

Matematisk-fysiske Skrifter
udgivet af
Det Kongelige Danske Videnskabernes Selskab
Bind 2, nr. 1

Mat. Fys. Skr. Dan. Vid. Selsk. 2, no. 1 (1962)

THEORY OF
IRREVERSIBLE PROCESSES

I. PARAMETERS OF SMALLNESS

BY

JOSEPH HIGGINS



København 1962

i kommission hos Ejnar Munksgaard

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Selskabets sekretariat og postadresse: Dantes Plads 5, København V.

The address of the secretariate of the Academy is:

*Det Kongelige Danske Videnskabernes Selskab,
Dantes Plads 5, København V, Denmark.*

Selskabets kommissionær: EJNAR MUNKSGAARD's Forlag, Nørregade 6,
København K.

The publications are sold by the agent of the Academy:

EJNAR MUNKSGAARD, *Publishers,*
6 Nørregade, København K, Denmark.

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Synopsis

In part I, the theory of irreversible processes proposed by PRIGOGINE and VAN HOVE is reviewed and the master equation is rederived directly in the phase space without reference to the Fourier space. In part II, the assumptions involved are closely examined with particular emphasis on the justification of the master equation as derived from the Liouville equation. It is demonstrated that the conditions of a parameter of smallness λ associated with the interaction potential energy and large time t compared to a collision time are neither necessary nor sufficient to justify the derivation of the master equation. A necessary, but physically restrictive condition is obtained, and the usefulness of the master equation is discussed.

Introduction

This is the first of several papers designed to investigate the logical relationship between the Liouville equation and equations describing irreversible processes. While there are many approaches to the development of such equations, they are usually based on philosophical assumptions and no attempt is made to justify analytically these assumptions from the Liouville equation. This, for example, is the case with KRAMERS' equations describing Brownian motion⁽¹⁾ for which the interaction is assumed to have a random character; or the master equation derived by BOGOLUBOV⁽²⁾, in which it is assumed that the equations describing nature have a Markovian character. Although these assumptions seem physically reasonable, they have not been derived from the Liouville equation. Consequently, the analytical conditions necessary to pass from the reversible properties of the Liouville equation (or the basic equations of motion) to the properties of equations describing irreversible processes are not known.

However, the theory of irreversible processes initiated by VAN HOVE⁽³⁾, BROUT and PRIGOGINE⁽⁴⁾, and further developed by PRIGOGINE and others^{(5), (6)}, is distinctive in that it represents an important analytical attempt to develop the equations for irreversible processes directly from the Liouville equation. In this theory, the Fourier space representation of the Liouville equation is studied and a general master equation is developed by assuming (1) a parameter of smallness λ associated with the interaction potential, (2) times t large compared to the average collision time, (3) a large number of particles $N \rightarrow \infty$ and infinite volume $\mathcal{V} \rightarrow \infty$ but finite concentration N/V , and (4) a weak restriction on the form of the initial density function $\varrho(0)$. Briefly, the Fourier transform of $\varrho(t)$ is expanded in powers of λ , the asymptotic forms of these terms for $\lambda \rightarrow 0$, $t \rightarrow \infty$, $N \rightarrow \infty$, $\mathcal{V} \rightarrow \infty$ are determined, and the dominant terms are selected out and summed to produce the master equation. In the first part of this paper (sections 1 and 2), the master equation is rederived directly in the phase space without the use of the Fourier space representation. While this derivation is less cumbersome, it should be emphasized that the logical structure and the assumptions involved are based entirely on the ideas originated by VAN HOVE and PRIGOGINE. The only significant difference in the derivation given here is that, by first summing the

selected terms in λ , a non-Markovian equation is obtained which reduces to the master equation when the limit $t \rightarrow \infty$ is taken.

But, in view of the reversible character of the Liouville equation which is not affected by parameters of smallness or large times, it is difficult to understand how the assumptions employed can give rise to the irreversible character of the master equation. In the second part of this paper (section 3), this problem is studied in conjunction with a close analysis of the derivation. Higher order terms in λ and t are examined and a condition is determined to justify the use of the asymptotic forms. The analysis demonstrates that the original assumptions are neither necessary nor sufficient to derive the master equation, while the new conditions appear to severely limit its practical value. However, the apparent discrepancies between the Liouville equation and the master equation are largely resolved and a closer relationship is established between the various theories of irreversible processes.

Part I: Derivation of the Master Equation

Section 1: Liouville Equation

1.1. General Assumptions

We shall consider a system of N particles, with momentum p_i and space coordinates x_i , contained in a cubic volume \mathcal{V} whose sides are of length $2L$, subject to the potential $V(\{x_i\})$. The potential is taken as a function of the relative positions and assumed to be pairwise additive:

$$V(\{x_i\}) = \frac{1}{2} \sum_{ij} V_{ij}(x_i - x_j), \quad (1.1.1)$$

from which it follows that the force on any particle is given by

$$\frac{\partial V}{\partial x_i} = \sum_j \frac{\partial V_{ij}}{\partial x_i} \quad (1.1.2)$$

and

$$\frac{\partial V_{ij}}{\partial x_i} = - \frac{\partial V_{ij}}{\partial x_j}. \quad (1.1.3)$$

Furthermore, we shall assume that the potential and forces vanish at infinity, i. e.,

$$V_{ij}(\pm \infty) = 0 \quad \text{and} \quad \frac{\partial V_{ij}}{\partial x_i}(\pm \infty) = 0. \quad (1.1.4)$$

The Hamiltonian for this system is

$$H = \sum_i \frac{p_i^2}{2m} + \lambda V(x_i), \quad (1.1.5)$$

where the mass of each particle has been taken equal to m . The parameter λ is introduced primarily as an expansion parameter.

The Liouville equation describes the time dependence of the phase space probability density function*, $\varrho(\{p_i\}, \{x_i\}, t)$, and is given by

$$\frac{\partial \varrho}{\partial t} + \sum_i \frac{p_i}{m} \frac{\partial \varrho}{\partial x_i} = \lambda \sum_i \frac{\partial V}{\partial x_i} \frac{\partial \varrho}{\partial p_i} \quad (1.1.6)$$

for the Hamiltonian (1.1.5).

* The words *density function* and *distribution function* are used interchangeably throughout the text, although strictly speaking the quantities referred to are always density functions.

1.2. Dimensional Changes

It is convenient to introduce new dimensions as follows:

$$V' = \frac{V}{RT}, \quad p'_i = \frac{p_i}{\sqrt{mRT}}, \quad t' = t \sqrt{\frac{RT}{m}} \quad (1.2.1)$$

where T is the temperature and R is the gas constant. In this case, the equilibrium density function becomes

$$\varrho_{eq} = C \exp \left[-\left(\frac{1}{RT} \right) \left(\sum_i \frac{p_i^2}{2m} + V \right) \right] = C' \exp \left[-\left(\frac{p_i'^2}{2} + V' \right) \right], \quad (1.2.2)$$

where C and C' are normalization constants. The Liouville equation (1.1.6) becomes

$$\frac{\partial \varrho}{\partial t'} + \sum_i p'_i \frac{\partial \varrho}{\partial x_i} = \lambda \sum_i \frac{\partial V'}{\partial x_i} \frac{\partial \varrho}{\partial p'_i}. \quad (1.2.3)$$

Henceforth we shall drop the primes, but consider that all quantities are expressed in these units so that equations (1.2.2) (right side) and (1.2.3) are the appropriate forms.

Finally, it is convenient to use a notation which applies specifically to a one-dimensional real space. Thus, \mathcal{V}° is interpreted as a length, and the summations in equation (1.2.3) extend from 1 to N . The results are easily extended to three dimensions, in which case x_i for $i = l \cdot 1, l \cdot 2, l \cdot 3$ are the three coordinates of the particle l and the summations extend from $i = 1$ to $3N$. Also the potentials $V(x_i - x_j)$ must be interpreted as functions of the three coordinates of each particle i and j . However, specific results derived here for one dimension are easily generalized and the general conclusions are not particularly affected by the dimensionality.

Section 2: Derivation of the Master Equation

2.1. Equations for the Reduced Density Function

From the set $[N]$ of N particles we choose a subset S consisting of s particular particles. These particles are labelled $(1, 2, \dots, s)$ and those in the set $[N-S]$ are labelled $(s+1, \dots, N)$. We define the S order coordinate-reduced density function by the equation

$$f_s = \mathcal{V}^{\circ s} \int \varrho dx_{s+1} dx_{s+2} \dots dx_N, \quad (2.1.1)$$

which means integration over the entire coordinate space of particles $s+1$ to N . The quantity \mathcal{V}° refers to the coordinate space volume (a length in one dimension). The introduction of the factor $\mathcal{V}^{\circ s}$ in the definition of f_s (2.1.1) is simply a recognition of the volume dependence of the normalization factors of the density func-

tions. In this connection, we are only interested in density functions of physical interest which behave similarly to the equilibrium distribution for the phase space limits. In accord with equation (1.2.2) the equilibrium density function behaves as

$$\varrho_{eq} \rightarrow 0 \quad \text{as} \quad p_i \rightarrow \pm \infty. \quad (2.1.2)$$

Since the potential energy functions of interest satisfy

$$\left. \begin{aligned} V_{ij}(x_i - x_j \rightarrow 0) &\quad \text{as} \quad x_i \rightarrow \pm \infty, \\ \varrho_{eq} &\rightarrow \frac{1}{\mathcal{V}^\circ} \varrho_{eq}^{N-1} \quad \text{as} \quad x_i \rightarrow \pm \infty, \end{aligned} \right\} \quad (2.1.3)$$

we have

where ϱ_{eq}^{N-1} denotes the equilibrium density function for $(N-1)$ particles. And as $\mathcal{V}^\circ \rightarrow \infty$, $\varrho_{eq} \rightarrow 0$ at the limits.

There are, of course, as many different f_s as there are ways of choosing a particular set $[S]$ from the set $[N]$ (order of particles plays no role). While these different f_s are always functions of a different set of coordinates (at least one particle must be different in each f_s), the f_s may or may not have the same functional form, depending on the symmetry of the problem. Also s can have any value from 0 to N , where $f_0 = f_0(p_1, \dots, p_N)$ and $f_N = \mathcal{V}^{\circ N} \varrho$.

To obtain the equations for the f_s from the Liouville equation we shall make use of the following facts:

$$\lim_{L \rightarrow \infty} \int_{-L}^{+L} \frac{\partial \varrho}{\partial x_i} dx_i = \lim_{L \rightarrow \infty} [\varrho(L) - \varrho(-L)] = 0 \quad (2.1.4)$$

because $\varrho(\pm \infty) = 0^*$. As $L \rightarrow \infty$, $\mathcal{V}^\circ \rightarrow \infty$, and to keep the problem meaningful, we must let $N \rightarrow \infty$ in such a way that the concentration $C = N/\mathcal{V}^\circ$ remains finite.

In addition, we note that

$$\left. \begin{aligned} \sum_{i=1}^N \frac{\partial V}{\partial x_i} \frac{\partial \varrho}{\partial p_i} &= \sum_{\substack{ij=1 \\ i \neq j}}^N \frac{\partial V_{ij}}{\partial x_i} \frac{\partial \varrho}{\partial p_i} = \sum_{\substack{ij=1 \\ i \neq j}}^S \frac{\partial V_{ij}}{\partial x_i} \frac{\partial \varrho}{\partial p_i} \\ + \sum_{i=1}^S \sum_{j=s+1}^N \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial \varrho}{\partial p_i} - \frac{\partial \varrho}{\partial p_j} \right] &+ \sum_{\substack{ij=s+1 \\ i \neq j}}^N \frac{\partial V_{ij}}{\partial x_i} \frac{\partial \varrho}{\partial p_i}, \end{aligned} \right\} \quad (2.1.5)$$

where we have used equations (1.1.2) and (1.1.3).

Integrating the Liouville equation (1.1.3) over the position coordinates of the particles in the set $[N-S]$, and using equations (2.1.1), (2.1.4), and (2.1.5), we obtain

* The same result is obtained if we assume $\varrho(L) = \varrho(-L)$ for $L \rightarrow \infty$.

$$\left. \begin{aligned} \frac{\partial f_s}{\partial t} + \sum_{i=1}^{S-1} p_i \frac{\partial f_s}{\partial x_i} &= \lambda \sum_{\substack{ij=1 \\ i \neq j}}^S \frac{\partial V_{ij}}{\partial x_i} \frac{\partial f_s}{\partial p_i} + \frac{\lambda}{\gamma^\circ} \sum_{i=1}^S \sum_{j=s+1}^N \int \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial f_{s+1}^{(j)}}{\partial p_i} - \frac{\partial f_{s+1}^{(i)}}{\partial p_j} \right] dx_j \\ &+ \frac{\lambda}{\gamma^{\circ 2}} \sum_{\substack{ij=s+1 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial f_{s+2}^{(ij)}}{\partial p_i} dx_i dx_j \end{aligned} \right\} \quad (2.1.6)$$

for $\gamma^\circ \rightarrow \infty$, $N \rightarrow \infty$ such that $N/\gamma^\circ = C$, where $f_{s+1}^{(j)}$ is a function of all the $p_i (i = 1, \dots, N)$, the x_i of the particles in the set $[S]$ and in addition x_j for j in the set $[N-S]$; similarly for $f_{s+2}^{(ij)}$. Equation (2.1.6) is valid for $(s = 1, \dots, N)$ and is the desired equation for the f_s .

The first three equations are

$$\frac{\partial f_0}{\partial t} = \frac{\lambda}{\gamma^{\circ 2}} \sum_{\substack{ij=1 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial f_2^{(ij)}}{\partial p_i} dx_i dx_j, \quad (2.1.7)$$

$$\left. \begin{aligned} \frac{\partial f_1^{(1)}}{\partial t} + p_1 \frac{\partial f_1^{(1)}}{\partial x_1} &= \frac{\lambda}{\gamma^\circ} \sum_{j=2}^N \int \frac{\partial V_{1j}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_j} \right] f_2^{(1j)} dx_j \\ &+ \frac{\lambda}{\gamma^{\circ 2}} \sum_{\substack{ij=2 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial f_3^{(ij)}}{\partial p_i} dx_i dx_j, \end{aligned} \right\} \quad (2.1.8)$$

$$\left. \begin{aligned} \frac{\partial f_2^{(12)}}{\partial t} + p_1 \frac{\partial f_2^{(12)}}{\partial x_1} + p_2 \frac{\partial f_2^{(12)}}{\partial x_2} &= \lambda \frac{\partial V_{12}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] f_2^{(12)} \\ &+ \frac{\lambda}{\gamma^\circ} \sum_{i=1}^2 \sum_{j=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] f_3^{(12j)} dx_j + \frac{\lambda}{\gamma^{\circ 2}} \sum_{\substack{i,j=3 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial f_4^{(12ij)}}{\partial p_i} dx_i dx_j, \end{aligned} \right\} \quad (2.1.9)$$

where the numbers in the parentheses $f_1^{(1)}$, $f_2^{(12)}$ refer to the particular particles not integrated over. The numbers can always be replaced by k, l as long as the summations exclude them specifically; thus

$$\sum_{i=1}^2 \sum_{j=3}^N \rightarrow \sum_{i=k, l} \sum_{j=1, (j \neq k, l)}^N.$$

2.2. Expression in Correlation Functions

We can always expand an arbitrary distribution function ϱ in terms of the correlation functions as

$$\varrho = \frac{1}{\gamma^{\circ N}} \left\{ g_0 + \sum_i g_1^{(i)} + \sum_P g_2^{(P)} + \sum_i \sum_{\substack{P \\ i \neq P}} g_1^{(i)} g_2^{(P)} + \sum_T g_3^{(T)} + \dots + g_N \right\}, \quad (2.2.1)$$

where the g_l are l^{th} order position correlation functions. The indices inside the parenthesis, as $g_2^{(1)}$, $g_2^{(P)}$, refer to the position coordinates of particular particles. The i, P, T represent the particle i , the pairs of particles (h, l) , the triplet (μ, ν, w) , etc., and the summations are combinations from the set $[N]$. All the g_l may be a function of the momenta of *all* the particles. In particular, g_0 is a function of the momenta only, $g_0 = g_0(p_1, p_2, \dots, p_N)$. According to their definition as correlation functions, we require that

$$\int_{-\infty}^{+\infty} g_l^{(1, \dots, l)} dx_\mu = 0 \quad \text{for} \quad \mu = 1, \dots, l. \quad (2.2.2)$$

We now limit our possible initial conditions by requiring that ϱ is a function of the relative coordinates only; i. e.,

$$\varrho = \varrho(\{x_i - x_j\}) \quad \text{for all } i \text{ and } j. \quad (2.2.3)$$

From the Liouville equation it is easily seen that, if this condition is satisfied at $t = 0$, then it is satisfied at all times. From (2.2.3) it follows that $g_1^{(i)} = 0$ and, hence, equation (2.2.1) reduces to

$$\varrho = \frac{1}{\gamma^N} \left\{ g_0 + \sum_P g_2^{(P)} + \sum_T g_3^{(T)} + \sum_{\substack{P_1 \\ P_1 \neq P_2}} \sum_{\substack{P_2 \\ P_1 \neq P_2}} g_2^{(P_1)} g_2^{(P_2)} + \sum_Q g_4^{(Q)} + \dots + g_N \right\}. \quad (2.2.4)$$

Using the definition of the f_s (2.1.1) and equation (2.2.2), we obtain from (2.2.4) that

$$f_s = \left\{ g_0 + \sum_P g_2^{(P)} + \sum_T g_3^{(T)} + \sum_{\substack{P_1 \\ P_1 \neq P_2}} \sum_{\substack{P_2 \\ P_1 \neq P_2}} g_2^{(P_1)} g_2^{(P_2)} + \sum_Q g_4^{(Q)} + \dots + g_s \right\}. \quad (2.2.5)$$

Specifically,

$$\left. \begin{aligned} f_0 &= g_0 \\ f_1 &= g_0 \end{aligned} \right\} \quad (2.2.6)$$

(which is independent of x_i in accord with condition (2.2.3))

$$\begin{aligned} f_2 &= g_0 + g_2^{(ij)} \\ f_3 &= g_0 + g_2^{(ij)} + g_2^{(ik)} + g_2^{(jk)} + g_3^{(ijk)}, \quad \text{etc.} \end{aligned}$$

These equations can be solved for the g_l and yield

$$\left. \begin{aligned} g_0 &= f_0 \\ g_1 &= 0 \\ g_2^{(P)} &= f_2^{(P)} - f_0 \\ g_3^{(T)} &= f_3 - \sum_P f_2^{(P)} + 2f_0^{(T)} \quad (P \in T). \end{aligned} \right\} \quad (2.2.7)$$

These equations could have been taken as a definition of the g_l and would yield equation (2.2.2). In fact, the g_l and the f_s form a one-to-one functional transformation of each other; the importance of this particular transformation is shown in section 2.3.

Note that

$$\iint h(x_i - x_j) g(x_i - x_j) dx_i dx_j = \mathcal{V}^\circ \int h(x) g(x) dx, \quad (2.2.8)$$

where h and g are arbitrary functions and the result depends on the limits of integration becoming infinite (i. e., $\mathcal{V}^\circ \rightarrow \infty$). Then, by substituting equations (2.2.6) into (2.1.6) and applying (2.2.8) as well as the condition (1.1.4), we obtain*

$$\begin{aligned} \frac{\partial g_0}{\partial t} &= \frac{\lambda}{\mathcal{V}^{\circ 2}} \sum_{\substack{ij=1 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial g_2^{(ij)}}{\partial p_i} dx_i dx_j & (2.2.9) \\ \frac{\partial g_2^{(12)}}{\partial t} + p_1 \frac{\partial g_2}{\partial x_1} + p_2 \frac{\partial g_2}{\partial x_2} &= \frac{\partial V_{12}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_0 + \frac{\partial V_{12}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_2 \\ + \sum_{j=1}^2 \sum_{i=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_2^{(ij)} dx_i &- \int \frac{\partial V_{12}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_2^{(12)} dx_1 dx_2 \\ + \sum_{j=1}^2 \sum_{i=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_3^{(12i)} dx_i & \\ + \sum_{i=3}^N \sum_{j=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial}{\partial p_i} [g_3^{(1ij)} + g_3^{(2ij)}] dx_i dx_j & \\ + g_2^{(12)} \sum_{i=3}^N \sum_{j=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial}{\partial p_i} g_2^{(ij)} dx_i dx_j & \\ + \sum_{i=3}^N \sum_{j=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] [g_2^{(1i)} g_2^{(2j)}] dx_i dx_j & \\ + \sum_{i=3}^N \sum_{j=3}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial}{\partial p_i} g_4^{(12ij)} dx_i dx_j & \end{aligned}$$

which are the equations for the g_0 and g_2 . The equations for the other g_i are obtained in the same way.

* That the equation for $\partial f_1 / \partial t$ (2.1.8) adds nothing new is easily seen by noting that

$$\begin{aligned} & \int \frac{\partial V_{ij}(x_i - x_j)}{\partial x_i} \frac{\partial f_3}{\partial p_i} [(x_i - x_j), (x_1 - x_i), (x_1 - x_j)] dx_i dx_j \\ &= \int \frac{\partial V_{ij}(x)}{\partial x_i} \frac{\partial f_3}{\partial p_i} [x, y - x, y] dx dy = \mathcal{V}^\circ \int \frac{\partial V_{ij}(x)}{\partial x_i} \frac{\partial f_2(x)}{\partial p_i} dx \\ & \text{since } \int f_3 [(x_i - x_j), (x_1 - x_i), (x_1 - x_j)] dx_1 = \mathcal{V}^\circ f_2^{(ij)} \end{aligned}$$

2.3. λ dependence

We shall now assume that the correlation functions can be expanded in powers of λ -as

$$\left. \begin{aligned} g_0 &= g_0^0 + \lambda g_0^1 + \lambda^2 g_0^2 + \dots \\ g_l &= \lambda^{l-1} [g_l^0 + \lambda g_l^1 + \lambda^2 g_l^2 + \dots] \quad \text{for } l \geq 2. \end{aligned} \right\} \quad (2.3.1)$$

That is, the l^{th} order correlation function has a λ dependence of no less than λ^{l-1} . Again, it is easy to prove that, if (2.3.1) is valid initially, it is true at all times. This is seen from equations (2.2.9) as well as from the Liouville equation; correlations are created by the operator $\lambda \left\{ \frac{\partial V}{\partial x_i} \frac{\partial}{\partial p_i} \right\}$, and an l^{th} order correlation requires the repeated application of this operator so that g_l can be created only with an order of λ^{l-1} . Consequently, if g_l has initially no λ dependence lower than λ^{l-1} , it will never have any. It is for this reason that we have transformed from the f_s to the g_l . The lowest order λ dependence of the g_l is preserved in time while the f_s will in general contain all powers of λ . It is important to note that equation (2.3.1) also applies to the equilibrium distribution

$$\left. \begin{aligned} \rho_{\text{eq}} &= C \exp \left[- \sum_i \frac{p_i^2}{2} - \frac{1}{2} \lambda \sum_{\substack{ij \\ i \neq j}} V_{ij}(x_i - x_j) \right] \\ &= C \left[\exp \left(- \sum_i \frac{p_i^2}{2} \right) \right] \left[1 + \frac{\lambda}{2} \sum_{\substack{ij \\ i \neq j}} V_{ij}(x_i - x_j) \right. \\ &\quad \left. + \frac{1}{2} \left(\frac{\lambda}{2} \right)^2 \sum_{P_1} \sum_{P_2} V(P_1) V(P_2) + \frac{1}{3!} \left(\frac{\lambda}{2} \right)^3 \sum_{P_1} \sum_{P_2} \sum_{P_3} V(P_1) (V(P_2) V(P_3) + \dots) \right], \end{aligned} \right\} \quad (2.3.2)$$

where C is a normalization factor and where we can have $P_1 = P_2 = P_3$ etc. From (2.3.2) it is clear that the g_l for the equilibrium distribution satisfy equation (2.3.1). This result is important, as it demonstrates that the equilibrium distribution has not been excluded by our choice of initial conditions.

2.4. *Solution of the Equations for the Correlation Functions*

We shall now solve equations (2.2.9) by iteration to the order λ^2 and for the following initial ($t = 0$) conditions:

$$\left. \begin{aligned} g_0^0(0) &= g_0^0(0) \neq 0 \\ g_0^m(0) &= 0 \quad \text{for } m \geq 1 \\ g_l^m(0) &= 0 \quad \text{for } l \geq 1. \end{aligned} \right\} \quad (2.4.1)$$

While these conditions satisfy the general restrictions (2.3.1) and (2.2.3), they are not preserved in time. They correspond to an initial distribution function $\varrho(t=0)$ which is a function of the momenta p_1, \dots, p_N alone and which is independent of λ .

Inserting equations (2.3.1) into equations (2.2.9) and equating powers of λ , we obtain

$$\frac{\partial g_0^0}{\partial t} = 0 \quad (2.4.2)$$

$$\frac{\partial g_0^1}{\partial t} = 0 \quad (2.4.3)$$

$$\frac{\partial g_0^2}{\partial t} = \frac{1}{\gamma^2} \sum_{\substack{ij=1 \\ i \neq j}}^N \int \frac{\partial V_{ij}}{\partial x_i} \frac{\partial g_2^0(ij)}{\partial p_i} dx_i dx_j \quad (2.4.4)$$

$$\frac{\partial g_2^0(12, t)}{\partial t} + p_1 \frac{\partial g_2^0(t)}{\partial x_1} + p_2 \frac{\partial g_2^0(t)}{\partial x_2} = \frac{\partial V_{12}}{\partial x_1} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_0^0(t). \quad (2.4.5)$$

Using the initial conditions (2.4.1), we obtain from (2.4.2)

$$g_0^0(t) = g_0^0(0), \quad (2.4.6)$$

from (2.4.3)

$$g_0^1(t) = 0, \quad (2.4.7)$$

and from (2.4.5)

$$g_2^0(t, 12) = \int_0^t \frac{\partial V_{12}}{\partial x_1}(x - pt') \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_0^0(0) dt' dx, \quad (2.4.8)$$

$$\text{where } x = x_1 - x_2 \quad \text{and} \quad p = p_1 - p_2;$$

putting (2.4.8) in (2.4.4), we have

$$\frac{\partial g_0^2}{\partial t} = \frac{1}{\gamma^2} \sum_{\substack{ij=1 \\ i \neq j}}^N \int_x \frac{\partial V_{ij}^{(x)}}{\partial x_i} \int_0^t \frac{\partial}{\partial p_i} \frac{\partial V_{ij}}{\partial x_i}(x - pt') \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(0) dt' dx, \quad (2.4.9)$$

where we have also applied equation (2.2.8).

Finally, we can add equations (2.4.2), (2.4.3), and (2.4.9) and write

$$\left. \begin{aligned} \frac{\partial g_0(t)}{\partial t} &= \frac{\partial}{\partial t} [g_0^0 + \lambda g_0^1 + \lambda^2 g_0^2] \\ &= \frac{\lambda^2}{\gamma^2} \sum_{\substack{ij=1 \\ i \neq j}}^N \int \frac{\partial V_{ij}(x)}{\partial x_i} \frac{\partial}{\partial p_i} \int_0^t \frac{\partial V_{ij}(x - pt')}{\partial x_i} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0(0) dt' dx, \end{aligned} \right\} \quad (2.4.10)$$

which is the expression for $g_0(t)$ valid to order λ^2 .

2.5. Extending the Solution

Equation (2.4.10) is the correct solution to order λ^2 for $\frac{\partial g_0(t)}{\partial t}$. However, it is not Markovian in that it depends on $g_0(0)$. This would appear to be easily rectified. We write equation (2.4.10) as

$$\frac{\partial g_0(t)}{\partial t} = \frac{\lambda^2}{\gamma^\circ} f(t, \bar{p}_\gamma) g_0(0), \quad (2.5.1)$$

where

$$f(t, \bar{p}_i, \bar{p}_j) = \sum_{\substack{ij=1 \\ i \neq j}}^N \int \frac{\partial V_{ij}(x)}{\partial x_i} \frac{\partial}{\partial p_i} \int_0^t \frac{\partial V_{ij}}{\partial x_i}(x-pt') dt' dx \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \quad (2.5.2)$$

is a differential operator in the momenta (denoted by \bar{p}_γ) as well as a function of t . Integrating equation (2.5.1) with respect to t yields

$$g_0(t) = g_0(0) + \frac{\lambda^2}{\gamma^\circ} F(t, \bar{p}_\gamma) g_0(0), \quad (2.5.3)$$

where

$$F(t, \bar{p}_\gamma) = \int_0^t f(t', \bar{p}_\gamma) dt'. \quad (2.5.4)$$

Solving equation (2.5.3) for $g_0(0)$ yields

$$g_0(0) = \frac{1}{1 + \frac{\lambda^2}{\gamma^\circ} F(t, \bar{p}_\gamma)} g_0(t), \quad (2.5.5)$$

which is an operator equation whose meaning is

$$g_0(0) = \left[1 - \frac{\lambda^2}{\gamma^\circ} F(t, \bar{p}_\gamma) + \left(\frac{\lambda^2}{\gamma^\circ} F(t, \bar{p}_\gamma) \right)^2 + \dots \right] g_0(t), \quad (2.5.6)$$

where the series is that for $1/1+x$. If we now assume that $F^n(t, \bar{p}_\gamma) g_0(t)$ is bounded for all t and \bar{p} with an upper bound U_n , and that λ is a parameter of smallness such that

$$1 \gg \frac{\lambda^2}{\gamma^\circ} U_1 \quad \text{and} \quad U_n \gg \frac{\lambda^2}{\gamma^\circ} U_{n+1} \quad \text{for all } n > 1, \quad (2.5.7)$$

then we can set

$$g_0(0) = g_0(t) \quad \text{to order } \lambda^2 \quad (2.5.8)$$

and equation (2.5.1) can be written as

$$\frac{\partial g_0(t)}{\partial t} = \frac{\lambda^2}{\gamma^\circ} f(t, \bar{p}_\gamma) g_0(t). \quad (2.5.9)$$

Subject to the condition (2.5.7), equation (2.5.9) is still valid to the order λ^2 . The method we have used to obtain equation (2.5.9) is known as the *resolvent method*; it amounts to an elimination of the initial condition in terms of the function and its derivatives, and is in fact the standard procedure for developing a differential equation from its solution. However, to obtain equation (2.5.9), we have made a double approximation: first by cutting off higher powers of λ according to equation (2.4.10), and second according to equation (2.5.8).

These particular approximations are not easily justified and would restrict equation (2.5.8) to cases of little physical interest. However, equation (2.5.9)¹ can be developed by another procedure for which the approximations seem to be physically reasonable at first sight. This procedure, introduced by PRIGOGINE⁽⁶⁾, involves the investigation and summation of all the terms in λ . To do this we examine the value of g_0^4 and in general g_0^{2n} ($n = 2, 3, \dots$). The term g_0^4 arises from g_2^3 according to equation (2.2.9). While there are many terms which contribute to g_2^3 , we shall only be interested in that which arises from g_0^2 . Solving the equations with the initial conditions (2.4.1) we obtain

$$g_0^4 = \left[\frac{\lambda^2}{\gamma^2} \right]^2 \sum_{\substack{ij=1 \\ i \neq j}}^N \int_0^t \int_x \frac{\partial V_{ij}(x)}{\partial x_i} \frac{\partial}{\partial p_i} \int_0^{t'} \frac{\partial V_{ij}}{\partial x_i}(x - p\tau) \times \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) F(t' - \tau) d\tau dt' g_0^0(0), \quad (2.5.10)$$

where $F(t)$ is defined by equation (2.5.4). Equation (2.5.10) can be written as

$$g_0^4 = \left[\frac{\lambda^2}{\gamma^2} \right]^2 \int_0^t f(t') * \int_0^{t'} f(t'') dt'' dt' g_0^0(0), \quad (2.5.11)$$

where $f(t)$ is defined by equation (2.5.2) and the operation is a type of convolution defined as

$$h(t) * g(t) = \int_0^t h'(\tau) g(t - \tau) d\tau, \quad (2.5.12)$$

where $h'(t) = \frac{dh(t)}{dt}$ is the derivative of $h(t)$, and $h(t)$ and $g(t)$ are arbitrary functions.

Note also that

$$h(t) * 1 = \int_0^t h'(\tau) d\tau = h(t) - h(0). \quad (2.5.13)$$

It is easily seen from equation (2.2.9) that some terms in g_0^{2n} arise from g_2^{2n-1} which in turn arises from the term $g_0^{2(n-1)}$. Thus the structure of the term g_0^{2n} is apparent from equation (2.5.11), and we obtain

$$\left. \begin{aligned}
 g_0(t) = & \left[1 + \alpha \int_0^t f(t') dt' + \alpha^2 \int_0^t f(t') * \int_0^{t'} f(t'') dt'' dt' \right. \\
 & \left. + \alpha^3 \int_0^t f(t') * \int_0^{t'} f(t'') * \int_0^{t''} f(t''') dt''' dt'' dt' + \dots \right] g_0(0),
 \end{aligned} \right\} \quad (2.5.14)$$

where $\alpha = \frac{\lambda^2}{\gamma^2}$.

Differentiating equation (2.5.14) with respect to t we obtain

$$\frac{\partial g_0(t)}{\partial t} = \alpha f(t) * \left[1 + \alpha \int_0^t f(t') dt' + \alpha^2 \int_0^t f(t') * \int_0^{t'} f(t'') dt'' dt' + \dots \right] g_0(0) \quad (2.5.15)$$

and, substituting equation (2.5.14) for the series, we have

$$\frac{\partial g_0(t)}{\partial t} = \alpha f(t) * g_0(t) = \alpha \int_0^t f'(\tau) g_0(t - \tau) d\tau. \quad (2.5.16)$$

Equation (2.5.16) represents a special solution of the general equation given by ZWANZIG⁽⁷⁾. Effectively certain terms in the λ expansion of Zwanzig's equation have been disregarded, but equation (2.5.16) retains the same general form. Equation (2.5.16) is still not Markovian, as it depends on the value of g_0 at the time $(t - \tau)$. It is closely related to equation (2.5.1) and can be made Markovian, in a similar manner, by replacing $g_0(t - \tau)$ by $g_0(t)$, in which case one again obtains equation (2.5.9) since $f(0) = 0$. But the necessary conditions to make this replacement are essentially the same as for deriving equation (2.5.9) and restrict the physics to cases of little interest.

However, the problem of making equation (2.5.16) Markovian can be related to an important property of the function $f(t)$ which is derived in the following section.

2.6. Properties of $f(t)$

For the function $f(t)$ we can write

$$f(t) = \alpha \sum_{\substack{ij=1 \\ i \neq j}}^N \frac{\partial}{\partial p_i} \Phi_{ij}(t, p) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right], \quad (2.6.1)$$

where

$$\Phi_{ij}(t, p) = \int_x \frac{\partial V_{ij}(x)}{\partial x} \int_0^t \frac{\partial V_{ij}}{\partial x} [x - pt'] dx dt'. \quad (2.6.2)$$

Carrying out the time integration of (2.6.2) and for convenience dropping the subscripts, we obtain

$$\Phi(t, p) = -\frac{1}{p} \int_x \frac{\partial V(x)}{\partial x} [V(x-pt) - V(x)] dx \quad (2.6.3)$$

or

$$\Phi(t, p) = -\frac{1}{p} \int_x \frac{\partial V(x)}{\partial x} V(x-pt) dx \quad (2.6.4)$$

since the last term in (2.6.3) vanishes when the x integration is carried out.

To investigate (2.6.4) we shall assume a specific form for $\partial V(x)/dx$, namely a force of constant magnitude a over a range $-b < x < b$ and zero elsewhere. This is illustrated in Figure 1 together with $V(x)$. Setting

$$j = pt,$$

the integration over x in equation (2.6.4) is easily carried out for this case and we obtain

$$\Phi(t, p) = +\frac{1}{p} \left\{ \begin{array}{ll} 0 & \text{for } |j| > 2b \\ \frac{1}{2} \frac{j}{|j|} a^2 [2b - |j|^2] & \text{for } b < |j| < 2b \\ \frac{1}{2} j a^2 [4b - 3|j|] & \text{for } 0 < |j| < b \end{array} \right\} \quad (2.6.5)$$

$$\text{a) } V(|x|) = \left\{ \begin{array}{ll} ab \left(1 - \frac{|x|}{b}\right) & \text{for } b \geq |x| \geq 0. \\ 0 & \text{for } |x| > b. \end{array} \right\}$$

$$\text{b) } \frac{\partial V(x)}{\partial x} = \left\{ \begin{array}{ll} -\frac{x}{|x|} & \text{for } b \geq |x| \geq 0 \\ 0 & \text{for } |x| > b \end{array} \right\}$$

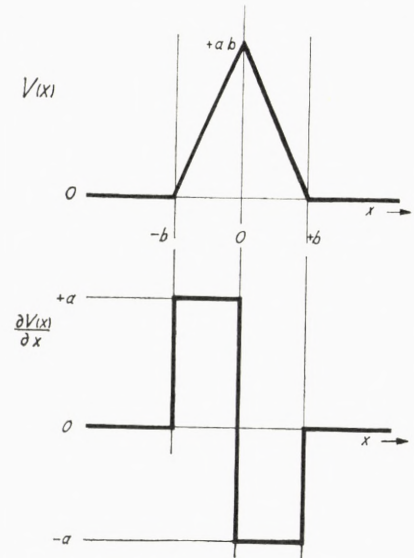


Fig. 1.

From equation (2.6.5) we see that $\Phi(t, p)$ behaves in a manner similar to a Dirac Delta, $\delta(p)$, function as t becomes large, since $\Phi(t, p)$ has a non-zero value only for $p < 2b/t$. To demonstrate that $\Phi(t, p)$ is a δ function for large t , we evaluate

$$I = \lim_{t \rightarrow \infty} \int_{-\infty}^{+\infty} \Phi(t, p) \mathfrak{N}(p) dp,$$

where $\mathfrak{N}(p)$ is an arbitrary function. By writing the integral as $\int_0^{\infty} + \int_{-\infty}^0$, changing p to $-p$ in the second integral and finally setting $p = j/t$, we obtain

$$I = \lim_{t \rightarrow \infty} \int_{j=0}^{\infty} \left\{ \begin{array}{ll} 0 & \text{for } |j| > 2b \\ \frac{1}{2} \frac{a^2}{j} [2b - j]^2 & \text{for } b < |j| < 2b \\ \frac{1}{2} a^2 [4b - 3j] & \text{for } 0 < |j| < b \end{array} \right\} \left[\mathfrak{N}\left(\frac{j}{t}\right) + \mathfrak{N}\left(-\frac{j}{t}\right) \right] dj \quad (2.6.6)$$

Since j is bounded by $0 < j < 2b$, if we carry through the limit $t \rightarrow \infty$, we have $\mathfrak{N}(j/t) \rightarrow \mathfrak{N}(0)$ and similarly $\mathfrak{N}(-j/t) \rightarrow \mathfrak{N}(0)$; evaluating the integral over j , we obtain

$$I = 4 a^2 b^2 (\ln 2) \mathfrak{N}(0)$$

so that we can write

$$\lim_{t \rightarrow \infty} \Phi(t, p) = 4 a^2 b^2 (\ln 2) \delta(p). \quad (2.6.7)$$

The condition that $t \rightarrow \infty$ will be studied in detail in a later section, but for the moment we shall follow the arguments given by PRIGOGINE: it is not necessary that $t \rightarrow \infty$. If we define the mean collision time t_c in terms of the mean velocity v_M of the particles as

$$t_c = \frac{2b}{v_M}, \quad (2.6.8)$$

then equation (2.6.7) will be approximately valid for $t \gg t_c$ as long as $\mathfrak{N}(p)$ is essentially constant for $0 < p < p_\beta$, where $p_\beta \ll p_M$.

In other words, $\Phi(t, p)$ becomes independent of t for $t \gg t_c$. We can write

$$\Phi(t, p) \approx \Phi(\infty, p) \quad \text{for } t \gg t_\beta \gg t_c$$

and, from equation (2.6.1), it follows that

$$f(t, p) \approx f(\infty, p) \quad \text{for } t \gg t_\beta. \quad (2.6.9)$$

For the problems considered here, t_c will be very small compared to times of interest, so that the condition $t \gg t_c$ presents no difficulty. Finally, for other interesting types of forces, the result will be essentially the same, replacing b by the mean interaction distance and a by the mean value of the force. The only important exception is the $1/r^2$ force which has such a large b that equation (2.6.7) is only valid for t of the order of relaxation times.

2.7. The Master Equation

With these properties for $f(t)$, it is now easy to demonstrate that equation (2.5.16) becomes Markovian for $t \geq t_\beta$. Integrating (2.5.16) by parts yields

$$\frac{\partial g_0(t)}{\partial t} = \alpha \left\{ f(t) g_0(0) - f(0) g_0(t) + \int_0^t f(\tau) g'(t-\tau) d\tau \right\}. \quad (2.7.1)$$

Noting that $f(0) = 0$, splitting the last integral into $\int_0^{t_\beta} + \int_{t_\beta}^t$ and using the property that $f(t) \cong f(\infty)$ for $t \geq t_\beta$, yields

$$\left. \begin{aligned} \frac{\partial g_0(t)}{\partial t} = \alpha \left\{ f(\infty) g_0(0) - \int_0^{t_\beta} f(\tau) g'_0(t-\tau) d\tau \right. \\ \left. - f(\infty) \int_{t_\beta}^t g'_0(t-\tau) d\tau \right\} \quad \text{for } t \geq t_\beta. \end{aligned} \right\} \quad (2.7.2)$$

An evaluation of the last integral gives

$$\frac{\partial g_0(t)}{\partial t} = \alpha \left\{ f(\infty) g_0(t-t_\beta) - \int_0^{t_\beta} f(\tau) g'_0(t-\tau) d\tau \right\} \quad \text{for } t \geq t_\beta. \quad (2.7.3)$$

This shows that $g'_0(t)$ is of order α so that both $g'_0(t)$ and $g_0(t)$ do not change very much in a time t_β which is small; hence, we can set $g_0(t-t_\beta) \approx g_0(t)$ and $g'_0(t-\tau) \approx g'_0(t)$. Finally, the last term in equation (2.7.3) is of order α as compared to the first term and can thus be neglected. While an exact condition for these approximations can be easily written down by expanding $g(t-t_\beta)$ in a power series of t_β , a more convenient necessary condition is that

$$\alpha F(t_\beta) g_0(t) \ll 1, \quad (2.7.4)$$

where $F(t)$ was previously defined by equation (2.5.4). If this condition holds, we can expect that our approximations are valid and equation (2.7.3) becomes

$$\frac{\partial g_0(t)}{\partial t} = \alpha f(\infty) g_0(t). \quad (2.7.5)$$

On replacing $f(\infty)$ by its value we have

$$\frac{\partial g_0(t)}{\partial t} = \frac{\lambda^2}{\gamma^\circ} \sum_{\substack{ij=1 \\ i \neq j}}^N \frac{\partial}{\partial p_i} \int_x \frac{\partial V_{ij}(x)}{\partial x} \int_{t'=0}^{\infty} \frac{\partial V_{ij}}{\partial x}(x-pt') dx dt' \times \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0(t) \quad (2.7.6)$$

which is identical with the Markovian master equation obtained by BROUT, PRIGOGINE, and VAN HOVE⁽⁴⁾, as is demonstrated in Appendix II.

Before comparing the details of this derivation with that given by PRIGOGINE, it is useful to review the application to the problem of Brownian motion.

2.8. *Brownian Motion*

The equation for the Brownian motion of a particle is easily derived from the master equation*. We consider a bath containing N_B particles at equilibrium. Another particle (P) of the same type** is introduced into this bath at $t = 0$ with a given momentum distribution $g_P(p_P, 0)$, and we wish to determine the time dependence of the distribution function g_P .

The momentum distribution for each particle is defined by

$$g_i(p_i, t) = \int_{-\infty}^{+\infty} g_0(\{p\}, t) \prod_{\substack{j=1 \\ j \neq i}}^N dp_j, \quad (2.8.1)$$

where $\int g_i(p_i, t) dp_i = 1$; that is, the g_i are normalized.

We now require that g_0 can be factorized into particle distribution functions, i. e.,

$$g_0(t) = \prod_{i=1}^N g_i(p_i, t). \quad (2.8.2)$$

Again, if (2.8.2) is valid at $t = 0$, it follows from the Liouville equation that it will be true for all t . Since the equilibrium distribution is factorizable, (2.8.2) will apply to Brownian particles if we require that the momentum of the particle P is initially uncorrelated with the momenta of the bath particles.

Since the particles are all of the same type, the interaction potentials $V_{ij}(x_i - x_j)$ will have the same functional form denoted by $V(x_i - x_j)$, and also the masses m_i will be the same. The derivation of the master equation requires that $\mathcal{V}^\circ \rightarrow \infty$ and hence $N \rightarrow \infty$. To make this a physically meaningful situation, we shall require that there exist N_B particles in the bath and n particles P undergoing Brownian motion. Thus,

$$N = N_B + n \quad (2.8.3)$$

as $\mathcal{V}^\circ \rightarrow \infty$, $N_B \rightarrow \infty$ and $n \rightarrow \infty$,
such that

$$\frac{N_B}{\mathcal{V}^\circ} = C_B \quad \text{and} \quad \frac{n}{\mathcal{V}^\circ} = C_P \quad \text{are finite.} \quad (2.8.4)$$

For practical problems we can usually set $n/N_B \simeq 10^{-23}$ (Avogadro's number). The physical interpretation of equations (2.8.4) can be taken either as (1) one system containing $\mathfrak{N} \cdot N_B$ bath particles (where $N_B \approx 10^{23}$) and $\mathfrak{N} \cdot n$ identical Brownian particles ($n \approx 1$), where $\mathfrak{N} \rightarrow \infty$ as $\mathcal{V}^\circ \rightarrow \infty$; or (2) approximately as \mathfrak{N} identical systems, each having a finite volume $\overline{\mathcal{V}^\circ}$ and containing N_B bath particles and n Brownian particles, where the number of systems becomes infinite ($\mathfrak{N} \rightarrow \infty$) and edge effects of the finite volume $\overline{\mathcal{V}^\circ}$ are neglected. Finally, since there are only two types of par-

* The procedure given here is identical to that used by PRIGOGINE (5), (8), (10).

** When the particle is not of the same type the equation is easily derived, but here this example suffices.

ticles, there will be only two different types of particle distribution functions, namely $g_P(p_{P_i}, t)$ for the Brownian particles, where g_P is the same for all these particles but the argument is the p_{P_i} for a particular one and $g_B(p_{B_i}, t)$ for the bath particles, similarly interpreted. Using equations (2.8.2) and (2.6.1), we obtain from the master equation

$$\left. \begin{aligned} \frac{\partial g_1(p_1)t}{\partial t} &= \alpha \sum_{i \neq j} \sum_{j=1}^N \int_{p_i, p_j = -\infty}^{+\infty} \frac{\partial}{\partial p_i} \Phi_{ij}(\infty, p) \\ &\times \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_i(p_i, t) g_j(p_j, t) \underbrace{dp_i dp_j}_{ij \neq 1} \end{aligned} \right\} \quad (2.8.5)$$

when the integration has been carried over all particles but 1, which is taken as some particular particle. The terms in the sum on the right-hand side of (2.8.5) can be broken down and evaluated as follows.

For i and $j \neq 1$, we have

$$\int \frac{\partial}{\partial p_i} \Phi_{ij} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_i g_j dp_i dp_j = \int \Phi_{ij}(p_i - p_j) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_i g_j \Big|_{p_i = -\infty}^{p_i = +\infty} dp_j = 0. \quad (2.8.6)$$

The last equality arises from the definition of (2.6.2) Φ_{ij} and the properties of $V(x)$, from which it follows that $\Phi_{ij} = 0$ for $p_i = \pm \infty$ for all $t \neq 0$ and all p_j except $p_j = \pm \infty$. We make the additional assumption that $g_j(p_j) = 0, \frac{\partial g_0}{\partial p_j} = 0$ for $p_j = \pm \infty$, which is necessary for g_i to be normalizable. The remaining terms of (2.8.5) are those for $i = 1$ or $j = 1$. For $j = 1$, we have

$$\int \frac{\partial}{\partial p_i} \Phi_{i1} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_1} \right] g_i g_1 dp_i = 0 \quad (2.8.7)$$

for the same reasons as (2.8.6). Finally, we have the terms for $i = 1$ which yield

$$\left. \begin{aligned} I_{1j} &= \int \frac{\partial}{\partial p_1} \Phi_{1j}(\infty, p) \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_j} \right] g_1 g_j dp_j \\ &= 4a^2 b^2 \ln 2 \int \frac{\partial}{\partial p_1} \delta(p_1 - p_j) \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_j} \right] g_1^{(p_1)} g_j^{(p_j)} dp_j, \end{aligned} \right\} \quad (2.8.8)$$

where we have now used the value of $\Phi_{ij}(\infty, p)$ given by equation (2.6.6). The last term in (2.8.8) has the obvious property that, if g_1 and g_j have the same functional form, then the term is zero. Thus, if particle 1 is a Brownian particle and particle j also, then the integral I_{ij} is zero. Similarly for the bath particles. We may thus write $I_{1j} = 0$ if 1 and j are the same types of particles. Utilizing these results, we have immediately

$$\frac{\partial g_P(p_1, t)}{\partial t} = C_B \beta \int \frac{\partial}{\partial p_1} \delta(p_1 - p_2) \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_P(p_1, t) g_B(p_2, t) dp_2 \quad (2.8.9)$$

and

$$\frac{\partial g_B(p_2, t)}{\partial t} = C_P \beta \int \frac{\partial}{\partial p_2} \delta(p_1 - p_2) \left[\frac{\partial}{\partial p_2} - \frac{\partial}{\partial p_1} \right] g_P(p_1, t) g_B(p_2, t) dp_1, \quad (2.8.10)$$

where $\beta = \lambda^2 4 a^2 b^2 \ln 2$ and C_B and C_P are the concentrations (equation 2.8.4). The label 1 refers to any one of the Brownian particles and the label 2 to any one of the bath particles.

We now make the additional assumption that the change in the distribution function of the bath particles is negligible in the times we are interested in (i. e., set $C_P = 0$ in 2.8.10) so that we may set

$$g_B(p_2, t) = g_B(p_2, 0) = g_{\text{eq}}(p_2) = \exp\left[-\frac{p_2^2}{2}\right]. \quad (2.8.11)$$

Equation (2.8.9) can then be written as

$$\left. \begin{aligned} \frac{\partial g_P(p_1, t)}{\partial t} &= C_B \beta \int \frac{\partial}{\partial p_1} \delta(p_1 - p_2) \\ &\times \left[g_{\text{eq}}(p_2) \frac{\partial g_P(p_1, t)}{\partial p_1} - g_P(p_1, t) \frac{\partial g_{\text{eq}}(p_2)}{\partial p_2} \right] dp_2. \end{aligned} \right\} \quad (2.8.12)$$

The integration over p_2 can be carried out to yield

$$\frac{\partial g_P(p_1, t)}{\partial t} = C_B \beta \left\{ \frac{\partial}{\partial p_1} [g_{\text{eq}}(p_1)] \left[\frac{\partial g_P(p_1, t)}{\partial p_1} + p_1 g_P(p_1, t) \right] \right\} \quad (2.8.13)$$

or

$$\frac{\partial g_P(p_1, t)}{\partial t} = C_B \beta [g_{\text{eq}}(p_1)] \left[\frac{\partial^2 g_P}{\partial p_1^2} + (1 - p_1^2) g_P \right], \quad (2.8.14)$$

which is the equation for the Brownian motion in *one dimension*. From equation (2.8.12) or (2.8.14) it is easily seen that $g_P(p_1, t)$ proceeds from its initial state $g_P(p_1, 0)$ to its final state which must be $g_{\text{eq}}(p_1)$. The details of the approach to the equilibrium distribution are given by equation (2.8.14). The procedure used here gives the various coefficients (as for friction) in terms of the mechanical properties of the particles.

2.9. Comparison with the Procedure Used by Prigogine

Aside from the fact that this derivation is carried out directly in the phase space without reference to the Fourier representation, there are several other differences with respect to the derivation given by PRIGOGINE et al.⁽⁶⁾ that are worth noting. In this derivation, the selection of higher-order terms in λ , namely g_0^{2n} , was

carried out by comparison with equation (2.5.6) and with the ultimate intention of demonstrating that equation (2.5.9) was actually contained in the complete expansion of $g_0(t)$. In the treatment given by PRIGOGINE, the Fourier transforms of all terms g_0^l are studied with respect to their asymptotic t , λ , N , and V dependence in the limits $t \rightarrow \infty$, $\lambda \rightarrow 0$ (where ∞ and 0 mean arbitrarily large and arbitrarily small, respectively) such that $\lambda^2 t$ remains finite and $N \rightarrow \infty$, $V \rightarrow \infty$ such that N/V^∞ remains finite. Thus, all non-zero terms containing $(\lambda^2 t)^n$ are retained while terms of order $\lambda^2 (\lambda^2 t)^n$ are dropped to this order in λ since they are negligible compared to the terms $(\lambda^2 t)^n$. In the next order of approximation all terms $\lambda (\lambda^2 t)^n$ must also be retained. Thus, the asymptotic dependence is taken as a selection rule. The necessity of this selection rule is clear, as we wish to develop an equation valid for small *but fixed* λ and arbitrarily large t so that the quantity $\lambda^2 t$ need not be small compared to $(\lambda^2 t)^2$. That is, λ and t are unrelated and, consequently, $\lambda^2 t$ can and will obtain arbitrarily large values*. Other terms such as $\lambda^3 t^2$ do not exist in the limit either because the Fourier coefficient is zero, or because they vanished as $N \rightarrow \infty$ and $V \rightarrow \infty$. In principle this is a very powerful procedure, for it contains within itself an immediate proof that the convergence conditions (as presented here) are satisfied.

The asymptotic time analysis is carried out on the Fourier transforms of the terms g_0^l as represented by equation (2.4.9). To indicate briefly the relation of that procedure to the phase space, we note that

$$\Phi(t, p) = \left. \begin{aligned} & \int_x \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x-pt') dt' dx \approx \int_x \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x-pt') dt' dx \quad \text{for } |p| > \varepsilon \\ & + t \int_x \left[\frac{\partial V(x)}{\partial x} \right]^2 dx \quad \text{for } 0 < |p| < \varepsilon. \end{aligned} \right\} (2.9.1)$$

The Fourier transform of the first integral has poles which lie off the real axis in the complex plane and these are discarded, whereas the second integral has a pole on the real axis and is retained. As pointed out by PRIGOGINE, the poles which lie off the real axis become negligible for $t \gg t_c$. This result is identical to that obtained with the rigorous analysis of $\Phi(t, p)$ (presented in section 2.6) which shows that the first integral in equation (2.9.1) can be effectively neglected for $t \gg t_c$ and, hence, that $\overline{g_0^2}$ behaves asymptotically as $t \delta(p) \overline{g_0(0)}$ (where the bar means the Fourier transform with respect to the x_i). In a similar manner it is shown by PRIGOGINE that $\overline{g_0^{(2n)}}$ behaves as $t^n \delta(p) \overline{g_0(0)}$. When these asymptotic terms are summed and differentiated with respect to t , the Fourier transform of equation (2.7.5) is obtained.

* This is an important point and it is the major distinction between the derivations given by ZWANZIG (7) and by PRIGOGINE. ZWANZIG requires that the quantity λt be small, a nonphysical condition, since λ is related to the size of the interaction potential energy which is time independent, and t necessarily becomes arbitrarily large. By summing all powers of λ/t , PRIGOGINE only requires that λ be small. However, the reader is referred to page 35 for a further discussion of these points.

One may wonder what happened to the convolution aspect of $g_0^{2^n}$. In the asymptotic analysis of these terms in the Fourier space, for example g_0^4 , one obtains both a δ and a δ' function. The latter is dropped as being negligible compared to the δ function. If retained it would have led to $g'(t)$ terms which have also been dropped in the treatment given here (see equations 2.7.3 and 2.7.4). It is worth mentioning that the result obtained by the resolvent method (eq. 2.5.6) is also used as a guide to enhance the proper selection and analysis of the terms g_0^l in the treatment given by PRIGOGINE.

Part II: Analysis of the Master Equation

Section 3: Analysis of the Master Equation

3.1. Discussion of the Master Equation

While we shall shortly investigate the approximations involved, it is important to realize the generality of the master equation (2.6.8) if the presentation is correct. The $\{x_i\}$ dependence of the initial distribution function $\varrho(0)$ is limited by the conditions (2.2.3) and (2.3.1), but the momentum distribution $g_0(\{p_{ij}\})$ is not restricted and can have any normalizable form. The master equation expresses the time dependence of $g_0(t)$ and is valid for λ small and $t \gg t_c$, as well as N and \mathcal{V}° becoming infinite such that concentrations remain finite. While not all physical systems will have a small λ , for purposes of discussion we shall allow λ to be made arbitrarily small, but not zero. The quantities λ and t are not related so that the master equation is valid no matter how large t becomes. Also we can take $g_0(t)$ as an approximation to $\varrho(t)$ in accord with equation (2.2.4), since all higher correlation functions ($g_2, g_3 \dots$) enter to higher orders in λ and can presumably be ignored for small λ^* . In effect, the master equation is another form of the Liouville equation valid when the stated conditions are satisfied. It is easily demonstrated that the entropy production (for $S(t) = - \int g_0 \ln g_0 \Pi_i dp_i$, where $g_0(t)$ is the solution of the master equation) is positive definite ($\partial S / \partial t > 0$). Furthermore, starting from any initial state $g_0(0)$, the distribution function will eventually approach a time independent state (as $t \rightarrow \infty$).

The nature of the solution is particularly easy to realize when the momentum distribution function is initially factorized (equation 2.8.2), in which case equation (2.8.5) can be applied. Starting from any initial set of $g_i(p_i, 0)$, after a short time ($t \gg t_c$), the only contributions to changing the functional forms $g_i(p_i, t)$ occur when $p_i = p_j$ and the time evolution proceeds until $g_i(p) = g_j(p)$ (that is, the functional forms become identical). At this point (which is $t = \infty$), the system is stationary, and all the g_i are functionally identical. Note that, in general, $g_i(p_i, 0) \neq g_i(p_i, \infty)$. The master equation does *not* possess an oscillatory solution.

* This approximate relationship between $\varrho(t)$ and $g_0(t)$ is not an explicit part of the theory as presented by PRIGOGINE, but it seems to be the source of some confusion in the literature as well as an interesting feature to investigate.

3.2. Difficulties with the Master Equation

However, we must recall the reversible properties of the Liouville equation, particularly the entropy production which is always zero and the existence of the Poincaré time at which the system returns to its original state. Since these properties do not depend on the size of λ , it is difficult to understand how the solution of the master equation, which is an approximation to the solution of the Liouville equation, can exhibit irreversible properties. As the Poincaré time depends on the number of particles N , this difficulty can be resolved by assuming that the Poincaré time becomes infinite for an infinite number of particles and hence can be forgotten, although the use of the master equation to describe real systems with a finite number of particles is implicitly limited to times much less than the Poincaré time*. The difference in the entropy production of the two equations is not explained.

There is still another difficulty. If all the particle density functions $g_i(p_i)$ have identical functional forms, *regardless* of what that form is (i. e., it need not be the equilibrium form), the momentum density function g_0 will not change in time according to the master equation (see eqs. 2.8.6, 2.8.8). Or, in the study of Brownian motion (section 2.8), if the density function of the bath particles g_B had *any* functional form, the Brownian particle would have approached this form as $t \rightarrow \infty$. This property of the master equation is in complete contradiction to the Liouville equation which states that, in general, such functions must change in time (except for the equilibrium density functions). This property of the Liouville equation does neither depend on the size of λ nor on whether the volume is finite or infinite. In view of these differences, we must conclude that the solution of the master equation is not an approximation to the solution of the Liouville equation $\varrho(t)$ nor to the corresponding momentum density function $g_0(t)$. Consequently, the derivation of the master equation starting from the Liouville equation cannot be justified with only the assumptions employed thus far.

3.3. Resolution of the Inconsistencies $-g_0$ as an approximation to ϱ .

The difference in entropy production between the Liouville equation and the master equation presents a problem only if g_0 is assumed to be equal to ϱ to the order λ . This possibility appears from equations (2.2.4) and (2.3.1) which state that

$$\varrho = \left[g_0^0 + \lambda \sum_P g_2^0 + \lambda^2 \sum_P g_2^1 \right] + \lambda^2 \left[g_0^0 + \lambda \sum_P g_2^2 + \lambda \sum_T g_3^0 \right] + \dots \quad (3.3.1)$$

Equation (3.3.1) is written so as to demonstrate that each term of higher order correlation functions, g_2^l , g_3^m , etc., can be compared to g_0^n and is of higher order in λ . If in *each* bracket the higher order terms can be neglected with respect to the first term for small λ , then ϱ can be replaced by g_0 . It is important to note that the

* This explanation was given by PRIGOGINE (4).

entire position dependence of ϱ is contained in the $g_l (l \geq 1)$, while g_0 expresses only a part of the momentum dependence.

To study this problem, we may start by examining the term g_2^0 which is given by equation (2.4.8) and can be written as

$$g_2^0(i, j, t) = -\frac{1}{p} [V(x-pt) - V(x)] \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(0) \quad (3.3.2)$$

after the time integration has been carried out. This term must be compared to $g_0^0(t) = g_0^0(0)$. For almost all density functions $g_0^0(0)$ of interest, the term g_2^0 will become arbitrarily large relative to g_0^0 as the p_i and p_j approach infinity. Specific examples are $g_0^0 = \prod_i g_i(p_i)$, where $g_i(p_i) = \delta(p_i - p_i')$ or $g_i(p_i) = \exp(-p_i^4)$. In the neighbourhood of $p = 0$, equation (3.3.2) reduces to

$$g_2^0(i, j, t) = +t \frac{\partial V(x)}{\partial x} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(0) \quad (3.3.3)$$

so that g_2^0 will become arbitrarily large as $t \rightarrow \infty$, even for $p = 0$. Finally, if $V(x)$ has an infinity as is the case for many potentials of physical interest, then g_2^0 will again become arbitrarily large when the arguments in (3.3.2) lie in the neighbourhood of these infinities. For any one of these reasons, it is clear that no matter how small λ is made, the term λg_2^0 will dominate the term g_0^0 for some values of $\{p_i\}$, $\{x_i\}$, and t so that it cannot be neglected. The same reasoning applies to each of the brackets of (3.3.1).

The importance of these higher-order correlation functions in regard to the entropy production is easily realized. If the expansion of ϱ given by (3.3.1) is inserted in the definition of the entropy, $S = \int \varrho \ln \varrho \prod_i dp_i dx_i$, and the entropy is then expanded in powers of λ , it is easy to demonstrate that $\partial S / \partial t = 0$ for all t and for each power of λ by using the values of the g_l derived from equations (2.2.9) in section 2.4.

We can conclude that $g_0(t)$ is not an approximation to $\varrho(t)$, regardless of how small λ may be. Consequently, there is no inconsistency in the different entropy productions associated with the Liouville equation and the master equation.

3.4. The Master Equation as an Equation for g_0

While $g_0(t)$ cannot be taken as an approximation to $\varrho(t)$, it is still possible that the g_0 , which satisfies the master equation, is a valid approximation to the g_0 which arises from the Liouville equation (1.1.6). However, we must still resolve the inconsistency which arises from the fact that stationary solutions g_0 of the master equation are not stationary solutions of the Liouville equation. Again we shall look at the higher-order terms in λ . We begin with the term g_0^2 which has an order λ^3 . This term arises from g_2^1 and, in the development of g_2^1 , we consider only the first term on the

right in equation (2.2.9). All other terms in this equation are of different powers in the concentrations, as indicated by the summation signs. Solving this reduced equation for g_2^1 , and inserting the result in equation (2.2.9), gives finally

$$\left. \begin{aligned} \frac{\partial g_0^3(t)}{\partial t} = \frac{\lambda^3}{\gamma^0} \sum_{ij} \frac{\partial}{\partial p_i} \int_{x=-\infty}^{+\infty} \frac{\partial V(x)}{\partial x} \int_0^t E(-p\tau) \frac{\partial V(x)}{\partial x} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \\ \int_0^{t-\tau} \frac{\partial V}{\partial x}(x-pt') dt' d\tau dx \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(t). \end{aligned} \right\} \quad (3.4.1)$$

The exact analysis of this term is carried out in Appendix II, and it is shown that equation (3.4.1) can be reduced to

$$\frac{\partial g_0^3(t)}{\partial t} = \frac{-2\lambda^3}{\gamma^0} \sum_{ij} \frac{\partial}{\partial p_i} \left\{ \frac{t}{p^2} I_{21}(j) + \frac{1}{p^3} I_{22}(j) \right\} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(0), \quad (3.4.2)$$

where $j = pt$ is confined to $|j| < 2b$. The character of $g_0^3(t)$ is already apparent from this equation which shows that $g_0^3(t)$ depends on $\lambda^3 t^2/p^2 + \lambda^3 t/p^3$ and has poles for $p = 0$ and $t = \infty$. Since the operators outside the brackets $\{ \}$ are identical with those for the term in $g_0^2(t)$ which depends on $\lambda^2 t/p$ (see eqs. 2.6.1 and 2.6.5), these terms can be compared directly. As the poles for g_0^3 are of higher order than for $g_0^2(t)$ we cannot expect that the higher-order terms can be neglected with respect to the lower-order terms, however small λ is made. But such analysis, while indicative of much that follows, is not rigorous. To determine the exact value of $\frac{\partial g_0^3}{\partial t}(t)$ for $t \rightarrow \infty$, we proceed as in section 2.6 by considering the integration over p_i . The complete evaluation of equation (3.4.2) for the constant force is carried out in Appendix II and yields

$$\frac{\partial g_0^3(t)}{\partial t} = -\lambda^3 \frac{4}{3} a^3 b^3 (1 - \ln 2) \sum_{ij} \frac{\partial}{\partial p_i} \delta(p_i - p_j) \frac{\partial^2}{\partial p_j^2} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0^0(0). \quad (3.4.3)$$

This equation shows that the asymptotic time dependence of $g_0^3(t)$ is $\lambda^3 t$ and, as pointed out by PRIGOGINE, can be neglected for small λ in comparison to $g_0^2(t)$ whose dependence is $\lambda^2 t$. However, a comparison of these terms on the basis of the time and λ dependence alone is not meaningful, since the momentum operator on the right of (3.4.3) is not identical with that which occurs in $g_0^2(t)$ (eqs. 2.6.1 and 2.6.7). Thus, if we again assume that $g_0(0)$ is factorized into $\prod_i g_i(p_i)$, then even if all the $g_i(p_i)$ have identical functional forms, $\partial g_0^3/\partial t$ will not in general* be zero, whereas we have

* There may well be particular functional forms which are exceptions to this statement, but, arbitrarily chosen, $g_i(p_i)$ (identical for all i) will *not* make $\partial g_0^3/\partial t = 0$. This is easily proved by picking particular forms for $g_i(p_i)$ and inserting them into equation (3.3.4).

already shown that $\partial g_0^2/\partial t = 0$ under this condition. This result affords the resolution of the difficulty discussed in the previous section, for the special factorized form is no longer a stationary solution of the extended master equation (i. e., the λ^3 term included). At the same time it demonstrates that the λ^3 term cannot in general be neglected relative to the λ^2 term, no matter how small λ is taken.

However we now have another difficulty. Equation (3.4.3) has done its job so well that even if we take all g_i identical and equal to the equilibrium form, i. e., $g_i(p_i) = g_{\text{eq}}(p_i) = C \exp\left(-\frac{P^2}{2}\right)$, we find that $\partial g_0^3/\partial t \neq 0$. This is at first rather difficult to understand since the equilibrium distribution is a time independent solution of the Liouville equation and g_{eq} is the correct form of the reduced equilibrium density function. Furthermore, of the terms which we have neglected, none can affect this result since they all occur to different powers of λ or C (concentration). However, the equilibrium distribution is given by equation (2.3.2) and is a function of the potential energy as well as the p_i . While this does not affect the momentum density functions g_{eq} , it does affect the initial conditions. The initial conditions thus far employed are incompatible with the fact that, at $t = 0$, the distribution function was the equilibrium distribution. Comparison with equation (2.3.2) shows that we must take

$$\left. \begin{aligned} g_0^0(0) &= g_0^0(0) \\ g_0^v &= 0 \quad \text{for } v > 0 \\ g_1^v &= 0 \quad \text{for all } v \\ g_2^0(0) &= -g_0^0(0) V(x) \\ g_2^1(0) &= g_0^0(0) V^2(x). \end{aligned} \right\} \quad (3.4.4)$$

For these initial conditions we obtain (see section 5.3)

$$\left. \begin{aligned} \frac{\partial g_0^3(t)}{\partial t} &= \frac{\lambda^3}{\gamma^2} \frac{8a^3 b^3}{3} \sum_{ij} \frac{\partial}{\partial p_i} \left\{ -\ln 2 \delta(p_i - p_j) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \right. \\ &+ (1 - \ln 2) \delta(p_i - p_j) \frac{\partial}{\partial p_j} - \frac{(1 - \ln 2)}{2} \delta(p_i - p_j) \frac{\partial^2}{\partial p^2} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \left. \right\} g_0^0(0). \end{aligned} \right\} \quad (3.4.5)$$

If we now assume that $g_0^0 = \prod_i g_{\text{eq}}(p_i)$, equation (3.4.5) gives

$$\frac{\partial g_0^3}{\partial t} = 0,$$

showing that the equilibrium density function is time independent. But equation (3.4.5) still retains the property that $\frac{\partial g_0^3}{\partial t}(t) \neq 0$ for arbitrary distributions $g_i(p_i)$, even if the functional forms are identical for all i . We shall consider the effects of

these higher-order terms in λ still further in section 3.6, but first it is important to investigate some of the other approximations involved in the derivation of the master equation.

3.5. The Value of the Collision Time

In the derivation of the master equation, it was necessary to assume the existence of a time t_β sufficiently large so that for all $t > t_\beta$ we could set $f(t) \approx f(\infty)$ (eq. 2.6.9). But we also had to assume that t_β was sufficiently small so that $g_0(t - t_\beta) \approx g_0(t)$ (eq. 2.7.4). It is necessary to investigate the requirements for which both these conditions can be satisfied simultaneously. To determine the largeness of t_β , we retain the next non-zero term which arises from the Taylor expansion of $[\Re(j/t) + \Re(-j/t)]$ in equation (2.6.6). In the place of equation (2.7.5) we obtain

$$\left. \begin{aligned} \frac{\partial g_0(t)}{\partial t} = \frac{1}{\mathcal{V}^\infty} \sum_{ij} \frac{\partial}{\partial p_i} \left\{ 4 a^2 b^2 \ln 2 \delta(p) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \right. \\ \left. + \frac{a^2 b^4}{2 t^2} \delta(p) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \frac{\partial^2}{\partial p_j^2} - \frac{a^2 b^4}{t^2} \delta(p) \frac{\partial}{\partial p_j} \right\} g_0(0), \end{aligned} \right\} \quad (3.5.1)$$

where the third term arises from the use of the new initial conditions discussed in section 3.4 (eqs. 3.4.1). We must choose t_β sufficiently large so that the terms in $1/t^2$ can be neglected with respect to the first term. Several features of the $1/t^2$ terms should be noted. First, while they occur to higher order in b (the range of the force) than the first term, they have the same a dependence (namely a^2) as the first term. Thus, it is necessary to assume that b^2/t^2 is small even to expect that these terms can be neglected. Secondly, the $1/t^2$ terms have the same property as the λ^3 terms; they do *not* vanish if $g_0(\{p_i\})$ is a factorized function with all factors having the same functional form, i. e., $g_0(p_i) = \prod_i g_i(p_i)$ with $g_i(p_i) = g_j(p_i)$, while the first term does vanish. In this case, $1/t^2$ terms can never be neglected except for $t_\beta = \infty$ (or $b = 0$ which is not allowed). But it should be noted that all terms vanish for g_0 equal to the equilibrium distribution.

To examine the conditions in t_β in further detail, we shall assume two types of particles, labelled α and β , having concentrations C_α and C_β . Furthermore, we shall assume that initially the density function $g(0)$ is factorized and that the two types of particles have the density functions

$$\left. \begin{aligned} g_\alpha(p_\alpha, t) = A_\alpha \exp \left[-\frac{p_\alpha^2}{2 \sigma_\alpha} \right] \\ g_\beta(p_\beta, t) = A_\beta \exp \left[-\frac{p_\beta^2}{2 \sigma_\beta} \right], \end{aligned} \right\} \quad (3.5.2)$$

where A_α and A_β are normalization constants and $\sigma_\alpha(t)$ and $\sigma_\beta(t)$ are parameters corresponding to the mean square deviation. For $\sigma_\alpha, \sigma_\beta = 1$, the density functions become the equilibrium density functions, while for $\sigma_\alpha, \sigma_\beta = 0$ they correspond to a delta function. The equations for $g_\alpha(p_\alpha, t)$ and $g_\beta(p_\beta, t)$ are developed in the same manner as for the case of Brownian motion (section 2.8) by integrating over all particles but the one of interest. Thus equation (3.5.1) yields

$$\left. \begin{aligned} \frac{\partial g_\alpha(p_\alpha, t)}{\partial t} = & \frac{\partial}{\partial p_\alpha} \left\{ 4 a^2 b^2 \ln 2 C_\beta \left[\frac{\partial g_\alpha(p_\alpha, t)}{\partial p_\alpha} g_\beta(p_\alpha, t) - g_\alpha(p_\alpha, t) \frac{\partial g_\beta(p_\alpha, t)}{\partial p_\alpha} \right] \right\} \\ & + \frac{a^2 b^4}{2 t^2} \left[C_\beta \frac{\partial g_\alpha(p_\alpha, t)}{\partial p_\alpha} \frac{\partial^2 g_\beta(p_\alpha, t)}{\partial p_\alpha^2} - C_\beta \frac{\partial^3 g_\beta(p_\alpha, t)}{\partial p_\alpha^3} g_\alpha(p_\alpha, t) \right. \\ & \left. + C_\alpha \frac{\partial g_\alpha(p_\alpha, t)}{\partial p_\alpha} \frac{\partial^2 g_\alpha(p_\alpha, t)}{\partial p_\alpha^2} - C_\alpha \frac{\partial^3 g_\alpha(p_\alpha, t)}{\partial p_\alpha^3} g_\beta(p_\alpha, t) \right] \\ & \left. + \frac{a^2 b^4}{t^2} \left[C_\beta \frac{\partial g_\beta(p_\alpha, t)}{\partial p_\alpha} g_\alpha(p_\alpha, t) + C_\alpha \frac{\partial g_\alpha(p_\alpha, t)}{\partial p_\alpha} g_\alpha(p_\alpha, t) \right] \right\} \quad (3.5.3) \end{aligned}$$

with a similar equation for $\partial g_\beta(p_\beta, t)/\partial t$ obtained from (3.5.3) by interchanging α and β . By inserting equations (3.5.2) into (3.5.3), the condition for neglecting the $1/t^2$ terms relative to the first term is readily obtained. For the $\partial g_\alpha/\partial t$ equation, we must require

$$\frac{b^2}{t_\beta^2} \left| \left\{ C_\alpha \left(1 - \frac{1}{\sigma_\alpha} \right) + C_\beta \left[\frac{1}{2} \frac{p_\alpha^2}{\sigma_\beta} \left(\frac{1}{\sigma_\beta} - \frac{1}{\sigma_\alpha} \right) + \frac{1}{2} \left(\frac{1}{\sigma_\alpha} - \frac{3}{\sigma_\beta} + 2 \right) \right] \right\} \right| \ll 4 \ln 2 C_\beta \left(1 - \frac{\sigma_\beta}{\sigma_\alpha} \right) \quad (3.5.4)$$

and for the $\partial g_\beta/\partial t$ equation the condition is the same as (3.5.4), but with α and β interchanged.

For the condition on the smallness of t_β , when $g_0(0)$ is factorized, we note that equation (2.7.3) reduces to two equations

$$\left. \begin{aligned} \frac{\partial g_\alpha(p_\alpha, t)}{\partial t} = & 4 a^2 b^2 \ln 2 C_\beta \frac{\partial}{\partial p_\alpha} \left\{ \frac{\partial g_\alpha(p_\alpha, t - t_\beta)}{\partial p_\alpha} g_\beta(p_\alpha, t - t_\beta) \right. \\ & \left. - g_\alpha(p_\alpha, t - t_\beta) \frac{\partial g_\beta(p_\alpha, t - t_\beta)}{\partial p_\alpha} \right\} \end{aligned} \right\} \quad (3.5.5)$$

and

$$\frac{\partial g_\beta(p_\beta, t)}{\partial t} = \text{same as above but } \alpha \rightleftharpoons \beta,$$

where we have neglected the integral term occurring in (2.7.3). The master equation is obtained by setting $t_\beta = 0$ in equations (3.5.5), and the conditions for doing this may be taken as

$$t_\beta \frac{\partial g_\alpha(t)}{\partial t} \ll g_\alpha(t) \quad t_\beta \frac{\partial g_\beta(t)}{\partial t} \ll g_\beta(t) \quad (3.5.6)$$

and correspond to the condition (2.7.4). To examine these conditions more fully, we shall use the functional forms given by (3.5.2) and determine $\partial g_\alpha(t)/\partial t$ from the master equation (i. e., 3.5.5. with $t_\beta = 0$). In that case, the conditions (3.5.6) become

$$\left| 4 a^2 b^2 \ln 2 t_\beta C_\beta g_\beta^{(p_\alpha)} \left[1 + p_\alpha^2 \left(\frac{1}{\sigma_\beta} - \frac{1}{\sigma_\alpha} \right) \right] \right| \ll 1 \quad (3.5.7)$$

and the same equation with $\alpha \rightleftharpoons \beta$, except that p_α is not changed.

The conditions (3.5.4) and (3.5.7) in the values of t_β are not necessarily compatible, regardless of how small (but not zero) the quantities a or b are chosen. Thus, if $\sigma_\beta = \sigma_\alpha \neq 1$, equation (3.5.4) can only be satisfied for $t_\beta = \infty$, while equation (3.5.7) requires $t_\beta = 0$, demonstrating that the master equation is not correct. This case is not surprising in view of our previous discussions, but it is now clear that σ_β and σ_α must be sufficiently different so that there will exist a t_β which satisfies both conditions. As another example, we can consider the case related to Brownian motion by taking $\sigma_\beta = 1$. In this case, the conditions (3.5.4) and (3.5.7) reduce to

$$b^2 \left| \frac{C_\alpha}{C_\beta} + \frac{1}{2} (p_\alpha^2 - 1) \right| \ll 4 \ln 2 \quad \text{for} \quad \frac{\partial g_\alpha}{\partial t} \quad (3.5.8)$$

$$\frac{1}{2} b^2 \left| \frac{p_\beta^2}{\sigma_\alpha^2} - \frac{3}{\sigma_\alpha} \right| \ll 4 \ln 2 \quad \text{for} \quad \frac{\partial g_\beta}{\partial t} \quad (3.5.9)$$

and

$$4 a^2 b^2 (\ln 2) t_\beta C_\beta g_\beta^{(p_\alpha)} \left| 1 + p^2 \left(1 - \frac{1}{\sigma_\alpha} \right) \right| \ll 1 \quad (3.5.10)$$

$$4 a^2 b^2 (\ln 2) t_\beta C_\beta g_\beta^{(p_\alpha)} \left| 1 + p^2 \left(\frac{1}{\sigma_\alpha} - 1 \right) \right| \ll 1, \quad (3.5.11)$$

where the first condition serves for neglecting the $1/t^2$ terms in the equation for $\partial g_\alpha(p_\alpha, t)/\partial t$, while the second applies to the equation for $g_\beta(p_\alpha, t)/\partial t$ and can be ignored if we wish to consider only the motion of the Brownian particle (i. e., g_α). The last two conditions apply to both equations. In any case, there are again no compatible values of t_β for $\sigma_\alpha = 0$; i. e., when the Brownian particle has initially a $\delta(p_\alpha)$ density function. Thus, we must assume that σ_α is sufficiently different from zero to satisfy the first, third, and fourth conditions. The second condition further restricts the value of σ_α , but is concerned with the equation for $g_\beta(p_\beta)$ describing the motion of the bath particles.

Furthermore, it should be recognized that the values of t_β which satisfy the conditions (3.5.7) also depend on the momentum (p_α or p_β). In general, it is necessary to restrict the range of momenta p_α for which the master equation can be considered correct. Thus, for large values of p_α , it is necessary to choose a large value of t_β to satisfy the condition (3.5.8); in fact $t_\beta \rightarrow \infty$ as $p_\alpha \rightarrow \infty$. However, this value of t_β will be compatible with equation (3.5.10) because of the presence of the factor $g_\beta(p_\alpha)$ in (3.5.10). While it is clear that we must choose a different value of t_β for each p_α , this presents no major problems, except to restrict the range of momenta for which the master equation is valid at a given time t . As t becomes larger, t_β for particular p_α can be made larger and we can neglect the terms in $1/t^2$ for a wider range of momenta.

Finally, we must realize that the values of σ used in the conditions (3.5.3) and (3.5.7) are time dependent. Thus, in the case of Brownian motion where, at $t = 0$, we take $\sigma_\beta(0) = 1$ and $\sigma_\alpha(0) \neq 1$, it will be possible to satisfy the conditions for some region of momentum if a and b are small. As was already pointed out in section 3.2, the master equation (eq. 3.5.1 *without* the $1/t^2$ terms) will drive the system to a state where $\sigma_\beta = \sigma_\alpha \neq 1$. As the system approaches this state the terms in $1/t^2$ will become increasingly important and finally dominate the other terms, as indicated by the fact that the conditions will no longer be satisfied. This result depends on the fact that $\sigma_\alpha \rightarrow \sigma_\beta$ exponentially in time, while we can only neglect the other terms to an order $1/t^2$.

3.6. Effect of Higher Order Terms in λ

In the previous section, we have concerned ourselves with an analysis of the condition necessary to reduce the non-Markovian equation (2.5.16) to the Markovian master equation (2.7.5). These equations only involved certain terms of order $(\lambda^2)^n$ and the reduction to the master equation primarily required conditions which allow these terms to be replaced by their asymptotic forms. In this section we shall examine the effect of higher-order terms in λ , such as $(\lambda^3)^n$, using the asymptotic forms of these terms without regard to the conditions necessary to justify these forms. In place of the master equation, we then obtain

$$\frac{\partial g_0(\{p_{ij}\}, t)}{\partial t} = \{\lambda^2 [2.7.6] + \lambda^3 [3.4.6]\} g_0(\{p_{ij}\}, t), \quad (3.6.1)$$

where the numbers in brackets refer to the operators given by those equations. The λ^2 terms are just those of the master equation. The only difference between the λ^3 term here and that given by equation (3.4.6) is that it now operates on $g_0(t)$ instead of $g_0(0)$. This replacement can be justified by examining and summing special terms of all orders in $(\lambda^3)^n$ and $(\lambda^2)^m (\lambda^3)^l$ in the same manner as for the derivation of the master equation given in sections 2.5 to 2.7.

As shown by equation (3.4.6), the λ^3 operator can be broken into two parts. One part (the first term of 3.4.6) has exactly the same form as the master equation and can always be ignored if λ is small (i. e. $\lambda^3 \ll \lambda^2$); but even if λ is not small, this term will not alter the form of the master equation, except for the change of the numerical coefficient from $(4\lambda^2 a^2 b^2 \ln 2)$ to $\left(4\lambda^2 a^2 b^2 \ln 2 \left[1 - \frac{2}{3} \lambda ab\right]\right)$. We shall ignore this term in the following. The other part of the λ^3 operator (the second and third terms of eq. 3.4.6) is identical with the terms in $1/t^2$ in equation (3.5.1); in fact it is only necessary to let the quantity in equation (3.5.1) go to

$$\frac{\alpha^2 b^4}{t^2} \rightarrow \alpha^3 b^3 [(\ln 2) - 1] \quad (3.6.2)$$

to obtain equation (3.6.1). As in section 3.5, we can assume that $g_0(0)$ is factorized and there exist only two types of particles, α and β . Equation (3.6.1) reduces to two simultaneous equations identical with the equation (3.5.3) when the substitution (3.6.2) is made. If we further assume that the density functions are represented by equation (3.5.2), then the conditions for neglecting the λ^3 terms become identical with the conditions (3.5.4) so long as we set

$$\frac{b^2}{t^2} \rightarrow ab [1 - \ln 2]. \quad (3.6.3)$$

The analysis of these conditions is essentially identical to that previously given, except that the λ^3 terms are not directly affected by the size of t . For any value of ab we must limit the momentum space and the nature of the density functions in order to neglect the terms in λ^3 . Finally, we must again realize that σ_α and σ_β are time dependent. The equation of motion for the density functions (eqs. 3.5.3 with 3.6.2) can be schematically written as

$$\left. \begin{aligned} \frac{\partial g_\alpha(p_\alpha, t)}{\partial t} &= \lambda^2 C_\beta(\sigma_\alpha = \sigma_\beta) + \lambda^3 C_\alpha(\sigma_\alpha = 1) \\ \frac{\partial g_\beta(p_\beta, t)}{\partial t} &= \lambda^2 C_\alpha(\sigma_\alpha = \sigma_\beta) + \lambda^3 C_\beta(\sigma_\beta = 1), \end{aligned} \right\} \quad (3.6.4)$$

where the equalities in parenthesis indicate the conditions under which the coefficients are zero. Thus, if we consider Brownian motion where initially $0 < \sigma_\alpha(0) \ll 1$ and $\sigma_\beta(0) = 1$, we can neglect the λ^3 terms for some range of momenta (λ is assumed small). But the effect of the λ^2 terms is to make $\sigma_\alpha = \sigma_\beta \neq 1$. As this state is approached, the λ^3 terms will dominate the motion. It is also clear that the λ^3 terms become important more rapidly for $\partial g_\beta / \partial t$ since they enter to an order C_β in that equation.

3.7. Discussion of the Analysis

The analysis given in this and the preceding section can be considered as a first-order analysis of the conditions necessary for the master equation to be correct. The presence of the λ^3 terms will affect the conditions necessary for the neglect or retention of the $1/t^2$ terms as well as the conditions for making the equation Markovian. Basically, it is also necessary to determine the condition for neglecting other terms which arose in the original expansion of the Liouville equation (2.2.9). In any case, the conditions we have determined already place the master equation in its proper perspective.

As in the case of Brownian motion, by imposing limitations on the momentum space, the time coordinate, and the nature of the initial distribution function, the motion of the system will be determined by the master equation (λ^2 terms). This motion is such that the system will approach a state (not the equilibrium state) where the master equation will be satisfied and where the λ^2/t^2 and λ^3 terms will become important in determining the motion of the system. When these terms are included we can expect that the system will approach a state (again, not the equilibrium state) which satisfies the collection of λ^2 , λ^2/t^2 and λ^3 terms and will require the retention of still higher order terms (λ^2/t^4 and λ^4). Furthermore, the equations (with λ^2/t^2 and λ^3 terms retained) are such that the system need not approach the new stationary states in a monotonic manner, but rather can undergo damped oscillations. When all orders of λ and t are retained, the system need no longer approach a stationary solution; instead, it will obtain an oscillatory solution. This effect will be further studied in a later paper for it relates to the Poincaré time and the entropy production.

However, there is one exception to the preceding discussion, which arises in the case of Brownian motion. If we assume that the concentration of the Brownian particles α is zero, then the bath particles β will remain at equilibrium, as shown by equation (3.6.4). While it is still necessary to impose limitations on the momentum-time space, the master equation will be correct within these limits and describe the motion of the Brownian particle to the final equilibrium state. The limitation on the momentum space involves p^2 and can be expressed as a condition on the energy, namely as $E_\alpha \ll kT$, where E_α is the energy of the particle. As was pointed out in section 3.6, even when λ is not small, the master equation (with only a change in numerical coefficients) may still be satisfied, although the momentum space will be more severely restricted. Still, it should be noted that any changes in the interaction potential or the Hamiltonian will affect the nature of these conditions, so that the particular form of the master equation may not be justified in regions of physical interest and some other form would have to be developed.

In view of these results, the similarity under certain conditions of the Brownian motion equation given here to equations derived by other techniques is not surprising. Thus, the stochastic derivation given by KRAMERS⁽¹⁾ assumes that the Brownian particle is affected by random forces in the bath which is not itself affected by the particle; and the final equation is intuitively subjected to the condition that $E_\alpha \ll kT$. The

derivation of a Brownian motion equation given by ROSENBLUTH⁽⁹⁾ is similar to the derivation given here. Starting from the Liouville equation an expansion is made in correlation functions and λ ; only the first iteration is carried out (in fact, only the $\lambda^2 t$ term is retained). The Brownian motion equation is then obtained by assuming that the bath particles are at equilibrium and are not disturbed, as well as that $t \rightarrow \infty$. This procedure is more direct and avoids the summation of all powers of $(\lambda^2 t)^n$ and the intermediate formulation of the master equation. A condition is imposed on the energy by requiring that the expansion be valid for average values; such a condition must be considered to be intuitive since it was not and cannot be used to analytically justify the application of the resulting equations. The resulting equation is identical with that obtained by use of the master equation. Finally, we may realize that the condition imposed by ZWANZIG in his derivation of the master equation, namely, that the quantity λt be small (see footnote p. 25), is actually required to justify the master equation. For the analysis presented here shows that the master equation is not valid after a time related to λ and the specific form of the initial density function.

The usefulness of the master equation is probably best discussed in terms of states of the density functions. Starting from some state for which the conditions are satisfied, the master equation will approximately describe the evolution of the system to some new state in which the conditions are no longer satisfied. If it happens that the two states are of physical interest, then the equation is useful. This is the case for a Brownian motion even when the ratio of particles is finite ($\approx 10^{23}$). The conditions (3.5.4) can be satisfied for initial states of physical interest and the evolution will be approximately described by the master equation until the state for $\sigma_\alpha = \sigma_\beta \neq 1$ is reached. This final state will be very near the equilibrium state, and the equation will be of physical importance. However, for other initial states which are not so closely related to the equilibrium state, the conditions will be more difficult to satisfy for problems of physical interest. It is worth noting that some form of time-coarse-graining in place of time limits ($t \rightarrow \infty$) may considerably reduce the stringency of the conditions while still yielding essentially the same equations; this will be discussed further in a later paper.

Section 4

Conclusions and Summary

The theory of irreversible processes developed by PRIGOGINE and others applies to infinite systems ($\mathcal{V} \rightarrow \infty$, $N \rightarrow \infty$) and is based on the assumption of a parameter of smallness associated with the interaction potential and the condition that t is large. It is further assumed that the initial density function $\varrho(\{p_i\}, \{x_i\}, 0)$ has a λ dependence similar to that of the equilibrium density function. The coordinate space Fourier transform of the solution of the Liouville equation $\varrho(\{p_i\}, \{x_i\}, t)$ is expanded in powers of λ , and the asymptotic time dependence of each term is studied. All terms having a dominant t dependence are selected out of the complete array. Thus, all powers of $(\lambda^2 t)^n$ are retained while terms such as $\lambda^3 t^2$ do not arise in the asymptotic

expansion. The asymptotic forms are then summed and lead immediately to the master equation which describes an irreversible process, since its solution implies a positive entropy production. In order to justify the use of the asymptotic forms, it is necessary to require that $t \gg t_c$, the collision time, which is assumed to be small in many cases of interest. Based on this derivation, the master equation would appear to be a representation of the Liouville equation, valid when λ is small, t is large, and the other weak restrictions are satisfied.

In part I of this paper (sections 1 and 2) we have rederived the master equation directly in the phase space, using only the conditions discussed above. It was demonstrated that the Fourier transform of the master equation obtained here is identical to that derived by PRIGOGINE. The only variation in the derivation given here was that the terms in $(\lambda^2 t)^n$ were summed before taking the limit of t large; this resulted in a *non*-Markovian equation closely related to the operational development of the master equation given by ZWANZIG. When the condition $t \gg t_c$ was imposed, this non-Markovian equation reduced to the Markovian master equation.

In view of the apparent generality of the master equation and its close relation to the Liouville equation, the differences in the properties of their solutions appear as inconsistencies. For example, the master equation basically describes the evolution of the momentum density function, $g_0(\{p_i\}, t)$, which would seem to be an approximation of the complete density function $\varrho(\{p_i\}, \{x_i\}, t)$ to the order λ ; as such it is difficult to understand the difference in entropy production of the two equations. As another example, the master equation possesses stationary solutions which are not stationary solutions of the Liouville equation. In part II (section 3), a detailed analysis of the master equation is given in order to resolve these inconsistencies. The analysis demonstrates that the assumptions used in the derivation of the master equation are by no means sufficient to justify the neglect of higher-order terms in λ (such as $\lambda^3 t$) neither for the expansion of $\varrho(t)$ nor g_0 , no matter how small λ is taken (but not zero). When these higher-order terms are retained the inconsistencies are removed.

The fundamental analytical error in the derivation of the master equation lies in the use of the asymptotic time dependence as the basis for selecting the dominant terms in λ . Every term in λ is a function of both t and $\{p_i\}$. This momentum dependence can be expressed as a differential momentum operator acting on the initial momentum density function $g_0(0, p_i)$ and such that higher terms in λ have higher order differential operators. While a particular term in λ may appear dominant for λ small and t large, the momentum dependence may make this term negligible, and some higher order term dominant. Furthermore, the lower order terms in λ always cause the density function $g_0(t, \{p_i\})$ to change such that the higher λ terms become dominant. Consequently, the selection rule based on λ , t dependence is not satisfactory and the momentum dependence of all terms must also be analyzed.

The preceding results do not directly affect the use of asymptotic forms for t large. The time dependence of any term in λ^n can be expanded about $t = \infty$ and pro-

duces terms in powers of l/t^2 which are associated with powers of the range b of the force. Again these terms also depend on the momentum $\{p_i\}$, and cannot in general be neglected, no matter how small b is made (but not zero) or how large t is made (but not infinite). This result shows that the Liouville equation cannot be reduced to a Markovian master equation for b small and t large without some additional conditions on the momentum density function. We may summarize these results as follows:

Even if the volume \mathcal{V} and the number of particles N are infinite, it is not possible to expand the density function $\varrho(\{p_i\}, \{x_i\}, t)$ which satisfies the Liouville equation, or the associated reduced density functions such as $g_0(\{p_i\}, t)$ or $g_i(p_i, t)$, in powers of a parameter of smallness, be it the magnitude of the force or the range of the force or the concentration, such that higher-order terms in the parameter can be neglected in describing the evolution of any of the density functions for all values of time, momentum (and/or position) or all initial states of the density function.

This conclusion represents a generalisation of a well-known theorem due to POINCARÉ. However, it does not exclude the possibility of establishing equations, such as the master equations, which can correctly describe the evolution when conditions are imposed on the range of time, the momentum space, and the initial state of the system. In this regard, a necessary condition for the master equation to hold was established and studied with particular emphasis on the problem of Brownian motion. It was shown that the condition can be satisfied by reasonable physical limitations on the range of momentum and initial distribution and that the master equation can be expected to describe the motion of the Brownian particle density function until it is *almost* at equilibrium. The condition also shows that even if λ is not small, the evolution of the density function may still be described by the master equation (with a change in numerical coefficients), although it will be necessary to impose stronger limits on the momentum space. That is, the condition that λ is small is neither necessary nor sufficient to justify the master equation. This result explains the close similarity of Brownian motion equations under certain conditions although these equations are obtained by widely different approaches such as the stochastic assumptions used by KRAMERS.

However, it must be realized that the condition developed here is only necessary; it may not be sufficient even for the case considered here. Furthermore, any change in the interaction potential or the Hamiltonian will affect the nature of the condition. Thus, the extension of the master equation to more complex systems by the use of action and angle variables^{(8), (10)} will yield very different conditions. Whether these conditions can be satisfied for cases of physical interest remains to be seen.

While the study carried out here has emphasized the one-dimensional case, the extension of the derivation of the master equation (section 2) to three dimensions

is trivial. The extension of the analysis (section 3) to three dimensions is more difficult as the integrals involved become complicated, and have not yet been evaluated. However, there is no indication, neither in the method nor in the results, that the general conclusions would be affected by the dimensionality.

Acknowledgements

While this study was primarily carried out after I left the Free University of Brussels, Belgium, I wish to thank Professor I. PRIGOGINE and his group for stimulating my interest in this subject as well as for affording me a most pleasant and instructive period during the year and a half I was there. Many of the ideas contained herein originated and were discussed at that time.

The further development and final formulation of this paper has been carried out at the Institute for Physical Chemistry in Copenhagen, where the interest and constructive comments of Dr. THOR A. BAK proved most valuable to me.

I also wish to thank Miss M. WHITE and Mrs. L. SEIFERT for their patience in the tedious job of typing and revising this manuscript.

This investigation was supported in part by a fellowship (AF-8313) from the National Institute of Arthritis and Metabolic Diseases, Public Health Service, and in part by the *Aeronautical Research Laboratories* of the Air Research and Development Command, United States Air Force, through its European Office.

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Section 5: Appendices

5.1. Appendix I: Solution of the equation

Equations of the type (2.4.4) are most easily solved by the use of a displacement operator

$$E(pt) = e^{pt \frac{\partial}{\partial x}} \quad (5.1.1)$$

which has the property

$$E(pt) f(x, p, t) = f[x + pt, p, t] \quad (5.1.2)$$

as well as the commutation properties

$$E(pt) \frac{\partial}{\partial t} f(x, p, t) = \left[\frac{\partial}{\partial t} E(pt) - p \frac{\partial}{\partial x} E(pt) \right] f(x, p, t) \quad (5.1.3)$$

$$E(pt) \frac{\partial}{\partial p} f(x, p, t) = \left[\frac{\partial}{\partial p} E(pt) - t \frac{\partial}{\partial x} E(pt) \right] f(x, p, t) \quad (5.1.4)$$

$$E(pt) g(p, t) \frac{\partial f}{\partial x}(x, p, t) = g(p, t) \frac{\partial}{\partial x} E(pt) f(x, p, t), \quad (5.1.5)$$

and

$$E(pt_1) E(pt_2) = E[p(t_1 + t_2)] \quad (5.1.6)$$

$$E(pt) g(x, p, t) h(x, p, t) = [E(pt) g(x, p, t)] [E(pt) h(x, p, t)]. \quad (5.1.7)$$

To solve the equation

$$\frac{\partial g(x, p, t)}{\partial t} + p \frac{\partial g(x, p, t)}{\partial x} = h(x, p, t) \quad (5.1.8)$$

we operate with $E(pt)$ and, after using the commutation properties (eq. 5.1.3), obtain

$$\frac{\partial}{\partial t} E(pt) g(x, p, t) = E(pt) h(x, p, t). \quad (5.1.9)$$

Integrating with respect to t , and noting that $E(0) = 1$, we have

$$E(pt) g(x, p, t) - g(x, p, 0) = \int_0^t E(pt') h(x, p, t') dt'. \quad (5.1.10)$$

Applying the inverse operator $E(-pt)$ yields

$$g(x, p, t) = E(-pt) g(x, p, 0) + E(-pt) \int_0^t E(pt') h(x, p, t') dt' \quad (5.1.11)$$

which can be written as

$$g(x, p, t) = g(x - pt, p, 0) + \int_0^t E[p(t-t')] h(x, p, t') dt'. \quad (5.1.12)$$

Finally, we may set $\tau = t - t'$ and obtain

$$g(x, p, t) = g(x - pt, p, 0) + \int_0^t h(x - p\tau, p, t - \tau) d\tau.$$

5.2. Appendix II: Evaluation of Higher-Order Terms in λ

1) In accord with equations (2.2.9) and (2.4.1) we obtain

$$\left. \begin{aligned} \frac{\partial g_0^3}{\partial t} = \frac{1}{\mathcal{Y}^c} \sum_{\substack{(2) \\ 2 \neq 1}} \frac{\partial}{\partial p_1} \int_x \frac{\partial V(x)}{\partial x} \int_0^t E(-p\tau) \frac{\partial V(x)}{\partial x} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] \\ \cdot \int_0^{t-\tau} \frac{\partial V}{\partial x}(x - pt') dt' d\tau dx \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_1(p_1) g_2(p_2), \end{aligned} \right\} \quad (5.2.1)$$

where $p = (p_1 - p_2)$ and the operator, $E(-p\tau)$, acts on everything to the right. Since this operator does not commute with the differential operator $[\partial/\partial p_1 - \partial/\partial p_2]$, it is easiest to carry through the latter operator and then apply $E(-p\tau)$. This yields

$$\frac{\partial g_0^3}{\partial t} = \frac{1}{\mathcal{Y}^c} \sum_{\substack{(2) \\ 2 \neq 1}} \frac{\partial}{\partial p_1} [I_1(t, p) \Phi_1(t, p_1, p_2) - 2I_2(t, p) \Phi_2(t, p_1, p_2)], \quad (5.2.2)$$

where

$$\left. \begin{aligned} \Phi_1(t, p_1, p_2) &= \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right]^2 g_1(p_1) g_2(p_2) \\ \Phi_2(t, p_1, p_2) &= \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] g_1(p_1) g_2(p_2) \end{aligned} \right\} \quad (5.2.3)$$

and

$$\left. \begin{aligned} I_1 &= \int_{x=-\infty}^{+\infty} \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x - p\tau) \int_0^{t-\tau} \frac{\partial V}{\partial x}[x - p(t' + \tau)] dt' d\tau dx \\ I_2 &= \int_{x=-\infty}^{+\infty} \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x - p\tau) \int_0^{t-\tau} t' \frac{\partial^2 V}{\partial x^2}[x - p(t' + \tau)] dt' d\tau dx. \end{aligned} \right\} \quad (5.2.4)$$

2) It is easily seen that the first integral (I_1) is zero. Note, first, that for an arbitrary function $F(t', \tau)$

$$\int_0^t \int_0^{t-\tau} F(t', \tau) dt' d\tau = \int_0^t \int_0^{t-t'} F(t', \tau) dt' d\tau, \quad (5.2.5)$$

since the area covered is the same and the two integrals differ only in the way it is covered. In the integral I_1 , change the integration variable x to $x' = x - p(t' + \tau)$ and we have

$$I_1 = \left. \begin{aligned} & \int_0^t \int_0^{t-\tau} \int_{x'=-\infty}^{+\infty} \frac{\partial V}{\partial x} [x' + p(t' + \tau)] \frac{\partial V}{\partial x} [x' + pt'] \frac{\partial V(x)}{\partial x} dx' dt' d\tau \\ & = \int_{x=-\infty}^{+\infty} \int_0^t \int_0^{t-\tau} \frac{\partial V(x)}{\partial x} \frac{\partial V}{\partial x} (x + p\tau) \frac{\partial V}{\partial x} [x + p(t' + \tau)] dt' d\tau dx, \end{aligned} \right\} \quad (5.2.6)$$

where the last integral has been obtained by applying equation (5.2.5), then interchanging the labels t' and τ and setting $x' = x$ because these are all dummy variables of integration. Adding equations (5.2.6) and (5.2.4) gives

$$I_1 = \frac{1}{2} \left. \begin{aligned} & \int_{x=-\infty}^{+\infty} \int_0^t \int_0^{t-\tau} \frac{\partial V(x)}{\partial x} \left\{ \frac{\partial V}{\partial x} (x - p\tau) \frac{\partial V}{\partial x} [x - p(t' + \tau)] \right. \\ & \quad \left. + \frac{\partial V}{\partial x} (x + p\tau) \frac{\partial V}{\partial x} [x + p(t' + \tau)] \right\} dt' d\tau dx. \end{aligned} \right\} \quad (5.2.7)$$

Note that $\partial V(x)/\partial x$ is an odd function, i. e., $\partial V(-x)/\partial x = -\partial V(x)/\partial x$; then it is immediately seen that the integral in (5.2.7) is an odd function of x and, hence,

$$I_1 = 0. \quad (5.2.8)$$

3) For the integral I_2 , we first make an integration by parts for the variable t' and obtain

$$I_2 = -\frac{1}{p} \int_x \frac{\partial V(x)}{\partial x} \frac{\partial V}{\partial x} (x - pt) \int_0^t \frac{\partial V}{\partial x} (x - p\tau) (t - \tau) d\tau dx + \frac{1}{p} I_1(pt) \quad (5.2.9)$$

and $I_1 = 0$ according to (5.2.8). Define

$$\bar{V}(x) = \int_{-\infty}^x V(x') dx' - \alpha, \quad (5.2.10)$$

where α is a constant chosen so as to make $\bar{V}(x)$ an odd function if $V(x)$ is an even function. Subsequently, an integration by parts over τ gives

$$\left. \begin{aligned} I_2 &= \frac{t}{p^2} \int_x \frac{\partial V(x)}{\partial x} V(x) \frac{\partial V}{\partial x}(x-pt) dx \\ &- \frac{1}{p^3} \int_x \frac{\partial V(x)}{\partial x} \frac{\partial V}{\partial x}(x-pt) [\bar{V}(x-pt) - \bar{V}(x)] dx. \end{aligned} \right\} (5.2.11)$$

The inclusion of α in the definition of \bar{V} (5.2.10) is allowed by (5.2.11) because of the difference which occurs. If the two terms of the second integral in (5.2.11) are separated and the variable of integration changed to $x' = x - pt$ in the first of these terms, we obtain

$$I_2 = +\frac{t}{p^2} I_{21} + \frac{1}{p^3} I_{22}, \quad (5.2.12)$$

where

$$I_{21} = - \int_x \frac{\partial V(x)}{\partial x} V(x) \frac{\partial V}{\partial x}(x-j) dx, \quad (5.2.13)$$

$$I_{22} = - \int_x \frac{\partial V(x)}{\partial x} \bar{V}(x) \left[\frac{\partial V}{\partial x}(x+j) - \frac{\partial V}{\partial x}(x-j) \right] dx, \quad (5.2.14)$$

and

$$j = pt. \quad (5.2.15)$$

4) Even and Odd Character.

Changing x to $x' = -x$ in equation (5.2.13), using the even and odd properties of $V(x)$ and $\partial V/\partial x$, and noting that $\int_{-\infty}^{+\infty} = - \int_{+\infty}^{-\infty}$, we obtain I_{21} as above, but with $x-j$ replaced by $x+j$. Adding this to I_{21} in (5.2.13), we can write

$$I_{21}(j) = -\frac{1}{2} \int_x \frac{\partial V(x)}{\partial x} V(x) \left[\frac{\partial V}{\partial x}(x-j) + \frac{\partial V}{\partial x}(x+j) \right] dx, \quad (5.2.16)$$

which is easily seen to be an even function of j ; i. e.

$$I_{21}(-j) = I_{21}(j), \quad (5.2.17)$$

while, from (5.2.14), we have that I_{22} is an odd function of j :

$$I_{22}(-j) = -I_{22}(j). \quad (5.2.18)$$

5) The exact evaluation of I_{21} and I_{22} for a constant force over a range $-b$ to b is not difficult. We have

$$\left. \begin{aligned} \frac{\partial V(x)}{\partial x} &= \begin{cases} \frac{-x}{|x|} a & 0 \leq |x| \leq b \\ 0 & b < |x| \end{cases} \\ V(x) &= \begin{cases} a(b - |x|) & 0 \leq |x| \leq b \\ 0 & b < |x| \end{cases} \\ \bar{V}(x) &= \begin{cases} \frac{x}{|x|} \frac{ab^2}{2} & b < |x| \\ \frac{a}{2} x [2b - |x|] & 0 \leq |x| \leq b \end{cases} \end{aligned} \right\} (5.2.19)$$

where α has been chosen to be $\alpha = ab^2/2$ according to the definition (5.2.10). The integrations for I_{21} and I_{22} are easily carried out and one obtains

$$\left. \begin{aligned} I_{21}(j) &= \begin{cases} +\frac{a^3}{2} (2b - |j|)^2 & b \leq |j| \leq 2b \\ +\frac{a^3}{2} \{2b^2 - [2b - |j|]^2\} & 0 \leq |j| < b \\ 0 & 2b < |j| \end{cases} \\ I_{22}(j) &= \begin{cases} +\frac{a^3 j}{3} [3b^2 - 6b|j| + j^2] & 0 \leq |j| < b \\ +\frac{a^3 j}{3|j|} [2b - |j|] [b^2 - 4b|j| + j^2] & b \leq |j| \leq 2b \\ 0 & 2b < |j|. \end{cases} \end{aligned} \right\} (5.2.20)$$

These functions are illustrated in figure 2.

6) To determine the meaning of I_2 , we may consider reducing g_0^3 by integration over all p_i for $i \neq 1$. This requires the evaluation of the integral

$$I = \int_{p_2 = -\infty}^{+\infty} I_2(p, t) \Phi_2(t, p_1, p_2) dp_2. \quad (5.2.21)$$

The integration over p_2 is easily transferred to an integration over p , by

$$p = (p_1 - p_2) \quad (5.2.22)$$

to give

$$I = \int_{p = -\infty}^{+\infty} I_2(p, t) \Phi_2(t, p_1, p) dp. \quad (5.2.23)$$

Finally, we can transform to

$$j = pt \quad (5.2.24)$$

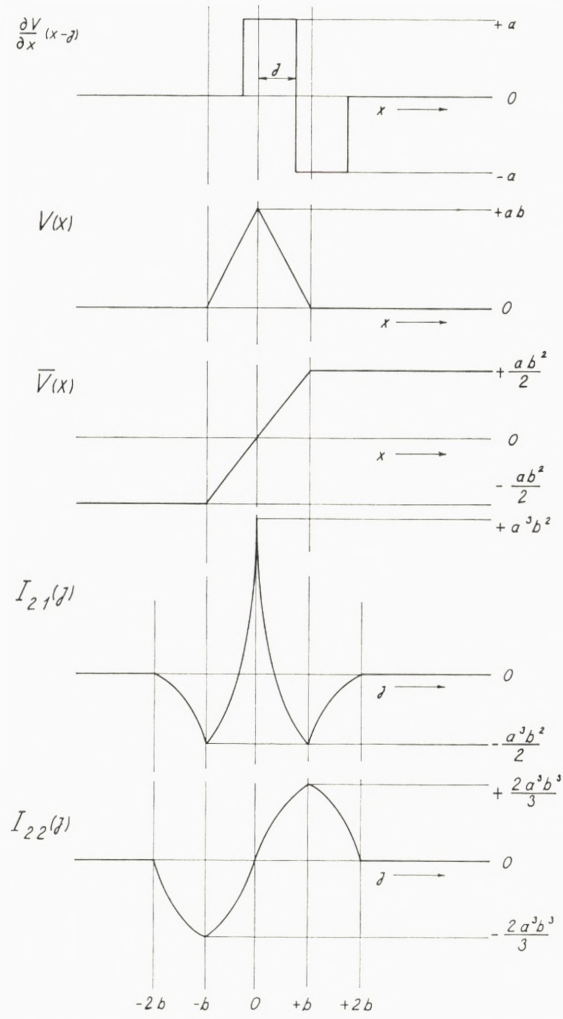


Figure 2: Illustration of the functions described by equations 5.2.19 and 5.2.20.

and have

$$I = \frac{1}{t} \int_{j=-\infty}^{+\infty} I_2\left(\frac{j}{t}, t\right) \Phi_2\left(t, p_1, \frac{j}{t}\right) dj. \quad (5.2.25)$$

Using the equation for I_2 (5.2.12), equation (5.2.24) becomes

$$I = t^2 \int_{-2b}^{+2b} \left[\frac{j I_{21}(j) + I_{22}(j)}{j^3} \right] \Phi_2\left(t, p_1, \frac{j}{t}\right) dj, \quad (5.2.26)$$

where we have noted that I_{21} and I_{22} are zero for $|j| > 2b$. The integral can now be broken into $\int_0^{2b} + \int_{-2b}^0$. Transforming $j \rightarrow -j$ in the second integral and using the even and odd properties of I_{21} and I_{22} , we obtain

$$I = t^2 \int_0^{2b} \left[\frac{j I_{21}(j) + I_{22}(j)}{j^3} \right] \left[\Phi_2 \left(t, p_1, \frac{j}{t} \right) + \Phi_2 \left(t, p_1, -\frac{j}{t} \right) \right] dj. \quad (5.2.27)$$

Finally, $\Phi_2 \left(t, p_1, \frac{j}{t} \right)$ and $\Phi_2 \left(t, p_1, -\frac{j}{t} \right)$ are expanded in a power series of j/t to yield

$$I = t^2 \int_0^{2b} \left[\frac{j I_{21}(j) + I_{22}(j)}{j^3} \right] \cdot \left[2 \Phi_2(t, p_1, 0) + \left(\frac{j}{t} \right)^2 \Phi_2''(t, p_1, 0) + \frac{1}{2 \cdot 3} \left(\frac{j}{t} \right)^4 \Phi_2^{IV}(t, p_1, 0) \right] dj, \quad (5.2.28)$$

where the primes (') on the Φ_2 denote derivatives with respect to p ; i. e., $\Phi_2'' = (\partial^2/\partial p^2) \Phi_2(t, p_1, p)$. Using the values of I_{21} and I_{22} given by (5.2.20) it is easy to carry out the integrations in (5.2.28) and show that

$$\int_0^{2b} \left[\frac{j I_{21}(j) + I_{22}(j)}{j^3} \right] dj = 0, \quad (5.2.29)$$

while

$$\int_0^{2b} \left[\frac{j I_{21}(j) + I_{22}(j)}{j} \right] dj = \frac{2 a^3 b^3}{3} (1 - \ln 2). \quad (5.2.30)$$

For all other terms in the series of (5.2.28) (namely $\Phi_2^{(2n)}$), the integral over j is finite (there are no poles in the integrand for these terms) while the t dependence is of order $(1/t_2)^{n-1}$; and as t becomes large such that $2b/t \ll 1$, all other terms can be neglected so long as we make the reasonable assumption that $\Phi_2^{(2n)}(t, p_1, 0)$ remains bounded for all t and p_1 .

Hence we have

$$I = \frac{2 a^3 b^3}{3} (1 - \ln 2) \Phi_2''(t, p_1, 0). \quad (5.2.31)$$

From the definition of Φ_2 we can therefore write

$$I_2 = \frac{2 a^2 b^3}{3} (1 - \ln 2) \delta(p_1 - p_2) \frac{\partial^2}{\partial p_2^2} \quad (5.2.32)$$

and thus

$$\left. \begin{aligned} \frac{\partial g_0^3}{\partial t} &= -\frac{\lambda^3 4 a^3 b^3}{3} (1 - \ln 2) \sum \frac{\partial}{\partial p_i} \delta(p_i - p_j) \\ &\quad \frac{\partial^2}{\partial p_j^2} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_i(p_i) g_j(p_j). \end{aligned} \right\} (5.2.33)$$

5.3. Appendix III: Effects of Equilibrium Type Initial Conditions

1) In this section, we calculate the equations for g_0 for a set of initial conditions in which the higher-order correlation functions g_l have a position dependence identical with the equilibrium distribution. Comparison with the expansion of the equilibrium distribution (eq. 2.3.2) shows that we must take

$$g_0^0(0) = g_0^0(0) \quad (5.3.1)$$

$$g_0^v = 0 \quad \text{for } v > 0$$

$$g_1^v = 0 \quad \text{all } v$$

$$g_2^0(0) = -g_0^0(0) V(x) \quad (5.3.2)$$

$$g_2^1 = g_0^0(0) V^2(x), \quad \text{etc.}, \quad (5.3.3)$$

$$\text{for all higher orders } g_2 \text{ and } g_1. \quad (5.3.4)$$

In section 5.3 we have developed the terms which arise from the initial conditions (5.3.1) and it is only necessary to add to those terms the one arising from the non-zero initial conditions (5.3.2), (5.3.3), and (5.3.4). To simplify the notation we shall let brackets [] represent all the terms previously calculated, where the number inside the brackets indicates the particular equation giving the value of these terms. Furthermore, we shall immediately replace $g_0^0(0)$ by $g_0(t)$ which is justified by selecting and summing various terms in higher powers of λ in the same manner as developed in sections 2.5 to 2.7.

2) Using equation (2.2.9) we obtain

$$g_2^0 = -V(x - pt) g_0^0(t) + [2.4.8] \quad (5.3.5)$$

which gives rise to

$$\frac{\partial g_0(t)}{\partial t} = -\frac{\lambda^2}{\mathcal{V}} \sum_{ij} \frac{\partial}{\partial p_i} \int_0^{\infty} \frac{\partial V(x)}{\partial x} V(x - pt') dt' dx g_0(t) + [2.4.10] \quad \text{to order } (\lambda^2)^n.$$

In the limit of $t \rightarrow \infty$, this term vanishes so that we are again left with our previous result (eq. 2.4.10).

3) However, if we now calculate the contribution to $\partial g_0^3/dt$, we obtain

$$\left. \begin{aligned} \frac{\partial g_0^3}{\partial t} = \sum_{\substack{ij \\ i \neq j}} \frac{1}{\mathcal{V}^2} \left\{ \frac{\partial}{\partial p_i} \int_x \frac{\partial V(x)}{\partial x} \int_0^t V^2(x-pt') dt' dx \right. \\ \left. - \frac{\partial}{\partial p_i} \int_x \frac{\partial V(x)}{\partial x} \int_0^t E(-p\tau) \frac{\partial V(x)}{\partial x} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] V[x-p(t-\tau)] d\tau dx \right\} g_0 \\ + [5.2.33] g_0. \end{aligned} \right\} \quad (5.3.7)$$

Here again the first term in the $\{ \}$ vanishes for $t \rightarrow \infty$, and it is the second term which is of interest.

Carrying through the operator $[\partial/\partial p_i - \partial/\partial p_j]$, equation (5.3.7) becomes

$$\frac{\partial g_0^3}{\partial t} = \sum_{ij} \frac{1}{\mathcal{V}^2} \left\{ \frac{\partial}{\partial p_i} (-) I_{31} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] g_0 + 2 \frac{\partial}{\partial p_j} I_{32} g_0 \right\} + [5.2.33], \quad (5.3.8)$$

where

$$I_{31} = \int_x \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x-p\tau) V(x-p\tau) d\tau dx \quad (5.3.9)$$

and

$$I_{32} = \int_x \frac{\partial V(x)}{\partial x} \int_0^t \frac{\partial V}{\partial x}(x-p\tau) [t-\tau] \frac{\partial V}{\partial x}(x-pt) d\tau dx. \quad (5.3.10)$$

4) A comparison of I_{32} with I_2 (eq. 5.2.9), Appendix II, shows

$$I_{32} = -pI_2 = -\frac{t}{p} I_{21} - \frac{1}{p^2} I_{22} \quad (5.3.11)$$

from equation (5.2.12). Proceeding as in section 5.2, we find that

$$\lim_{t \rightarrow \infty} \int_{-\infty}^{+\infty} I_{32}(p_1, t) \Phi(t, p_1, p) dp = -\frac{4a^3 b^3}{3} (1 - \ln 2) \Phi'(t, p_1, 0) \quad (5.3.12)$$

so that we can write

$$I_{32} = +\frac{4a^3 b^3}{3} (1 - \ln 2) \delta(p_1 - p_2) \frac{\partial}{\partial p}. \quad (5.3.13)$$

5) The integral I_{31} is easily reduced to

$$I_{31} = \frac{1}{4p} \int V_{(x)}^2 \left[\frac{\partial V}{\partial x}(x-j) - \frac{\partial V}{\partial x}(x+j) \right] dx \quad (5.3.14)$$

and integration over x gives

$$I_{31} - \frac{1}{2p} (-) \left. \begin{array}{l} 0 \quad \text{for} \quad 2b \leq |j| \\ \frac{\alpha^3 j}{3 |j|} [2b - |j|]^3 \quad b < |j| < 2b \\ \frac{\alpha^3 j}{3} [6b(b - |j|) + j^2] \quad 0 \leq |j| \leq b. \end{array} \right\} \quad (5.3.15)$$

Finally,

$$\lim_{t \rightarrow \infty} \int_{+\infty}^{-\infty} I_{31}(p, t) \Phi(p) dp = \frac{8\alpha^3 b^3}{3} \ln 2 \Phi(0) \quad (5.3.16)$$

so we can write

$$I_{31} = \frac{8\alpha^3 b^3}{3} \ln 2 \delta(p_1 - p_2). \quad (5.3.17)$$

6) Equation (5.3.8) can then be written as

$$\left. \begin{array}{l} \frac{\partial g_0^3}{\partial t} = \frac{1}{\mathcal{V}} \sum_{ij} \frac{\partial}{\partial p_i} \left\{ -\frac{8\alpha^3 b^3}{3} \ln 2 \delta(p_1 - p_2) \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] \right. \\ \quad \left. + \frac{8\alpha^3 b^3}{3} (1 - \ln 2) \delta(p_1 - p_2) \frac{\partial}{\partial p_2} \right. \\ \quad \left. - \frac{4\alpha^3 b^3}{3} (1 - \ln 2) \delta(p_1 - p_2) \frac{\partial^2}{\partial p_2^2} \left[\frac{\partial}{\partial p_1} - \frac{\partial}{\partial p_2} \right] \right\} g_0^0. \end{array} \right\} \quad (5.3.18)$$

If we further assume that g_0^0 is factorized, i. e.,

$$g_0^0 = \prod_i {}^{(i)}g(p_i) \quad (5.3.19)$$

such that

$$\int {}^{(i)}g(p_i) dp_i = 1, \quad (5.3.20)$$

we obtain

$$\left. \begin{array}{l} \frac{\partial {}^{(i)}g^3}{\partial t} = \frac{1}{\mathcal{V}} \sum_{ij} \frac{\partial}{\partial p_i} \left\{ -\frac{8\alpha^3 b^3}{3} \ln 2 \int \delta(p_i - p_j) \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] {}^{(i)}g^0 {}^{(j)}g^0 dp_j \right. \\ \quad \left. + \frac{8\alpha^3 b^3}{3} (1 - \ln 2) \int \delta(p_i - p_j) \frac{\partial}{\partial p_j} {}^{(i)}g^0 {}^{(j)}g^0 dp_j \right. \\ \quad \left. - \frac{4\alpha^3 b^3}{3} (1 - \ln 2) \int \delta(p_i - p_j) \frac{\partial^2}{\partial p_j^2} \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] {}^{(i)}g^0 {}^{(j)}g^0 dp_j \right\}. \end{array} \right\} \quad (5.3.21)$$

Finally, if we assume that *all* particles were at equilibrium initially, we have

$${}^{(i)}g^0(p_i) = C \exp \left[-\frac{p_i^2}{2} \right] = {}^{(i)}g_{\text{eq}} \quad \text{for all } i. \quad (5.3.22)$$

Inserting this in equation (5.3.21), we find that the first term on the right is zero while the second and third terms give

$$\frac{\partial g^3}{\partial t} = \frac{N}{\mathcal{V}^\circ} \frac{\partial}{\partial p_i} \left\{ \frac{8a^3 b^3}{3} (1 - \ln 2) [-p_1] - \frac{4a^3 b^3}{3} (1 - \ln 2) [-2p_1] \right\} {}^{(i)}g_{\text{eq}} {}^{(j)}g_{\text{eq}} = 0. \quad (5.3.23)$$

5.4. Appendix IV: Identity of the Master equations

1) In this section a proof is given to demonstrate that the master equation obtained by PRIGOGINE and the master equation (2.7.6) presented here are in fact identical. For a problem in one dimension, the master equation is given by PRIGOGINE as

$$\frac{\partial g^0}{\partial t} = \lambda^2 \sum_{ij} \int dk |V_k|^2 k \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) \delta_- [k(p_i - p_j)] k \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) g_0(p, t), \quad (5.4.1)$$

where

$$V_k = \lim_{\mathcal{V}^\circ \rightarrow \infty} \frac{1}{\mathcal{V}^{\circ 1/2}} \int e^{-ikx} V(x) dx \quad (5.4.2)$$

and \mathcal{V}° is the volume.

From the definition of V_k , we readily obtain

$$\frac{1}{\mathcal{V}^{\circ 1/2}} \int e^{-ikx} \frac{\partial V(x)}{\partial x} dx = + \frac{ik}{\mathcal{V}^{\circ 1/2}} \int e^{-ikx} V(x) dx = \frac{ik}{\mathcal{V}^{\circ 1/2}} V_k \quad (5.4.3)$$

and, hence,

$$k^2 |V_k|^2 = \frac{1}{\mathcal{V}^\circ} \int e^{-ikx} \frac{\partial V(x)}{\partial x} dx \int e^{+ikx'} \frac{\partial V(x')}{\partial x'} dx'. \quad (5.4.4)$$

From its definition we may set

$$\delta_- [k(p_i - p_j)] = \int_0^\infty e^{+ik(p_i - p_j)t'} dt'. \quad (5.4.5)$$

Inserting equations (5.4.4) and (5.4.5) in (5.4.1), we obtain

$$\left. \begin{aligned} \frac{\partial g_0[\{p_i\}, t]}{\partial t} &= \frac{\lambda^2}{\mathcal{V}^\circ} \sum_{i < j} \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) \int_{t=0}^\infty \int_{x'} \int_x \int_{k=-\infty}^{+\infty} dk e^{-ik(x-x'-pt')} \\ &\cdot \frac{\partial V(x)}{\partial x} \frac{\partial V(x')}{\partial x'} dx dx' dt' \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) g_0(\{p_i\}, t). \end{aligned} \right\} \quad (5.4.6)$$

This equation is found in reference (11) as equation (1.14), page 557. As shown by PRIGOGINE (5), the $\pi\delta(kp)$ which occurs there should be corrected to read $\delta_-(kp)$.

Performing the integration over k gives

$$\left. \begin{aligned} \frac{\partial g_0}{\partial t} &= \frac{\lambda^2}{\mathcal{V}^0} \sum_{ij=1}^N \frac{\partial}{\partial p_i} \int_x \int_{x'} \int_{t=0}^{\infty} \delta(x-x'-pt) \\ &\cdot \frac{\partial V(x)}{\partial x} \frac{\partial V(x')}{\partial x} dx dx' dt \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) g_0(\{p_i\}, t), \end{aligned} \right\} \quad (5.4.7)$$

where we have noted that

$$\left. \begin{aligned} \sum_{i < j} \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) &= 1/2 \sum_{ij=1}^N \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \left[\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right] \\ &= 1/2 \left[\sum_{ij=1}^N \frac{\partial}{\partial p_i} \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) - \sum_{ij=1}^N \frac{\partial}{\partial p_j} \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) \right] \\ &= \sum_{ij=1}^N \frac{\partial}{\partial p_i} \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right). \end{aligned} \right\} \quad (5.4.8)$$

Finally, integrating equation (5.4.7) over x' yields

$$\frac{\partial g_0}{\partial t} = \frac{\lambda^2}{\mathcal{V}^0} \sum_{ij=1}^N \frac{\partial}{\partial p_i} \int_x \int_{t=0}^{\infty} \frac{\partial V(x)}{\partial x} \frac{\partial V}{\partial x}(x-pt) dx dt \cdot \left(\frac{\partial}{\partial p_i} - \frac{\partial}{\partial p_j} \right) g_0(\{p_i\}, t) \quad (5.4.9)$$

which is identical with equation (2.7.6).

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