by an orthogonal matrix O_{ij} such that

$$O_{i\ell} E_{\ell k} O_{jk} = d_i^2 \delta_{ij}$$

where $d_i > 0$. Define D_{ij} by $D_{ij} = d_i \delta_{ij}$. Finally, define

a'_i by $a'_i = D_{ij} O_{jk} a_k$. Putting this in (III) gives

$$\begin{aligned} W_1(a') &= W_0 \exp\left[-\frac{1}{2} a'_\ell d_\ell^{-1} O_{\ell i} E_{ij} a'_k d_k^{-1} O_{kj}\right] \\ &= W_0 \exp\left[-\frac{1}{2} a'_\ell a'_\ell\right] . \end{aligned} \quad (\text{IV})$$

Therefore, $E'_{ij} = \delta_{ij}$. The dynamical equations (I) become

$$\dot{a}'_i = -D_{i\ell} O_{\ell k} G_{kj} O_{mj} D_{mn}^{-1} a'_n + D_{ij} O_{jk} \tilde{F}_k . \quad (\text{V})$$

Therefore,

$$G'_{ij} = D_{il} O_{lk} G_{kn} O_{mn} D_{mj}^{-1} .$$

Since S_{ij} was semi-positive definite it follows from Chapter I that the eigenvalues of G_{ij} all have non-negative real parts. This guarantees that the solutions to (I) converge asymptotically in time. From

$$\|G' - \lambda I\| = \|D O G O^{-1} D^{-1} - \lambda I\| = \|D O (G - \lambda I) O^{-1} D^{-1}\| = \|G - \lambda I\|$$

it follows that G_{ij} and G'_{ij} have the same eigenvalues which implies that the solutions to (V) must also converge asymptotically in time.

Furthermore,

$$\begin{aligned} \langle \tilde{F}'_i(t) \tilde{F}'_j(s) \rangle &= D_{il} O_{lm} D_{jk} O_{kn} \langle \tilde{F}_m(t) \tilde{F}_n(s) \rangle = \\ &= D_{il} O_{lm} D_{jk} O_{kn} [G_{mp} E_{pn}^{-1} + E_{mp}^{-1} G_{pn}^+] \delta(t-s) = [G'_{il} E_{lj}^{-1} + E_{il}^{-1} G_{lj}^+] \delta(t-s) = \\ &= [G'_{ij} + G_{ij}^{+1}] \delta(t-s) = 2S'_{ij} \delta(t-s) . \end{aligned}$$

As a final step, S'_{ij} may be diagonalized by a unitary transformation U_{ij} . The net result is that (I) may always be transformed into the form

$$\dot{a}_i + A_{ij} a_j = -\lambda_i a_i + \tilde{F}_i \quad (VI)$$

where A_{ij} is antisymmetric and the λ_i 's are all non-negative

and real. The \tilde{F}_i 's satisfy

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2\lambda_i \delta_{ij} \delta(t-s) . \quad (\text{VII})$$

Note that for convenience the same notation is used in (I), (II), (VI) and (VII) whereas in fact the a_i 's of (VI) are different from those in (I) and are obtained by the series of transformations described above. Equations (VI) and (VII) are called the canonical representation of the process.

The canonical representation (VI) qualifies for contraction when the spectrum of λ_i 's breaks up into at least two distinct groups on the basis of size. This obtains when some of the λ_i 's are zero whereas others are not. Assume that the first n λ_i 's are zero. The index α will be used for these n λ_i 's whereas the index i will be used for all the others. The a_i 's are expanded in powers of a scaling parameter $\frac{1}{\theta}$.

$$a_i = a_i^{(0)} + \frac{1}{\theta} a_i^{(1)} + \frac{1}{\theta^2} a_i^{(2)} + \dots . \quad (\text{VIII})$$

Let $\lambda_i = \theta \tilde{\lambda}_i$ define $\tilde{\lambda}_i$ which is taken to be of order zero in θ . The \tilde{F}_i 's are also taken to be of order zero in θ . The time derivative, $\frac{d}{dt}$, is formally expanded as

$$\frac{d}{dt} \rightarrow \frac{d_0}{dt} + \frac{1}{\theta} \frac{d_1}{dt} + \frac{1}{\theta^2} \frac{d_2}{dt} + \dots . \quad (\text{IX})$$

Putting (VIII) and (IX) into (VI) gives to equal orders in the series of equations

$$-\tilde{\lambda}_i a_i^{(0)} = 0 \quad (\text{X})$$

$$\frac{d}{dt} a_i^{(0)} + A_{ij} a_j^{(0)} = -\bar{\lambda}_i a_i^{(1)} + \tilde{F}_i \quad (\text{XI})$$

$$\frac{d}{dt} a_i^{(1)} + \frac{d}{dt} a_i^{(0)} + A_{ij} a_j^{(1)} = -\bar{\lambda}_i a_i^{(2)} \quad (\text{XII})$$

Equation (X) has the solution $a_\alpha^{(0)}$ for $\alpha = 1, 2, \dots, n$ since

$$\bar{\lambda}_\alpha = 0 \text{ for } \alpha = 1, 2, \dots, n \text{ and } a_i^{(0)} = 0 \text{ for } i > n \text{ since } \bar{\lambda}_i \neq 0$$

for $i > n$. From (VII) $\tilde{F}_\alpha = 0$ for $\alpha = 1, 2, \dots, n$ so that the solubility conditions for (XI) are

$$\frac{d}{dt} a_\alpha^{(0)} + A_{\alpha\beta} a_\beta^{(0)} = 0 \quad (\text{XIII})$$

The uniqueness conditions for (XI) are simply $a_\alpha^{(1)} = 0$ for $\alpha = 1, 2, \dots, n$. The solutions to (XI) are, therefore,

$$a_i^{(1)} = -\frac{1}{\bar{\lambda}_i} [A_{i\alpha} a_\alpha^{(0)} - \tilde{F}_i] \text{ for } i > n \quad (\text{XIV})$$

The solubility conditions for (XII) are

$$\frac{d}{dt} a_\alpha^{(0)} + A_{\alpha j} a_j^{(1)} = 0 \quad (\text{XV})$$

Substituting (XIV) into (XV) gives

$$\frac{d}{dt} a_\alpha^{(0)} = A_{\alpha j} \frac{1}{\bar{\lambda}_j} A_{j\beta} a_\beta^{(0)} - A_{\alpha j} \frac{1}{\bar{\lambda}_j} \tilde{F}_j \quad (\text{XVI})$$

Combining (XIII) and (XVI) and taking

$$\frac{d}{dt} = \frac{d_o}{dt} + \frac{1}{\theta} \frac{d_1}{dt}$$

up to order one in $\frac{1}{\theta}$ gives the equations

$$\frac{d}{dt} a_{\alpha}^{(o)} + A_{\alpha\beta} a_{\beta}^{(o)} = - A_{j\alpha} \frac{1}{\lambda_j} A_{j\beta} a_{\beta}^{(o)} + A_{j\alpha} \frac{1}{\lambda_j} \tilde{F}_j \quad . \quad (XVII)$$

Note that if

$$S_{\alpha\beta} = A_{j\alpha} \frac{1}{\lambda_j} A_{j\beta}$$

is taken as a definition of $S_{\alpha\beta}$ then $S_{\alpha\beta}$ is symmetric and at least semipositive definite. The sum over j indicated by the repeated index is from $j > n$ to $j = \infty$ as is implied by (XIV) and (XV).

Finally, defining \tilde{F}'_{α} by

$$\tilde{F}'_{\alpha} = A_{j\alpha} \frac{1}{\lambda_j} \tilde{F}_j$$

it is easily verified from (VII) that

$$\langle \tilde{F}'_{\alpha}(t) \tilde{F}'_{\beta}(s) \rangle = 2S_{\alpha\beta} \delta(t-s) \quad .$$

Therefore, (XVII) has the form of a stationary Gaussian Markov process which was what was desired to be shown.

- 4) Note that in (48) the matrix $Q_{\alpha\beta}^{\mu}$ appears in both $P_{\alpha\beta}^{(2)}$ and $q_{\alpha}^{(2)}$.

This type of symmetry relationship is quite general in each order of approximation and may be viewed as a kind of generalized

Onsager reciprocity relation. For Burnett it was already noticed in the literature.

5) The integral theorems are: given any scalar function $F(p)$, then

$$\begin{aligned} \int f_{\text{eq.}}(p) F(p) p_i p_j \langle p_\alpha p_\beta \rangle dp &= \int f_{\text{eq.}}(p) F(p) \langle p_i p_j \rangle \langle p_\alpha p_\beta \rangle dp = \\ &= \frac{1}{15} (\delta_{i\alpha} \delta_{j\beta} + \delta_{i\beta} \delta_{j\alpha} - \frac{2}{3} \delta_{ij} \delta_{\alpha\beta}) \int f_{\text{eq.}}(p) F(p) p^4 dp \end{aligned}$$

and

$$\int f_{\text{eq.}}(p) F(p) p_i p_j dp = \frac{1}{3} \delta_{ij} \int f_{\text{eq.}}(p) F(p) p^2 dp .$$

See L. Waldmann, Handbuch der Physik, Volume 12, pp. 388-389.

6) See Uhlenbeck and Ford, Lectures in Statistical Mechanics, American Mathematical Society (1963), p. 85.

7) See C. S. Wang Chang and G. E. Uhlenbeck, Report of the Eng. Res. Inst., University of Michigan (1952).

CHAPTER V

Prolegomena

A. Introduction

In this chapter a number of topics and questions will be discussed which are suggested by the development up to this point but which are otherwise unrelated. Some of the questions arise if it is desired to generalize the theory to open systems, or to multicomponent systems wherein chemical reactions can occur. Not all of the questions have been fully answered and an exhaustive account will not be presented. In this sense, only the prolegomena for a future theory are presented.

In Section B the entropy production in closed systems is discussed and its relationship to the second law of thermodynamics is analysed. In Section C open systems are introduced and again the question of entropy production is discussed. A general entropy reduction theorem is proved for open systems, and the relation of this to the minimum dissipation theorems of Onsager and Prigogine is discussed. In Section D the question is raised whether for an open system with time independent inputs, the input and output terms can be replaced by appropriate boundary conditions asymptotically in time when a steady state is achieved. Although this question is not answered in general a simple example is worked out in which such a replacement is achieved. In Section E it is shown that close to equilibrium the equations for chemical reaction kinetics are of the form of a stationary Gaussian Markov process. This permits the introduction of fluctuating chemical forces leading to a stochastic form of the chemical rate equations. In this case the consideration of open systems is especially appropriate.

B. Entropy Production in Closed Systems

The systems discussed in the preceding chapters did not exchange physical quantities with the external environment and are, therefore, closed systems. Such systems have been characterized by n variables $a_i(t)$, for $i = 1, 2, \dots, n$, which satisfy the equations

$$\dot{a}_i + A_{ij} a_j = -S_{ij} a_j + \tilde{F}_i \quad (1)$$

when the behavior of the systems is close enough to equilibrium. Using

$$G_{ij} = S_{ij} + A_{ij} \quad \text{and} \quad 2Q_{ik} = G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{kj}^+ ,$$

the correlation formulae for the \tilde{F}_i 's are

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2Q_{ij} \delta(t-s) . \quad (2)$$

The $W_1(a)$ distribution for the process described by (1) and (2) is

$$W_1(a) = W_o \exp[-a_i E_{ij} a_j] . \quad (3)$$

Invoking the Boltzmann-Planck relation for the entropy, $S = K_B \ln W_1$ gives an expression for the entropy which is

$$S = S_o - \frac{1}{2} K_B a_i E_{ij} a_j \quad (4)$$

where $S_o = K_B \ln W_o$. The question now arises whether or not in the approach to equilibrium, which is characterized by $a_i = 0$, the entropy

increases monotonically to S_0 as might be expected from the usual interpretation of the second law of thermodynamics. It will be shown that this is not the case, so that the second law must be interpreted more subtly.

To begin with, the entropy fluctuates just like the other thermodynamical variables. Therefore, it is likely that the second law should be applied to the average value of the entropy at a time t . The average value at time t is given by

$$\langle S(t) \rangle = K_B \int P_2(a^0 | at) \ln W_1(a) da \quad . \quad (5)$$

From (5) two points must be carefully noted. The first is that the equilibrium value of $\langle S \rangle$ is not S_0 but is

$$\langle S \rangle_{eq.} = K_B \int W_1(a) \ln W_1(a) da = S_0 - \frac{n}{2} K_B \quad . \quad (6)$$

This is less than S_0 by $\frac{n}{2} K_B$. The second point is that $\frac{d}{dt} \langle S(t) \rangle$ is not strictly positive in general; that is, the approach of $\langle S(t) \rangle$ to $S_0 - \frac{n}{2} K_B$ is not strictly monotone. $\langle S(t) \rangle$ may be explicitly computed and written in terms of two contributions

$$\langle S(t) \rangle = S_A(t) + S_C(t) \quad . \quad (7)$$

$S_A(t)$ is the entropy of the average values of the a_i 's

$$S_A(t) = S_0 - \frac{1}{2} K_B \langle a_i(t) \rangle E_{ij} \langle a_j(t) \rangle \quad . \quad (8)$$

$S_C(t)$ is the entropy of the correlations of the deviations of the a_i 's from their average values at time t . S_A would be the entropy if there were no fluctuations. What can now be proved is that S_A is monotonically increasing going from $S(o)$ up to S_o whereas S_C is monotonically decreasing going from 0 down to $-\frac{n}{2}K_B$. In general their sum, $\langle S(t) \rangle$, is simply not monotone, although because S_A dominates S_C , it is nearly so that $\langle S(t) \rangle$ is monotonically increasing. When specializing to the Onsager theory for even variables only, it is possible to prove that even $S_A + S_C$ is monotonically increasing if the initial state satisfies $S(o) < S_o - \frac{n}{2}K_B$. In most cases approximating $\langle S(t) \rangle$ by S_A is probably reasonable and then the usual statement of the second law is valid provided that one takes $S_o - \frac{n}{2}K_B$ for the equilibrium value.

C. Open Systems and Entropy Production

One way to describe systems which interact with an outside environment is to introduce input and output terms into the basic equations and thereby start from

$$\frac{d}{dt} a_i + A_{ij} a_j = -S_{ij} a_j - O_{ij} a_j + I_i + \tilde{F}_i. \quad (9)$$

The input terms, I_i are in general positive and prescribed functions of the time. The output terms, $O_{ij} a_j$, depend on the time through the a_j 's only and the matrix O_{ij} is positive definite. This difference in form between the inputs and the outputs reflects the fact that usually the outputs depend on the state of the systems whereas the inputs depend only on the state of the environment, which is independent of the state of the system. It is not claimed that (9) in any way exhausts the

possibilities for introducing an interaction of a system with its environment, but for the present purposes (9) is general enough.

The special case of time independent inputs, I_i , will be considered first. Denoting $A_{ij} + S_{ij} + O_{ij}$ by G_{ij} the solution to (9) may be written as

$$a_i(t) = [e^{-Gt}]_{ij} a_j(0) + [e^{-Gt}]_{ij} \int_0^t [e^{Gs}]_{jk} \tilde{F}_k(s) ds + G_{ik}^{-1} I_k - [e^{-Gt}]_{ij} G_{jk}^{-1} I_k. \quad (10)$$

The positive definiteness of S_{ij} and O_{ij} guarantees that (10) converges asymptotically in time and it follows that

$$\lim_{t \rightarrow \infty} a_i(t) = G_{ik}^{-1} I_k. \quad (11)$$

Consequently, a steady state characterized by non-zero average values for the a_i 's develops asymptotically in time. This is to be contrasted with the asymptotic behavior of a closed system which in full equilibrium is characterized by the value zero on the average for every a_i .

It is of special interest to look at entropy production in this case of time independent inputs. From (10) it follows that

$$\lim_{t \rightarrow \infty} \langle a_i(t) a_j(t) \rangle = E_{ij}^{-1} + [G_{ik}^{-1} I_k][G_{jl}^{-1} I_l]. \quad (12)$$

Using (12) in (4) the asymptotic value of $\langle S \rangle$ is given by

$$\lim_{t \rightarrow \infty} \langle S \rangle = S_o - \frac{n}{2} K_B - \frac{1}{2} K_B E_{ij} [G_{ik}^{-1} I_k][G_{jl}^{-1} I_l]. \quad (13)$$

The last term on the right is negative since E_{ij} is positive definite. Therefore, the asymptotic value of $\langle S \rangle$ is actually less than the

corresponding value for a closed system. This means that if inputs are suddenly impressed on a closed system in equilibrium, then the entropy will decrease in time. In general the time course is not monotone but always has the asymptotic consequence of entropy reduction.

For time dependent inputs the analysis of entropy production is not significantly more difficult than in the preceding special case. Generally no asymptotic state is achieved since the inputs continuously vary with time. However, it can again be shown that if the system is initially in equilibrium then turning on inputs and outputs results in a reduction of the entropy. The value of the entropy continuously changes with time and has no asymptotic value in general, but whatever its value, it is always less than the initial equilibrium value.

Both open and closed systems are stable against weak perturbations. This is so because the weak perturbations may be considered to be time dependent inputs of short duration in time. Consequently, their initial influence on the system exponentially decays away until it becomes negligibly small. Therefore, the perturbed state returns to its unperturbable values which is the essence of stability.²⁾

As a final point it is often attractive to associate a view of the concept of order with entropy. High entropy is identified with low order and low entropy is identified with high order. The entropy reduction theorem presented above suggests that open systems which were initially closed and in equilibrium become internally ordered by virtue of the inputs and outputs subsequently imposed on them. It is the opinion of this author that many physical processes, particularly in biology and chemistry, illustrate this point. Consider, for example, the order and stability of metabolic cycles, such as the tricarboxylic acid pathway in biochemistry, which are driven by specific energy rich metabolites as inputs and which produce low energy metabolic end products as outputs.

Another example is electron transport during oxidative phosphorylation which achieves a steady state when driven by a constant input, and which shows oscillations when the steady state is weakly perturbed, thereby manifesting the stability of the steady state.

D. The Problem of Boundary Conditions

In Chapter II, Section D, the problem of the effect of hydrodynamical fluctuations on the motion of a solid body moving through a fluid was discussed and it was remarked there that the application of the Landau and Lifshitz formulae to such problems of steady state flow implies an extension of the theory to open systems. Clearly, for the steady state flow around a body, both the body and the surface at infinity are sources and sinks of fluid particles and momenta and should, therefore, be described by extra input and output terms in the hydrodynamical equations. However, it is customary and also physically reasonable not to add inputs and outputs but instead to describe the effect on the steady state of the body and of the prescribed flow at infinity by surface boundary conditions. In Chapter II, this is precisely what was done and it was shown to lead to a derivation of the Langevin equation. The question, therefore, arises whether or not the two procedures are equivalent and especially whether or not the boundary conditions can be derived from the appropriate description of the inputs and outputs effective near the surfaces considered when the system is in a steady state.

This question is not discussed here in all generality. However, a simple example follows which may elucidate how boundary conditions can obtain from appropriate inputs and outputs in a steady state.

Consider a gas contained between two parallel plates at $x = \pm \frac{1}{2}L$. Let the equilibrium temperature of the gas be T_{eq} and suppose that

the temperature of the plate at $x = +\frac{1}{2}L$ is raised to $T_{eq.} + \frac{1}{2}\Delta T$ whereas the temperature of the plate at $x = -\frac{1}{2}L$ is lowered to

$T_{eq.} - \frac{1}{2}\Delta T$. Since the plates exchange energy with the gas, the gas must be considered an open system. It is desired to compute the temperature profile in the gas when the steady state has been achieved at $t = \infty$.

Assume that the interaction of the gas with the plates can be described as follows. In a planar region of thickness σ , which is small compared with L , located between $x = -\frac{1}{2}L$ and $x = -\frac{1}{2}L + \sigma$, all molecules entering the region are converted from whatever velocity distribution they have to a Maxwell distribution with temperature

$T_{eq.} - \frac{1}{2}\Delta T$. Similarly, between $x = +\frac{1}{2}L - \sigma$ and $x = +\frac{1}{2}L$ the molecules are converted to a Maxwell distribution with temperature

$T_{eq.} + \frac{1}{2}\Delta T$. It is assumed that ΔT is sufficiently small that the behavior of the gas may be described by the linearized Navier-Stokes equations, which will now be augmented by input and output terms in the two boundary regions just described. Since the average velocity can be taken to be zero everywhere and since no particles are put into or taken out of the gas, only the energy or temperature equation needs to be considered.³⁾ In one dimension it becomes at $t = \infty$

$$-K \frac{d^2 T(x)}{dx^2} = -\frac{3}{2} n_{eq.} K_B [\alpha_+(x) + \alpha_-(x)] T(x) + \frac{3}{2} n_{eq.} K_B [\alpha_+(x) - \alpha_-(x)] \frac{1}{2} \Delta T. \quad (14)$$

The righthand side terms are the inputs and outputs. The functions $\alpha_+(x)$ and $\alpha_-(x)$ are equal to α in the σ -regions at $x = +\frac{1}{2}L$ and $x = -\frac{1}{2}L$ respectively. Elsewhere they are zero. α must have the dimensions of a reciprocal time and is assumed to be of order

$\frac{U_{th.}}{\Lambda}$ where $U_{th.}$ is the mean thermal velocity and Λ is the mean free path. It is reasonable also to assume that σ is of order Λ . Note that (14) is of the general form given by (9) without fluctuations by identifying

$$a_i \rightarrow T(x) \quad ,$$

$$A_{ij} = 0 \quad ,$$

$$S_{ij} \rightarrow S(x, y) = -K \frac{d^2}{dx^2} \delta(x-y) \quad ,$$

$$O_{ij} a_j \rightarrow [\alpha_+(x) + \alpha_-(x)] \frac{3}{2} n_{eq.} K_B T(x) \quad ,$$

and

$$I_i \rightarrow [\alpha_+(x) - \alpha_-(x)] \frac{3}{2} n_{eq.} K_B \frac{1}{2} \Delta T \quad .$$

Equation (14) clearly separates into three equations, one for each of the three regions contained between $x = -\frac{1}{2} L$ and $x = +\frac{1}{2} L$. In the $\alpha_-(x)$ region the equation is

$$K \frac{d^2 T_-(x)}{dx^2} = \frac{3}{2} n_{eq.} K_B \alpha_- T_-(x) + \frac{3}{2} n_{eq.} K_B \alpha_- \frac{1}{2} \Delta T \quad . \quad (15)$$

In the $\alpha_+(x)$ region the equation is

$$K \frac{d^2 T_+(x)}{dx^2} = \frac{3}{2} n_{eq.} K_B \alpha_+ T_+(x) - \frac{3}{2} n_{eq.} K_B \alpha_+ \frac{1}{2} \Delta T \quad . \quad (16)$$

In the region between $x = -\frac{1}{2}L + \sigma$ and $x = +\frac{1}{2}L - \sigma$ the equation is

$$K \frac{d^2 T(x)}{dx^2} = 0 \quad . \quad (17)$$

The temperature conditions given in the beginning for the two plates gives the boundary conditions

$$T_-(-\frac{1}{2}L) = -\frac{1}{2}\Delta T \quad \text{and} \quad T_+(\frac{1}{2}L) = +\frac{1}{2}\Delta T \quad . \quad (18)$$

In addition the temperature profile must be continuous throughout the gas which gives the two conditions

$$T_-(-\frac{1}{2}L + \sigma) = T(-\frac{1}{2}L + \sigma) \quad \text{and} \quad T_+(\frac{1}{2}L - \sigma) = T(+\frac{1}{2}L - \sigma) \quad . \quad (19)$$

Finally, at the two interfaces between the three regions of the gas there should be no source of heat flux which results in the additional two conditions

$$T'_-(-\frac{1}{2}L + \sigma) = T'(-\frac{1}{2}L + \sigma) \quad \text{and} \quad T'_+(\frac{1}{2}L - \sigma) = T'(+\frac{1}{2}L - \sigma) \quad . \quad (20)$$

The conditions (18) through (20) are independent and sufficient to uniquely determine the solutions to equations (15) through (17). Putting

$$K\lambda^2 = \frac{3}{2} n_{eq} K_B \alpha$$

it is easily found that

$$T(x) = \left[\frac{\Delta T}{L-2\sigma} + 2B \frac{1}{L-2\sigma} e^{-\frac{1}{2} \lambda L} (e^{\lambda \sigma} - e^{-\lambda \sigma}) \right] x$$

$$T_+(x) = -B e^{-\frac{1}{2} \lambda L} (e^{\lambda(x-\frac{1}{2} L)} - e^{-\lambda(x-\frac{1}{2} L)}) + \frac{1}{2} \Delta T \quad (21)$$

$$T_-(x) = -B e^{-\frac{1}{2} \lambda L} (e^{\lambda(x+\frac{1}{2} L)} - e^{-\lambda(x+\frac{1}{2} L)}) - \frac{1}{2} \Delta T$$

where

$$B = -\frac{\Delta T}{L-2\sigma} \left[\frac{2e^{-\frac{1}{2} \lambda L}}{L-2\sigma} (e^{\lambda \sigma} - e^{-\lambda \sigma}) + \lambda e^{-\frac{1}{2} \lambda L} (e^{\lambda \sigma} - e^{-\lambda \sigma}) \right]^{-1}.$$

It can be shown that λ is of order L^{-1} so that $\sigma \ll L$ and

$\lambda L \gg 1$. Therefore, $T(x) \approx \Delta T \frac{x}{L}$ which is the result obtained without inputs and outputs using only boundary conditions at the two plates given by

$$T(-\frac{1}{2} L) = -\frac{1}{2} \Delta T \quad \text{and} \quad T(+\frac{1}{2} L) = +\frac{1}{2} \Delta T.$$

Therefore, inputs and outputs give a modified solution closely approximating the customary boundary value solution but also containing boundary layer behavior.

The generality of the situation just presented needs to be explored further with other examples.

E. Chemical Reaction Kinetics

For a multicomponent system in which a number of chemical reactions can occur, it can be shown that if transport of the different

molecular species can be neglected, then it follows from the law of mass action that close to equilibrium the regression of the concentrations to their equilibrium values has the standard form of the regression equations for a stationary Gaussian Markov process. This suggests the introduction of fluctuating chemical forces and leads to a stochastic interpretation of the usual reaction rate equations. The corresponding fluctuation dissipation theorem is of special interest and may perhaps have practical applications.

Consider a large number of molecular species, M_i , which are numbered by a latin index. Let their concentrations be C_i which in equilibrium has the value of $C_i^{eq.}$ and write $a_i = C_i - C_i^{eq.}$ for deviations from the equilibrium values. The equilibrium is determined by a large number of chemical reactions which are distinguished using a Greek index. Of course, several distinct reactions may have one or more molecular species in common. Suppose that in the α^{th} reaction there are n_α reactants forming the set R_α and m_α products forming the set P_α .⁴⁾ The forward rate constant for the reaction is denoted by K_α^+ and the backward rate constant is denoted by K_α^- . The equilibrium condition for reaction α is given by

$$K_\alpha^+ \prod_{i \in R_\alpha} C_i^{eq.} = K_\alpha^- \prod_{j \in P_\alpha} C_j^{eq.} \quad (22)$$

Since according to the law of mass action, the rate of a chemical reaction is proportional to the product of the concentrations, close to equilibrium a forward reaction current can be defined by

$$\begin{aligned} J_\alpha(R_\alpha | P_\alpha) &= K_\alpha^+ \prod_{i \in R_\alpha} C_i^{eq.} \sum_{l \in R_\alpha} \frac{a_l}{C_l^{eq.}} - K_\alpha^- \prod_{j \in P_\alpha} C_j^{eq.} \sum_{k \in P_\alpha} \frac{a_k}{C_k^{eq.}} \\ &= K_\alpha^+ \prod_{i \in R_\alpha} C_i^{eq.} \left[\sum_{l \in R_\alpha} \frac{a_l}{C_l^{eq.}} - \sum_{k \in P_\alpha} \frac{a_k}{C_k^{eq.}} \right] \end{aligned} \quad (23)$$

where (22) was used to obtain the second equality. The linearized mass action laws then take the form

$$\dot{a}_k = \sum_{\alpha} \sum_{j \in P_{\alpha}} J_{\alpha}(R_{\alpha} | P_{\alpha}) \delta_{jk} - \sum_{\alpha} \sum_{i \in R_{\alpha}} J_{\alpha}(R_{\alpha} | P_{\alpha}) \delta_{ik} . \quad (24)$$

The Kronecker δ -functions pick out all the reactions in which molecular species M_k participates. The first term on the righthand side of (24) has species M_k participating as a product whereas the second term has species M_k participating as a reactant.

Putting (23) into (24) leads to the equation

$$\dot{a}_k = - G_{kl} a_l \quad (25)$$

where G_{kl} is given by

$$G_{kl} = - \sum_{\alpha} (K_{\alpha}^{+} \prod_{i \in R_{\alpha}} C_i^{eq.}) \left[\sum_{j \in P_{\alpha}} \delta_{jk} - \sum_{i \in R_{\alpha}} \delta_{ik} \right] \left[\sum_{m \in R_{\alpha}} \frac{\delta_{ml}}{C_m^{eq.}} - \sum_{n \in P_{\alpha}} \frac{\delta_{nl}}{C_n^{eq.}} \right] . \quad (26)$$

Clearly, G_{kl} can always be written as $G_{kl} = A_{kl} + S_{kl}$ where A_{kl} is antisymmetric and S_{kl} is symmetric. Moreover, since the mass action laws near equilibrium produce regression of all concentration deviations, a_i , to zero, it follows that the S_{kl} determined by G_{kl} must be positive definite. Therefore, the linearized mass action laws are of the form of the average regression equations for a stationary Gaussian Markov process. Fluctuating forces, \tilde{F}_i may be added to (25) giving an O-U process

$$\dot{a}_i = - G_{ij} a_j + \tilde{F}_i . \quad (27)$$

The correlations of the \tilde{F}_i 's are given by

$$\langle \tilde{F}_i(t) \tilde{F}_j(s) \rangle = 2Q_{ij} \delta(t-s) \quad . \quad (28)$$

The matrix Q_{ij} is determined from the fluctuation-dissipation theorem

$$2Q_{ij} = G_{ik} E_{kj}^{-1} + E_{ik}^{-1} G_{kj}^+$$

once E_{ij} is known. To obtain E_{ij} it is necessary to compute the entropy for chemical reaction kinetics.

The affinity for the α^{th} reaction is defined by

$$A_\alpha = \sum_{i \in R_\alpha} \mu_i - \sum_{j \in P_\alpha} \mu_j \quad (29)$$

where μ_i is the chemical potential of the molecular species M_i . Near equilibrium μ_i is a linear function of the concentrations and A_α becomes

$$A_\alpha = K_B T_{\text{eq.}} \left[\sum_{i \in R_\alpha} \frac{a_i}{C_i^{\text{eq.}}} - \sum_{j \in P_\alpha} \frac{a_j}{C_j^{\text{eq.}}} \right] \quad . \quad (30)$$

The entropy production, \dot{S} is given for reaction kinetics by

$$T_{\text{eq.}} \dot{S} = \sum_\alpha A_\alpha J_\alpha (R_\alpha | P_\alpha) \quad . \quad (31)$$

Using

$$E_{ij} = \frac{1}{C_i^{\text{eq.}}} \delta_{ij}$$

in

$$S = S_o - \frac{1}{2} K_B a_i E_{ij} a_j$$

reproduces the expression (31) when substitutions are made using (23), (25), and (30). Using this value for E_{ij} and (26) in the fluctuation-dissipation theorem gives

$$Q_{ij} = \sum_{\alpha} (K_{\alpha}^{+} \prod_{i \in R_{\alpha}} C_i^{eq}) \left[\sum_{n \in P_{\alpha}} \delta_{ni} \sum_{\ell \in P_{\alpha}} \delta_{\ell j} - \sum_{m \in R_{\alpha}} \delta_{mi} \sum_{k \in R_{\alpha}} \delta_{kj} \right]. \quad (32)$$

For two molecular species M_i and M_j , Q_{ij} gets non-zero contributions whenever both M_i and M_j molecules are simultaneously reactants or simultaneously products in some reaction.

Using (32) in solutions to (27), the correlations in concentration fluctuations may be computed. These fluctuations create fluctuations in the dielectric constant of the medium in which the reactions are occurring and therefore effect light scattering measurements. It is in this way that these results may find application.

Finally, the considerations of both sections B and C of this chapter may be applied to this case. In the case of open systems the inputs and outputs are molecular species. The proper treatment of metabolic pathways thermodynamically requires considering them as open systems. Such a treatment is indicated by the approach outlined in this section when extended to open systems as in section C. Ultimately, it is desired to combine the results of this section, extended to open systems, with the results of Chapter II so that transport of molecular species involved in chemical reactions may be characterized as well. This, however, remains to be done.

NOTES

- 1) For another discussion of this point see: S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North-Holland, (1962), Chapter VII, 8.
- 2) The preceding remarks concerning steady states and their inherent stability have been approached from a somewhat different direction by both Onsager and Prigogine. For steady states a least dissipation of entropy theorem is provable. See L. Onsager, *Physical Review*, Vol. 37, (1931) and I. Prigogine, *Thermodynamics of Irreversible Processes*, Interscience, (1961), Chapter VI. Onsager and Machlup have also used the least dissipation theorem to characterize the probability of a given path which a system might follow in its approach to equilibrium. See L. Onsager and S. Machlup, *Physical Review*, Vol. 91, No. 6, (1953), Section 4.
- 3) Actually all of the Navier-Stokes equations need to be considered. However, the continuity equation at $t = \infty$ leads to $\frac{\partial}{\partial x_\alpha} u_\alpha = 0$. This in turn eliminates the $\frac{\partial}{\partial x_\alpha} u_\alpha$ term in the temperature equation, as is indicated in (18). The u_α equation can then be shown to lead to $u_\alpha = 0$ everywhere. The details of these events only detract from the main point and are, therefore, omitted.
- 4) The stoichiometry of each reaction is not explicitly manifested. This is for notational convenience, and molecular species which occur multiply in a given reaction do not effect the results as presented.

Dear Nancy,

These reports are C.D.'s. However,
please not state on C.D.s - even
once we will be making them
permanently.

Sincerely,
Dorothy

