A CRITICAL COMPARISON OF SOME THEORIES OF CLASSICAL IRREVERSIBLE STATISTICAL MECHANICS

BY

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ABSTRACT

The infinite order perturbation theory of Prigogine and coworkers is used, with some modifications, to discuss the theories of classical irreversible processes due to Bogoliubov, Sandri & Frieman, and Mazur & Biel. The latter authors use the BBKGY hierarchy of equations as a starting point. Accordingly, to discuss these theories the infinite order perturbation theory is written out in such a way that it relates easily to the BBKGY hierarchy. The nature of the assumptions involved in the theories of Bogoliubov and Sandri & Frieman become particularly clear when compared with the infinite order perturbation expansion. The relation of the theory of Mazur & Biel with the cluster expansion of Green is also elucidated.

TABLE OF CONTENTS

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INTRODUCTION.

Several attempts have been made to understand irreversible processes starting from the Liouville equation. In (1946) Bogoliubov[1] proposed a novel and interesting perturbation expansion method. His theory has however remained controversial. Our central aim in this work is to clarify Bogoliubov's expansion method. To do this we apply infinite order perturbation theory using the more recent (1959) diagram techniques developed by Prigogine and coworkers.[2] In particular we use with some modification the infinite order perturbation theory as written out by Severne.[3] We discuss the necessary restrictions on infinite order perturbation theory in order to obtain Bogoliubov's expansion. In this same spirit we also discuss the theories of Sandri & Frieman[4,5] and Mazur & Biel.[6]

Efforts to establish possible connections between Bogoliubov's theory and infinite order perturbation theory began a early as (1961) by Prigogine and Resibois.[7] The problem has also been considered by Stecki & Taylor[8] (1965), Brocas & Resibois[9] (1966), and Braun & Garcia-Colin[10] (1966). These authors use the Master Equation[2] approach and have compared their results with Bogoliubov's expansion. Bogoliubov starts by deriving the well known BBKGY hieracchy[1] of equations. For this reason we choose to write out the infinite order perturbation expansion in such a way that it relates easily to the BBKGY hierarchy and it is our opinion

that these expansions elucidate Bogoliubov's approximation more clearly than does the Master Equation approach.

We will be discussing a classical system of many particles. We spacialize to consider systems of identical particles which interact through a central two body potential with no external fields on the system. Our starting point will be the basic evolution equation of statistical mechanics, the Liouville equation. In Chapter II we formally solve the Liouville equation and write the answer as a perturbation series. Since it has shown considerable promise in the literature; we introduce first-, second-, and higher-order distribution functions defined by integrating the solution to Liouville's equation over coordinates and momenta of all but the particle one, two, etc. To simplify our method of writing these perturbation series we introduce in Chapter III our definitions of diagrams which are similar to those of Prigogine and coworkers. In this Chapter III we perform some simplifications and we find that our expansion relates easily to the BBKGY hierarchy of equations which couple the reduced distribution functions. Also in Chapter III we introduce the Cluster expansion[11] of the distribution functions which we find particularly useful to expand the statistical initial condition needed for the solution of the Liouville equation.

In successful theories of irreversible statistical mechanics the dependence of the distribution functions

upon the one body distribution function has played a dominant role. In Chapter IV we work out this this dependence in detail; we obtain the dependence by performing a particular summation of diagrams. In the later part of the chapter we show that this summation is necessary to determine the long time behavior of the system. That is, the long time behavior of a physical system is determined through the one body distribution function.

In Chapter V we specialize the theory to consider systems for which only small clusters of particles interact simultaneously. Such a situation occurs for dilute systems or for systems where the particles interact through short range forces. We call such systems short-range systems, and we carry out the calculations to include all two and three particle collision effects. We find that a valuable guide for selecting and summing diagrams is the hierarchy of equations, similar to the BBKGY hierarchy, that couple the cluster expansion coefficients that were introduced in Chapter III. We begin Chapter V by deriving this hierarchy of equations in a form which is useful for our purposes. These equations have formerly been obtained by Green.[11]

The equations of Chapter IV and V are non-Markowian. A method for finding well behaved Markowian approximations has not to our knowledge been satisfactorily determined in the literature. In Chapter VI we produce a Markowian approximation procedure that relates most easily to methods found in the literature. We point out some asymptotic

divergence difficulties of this method.

In Chapter VII we discuss Bogoliubov's theory. We begin by writing a résumé of his theory. Then we develop from the knowledge of the former chapters an expansion method that we feel most nearly as possible follows Bogoliubov's expansion, and we solve our equations side by side with those of Bogoliubov. What we do is determine if it is possible to time coarse grain the distribution functions by a certain approximation of the fine grain behavior. We determine the necessary restrictions on our expansions needed to obtain Bogoliubov's; this amounts to a discussion of Bogoliubov's asymptotic boundary conditions. We find however that a meaningful asymptotic limit cannot be found.

In Chapter VIII we discuss the theory of Sandri & Frieman[4,5] which they call the method of extension. We find that thier theory is another approximation that can be obtained from our coarse graining procedure introduced in Chapter VII.

In Chapter IX we discuss the theory of Mazur & Biel.[6] The relation of their theory to the Cluster expansion of Green[11] is elucidated.

In Chapter X we give some concluding remarks.

Figure I is a synoptic diagram of the organization of this thesis.

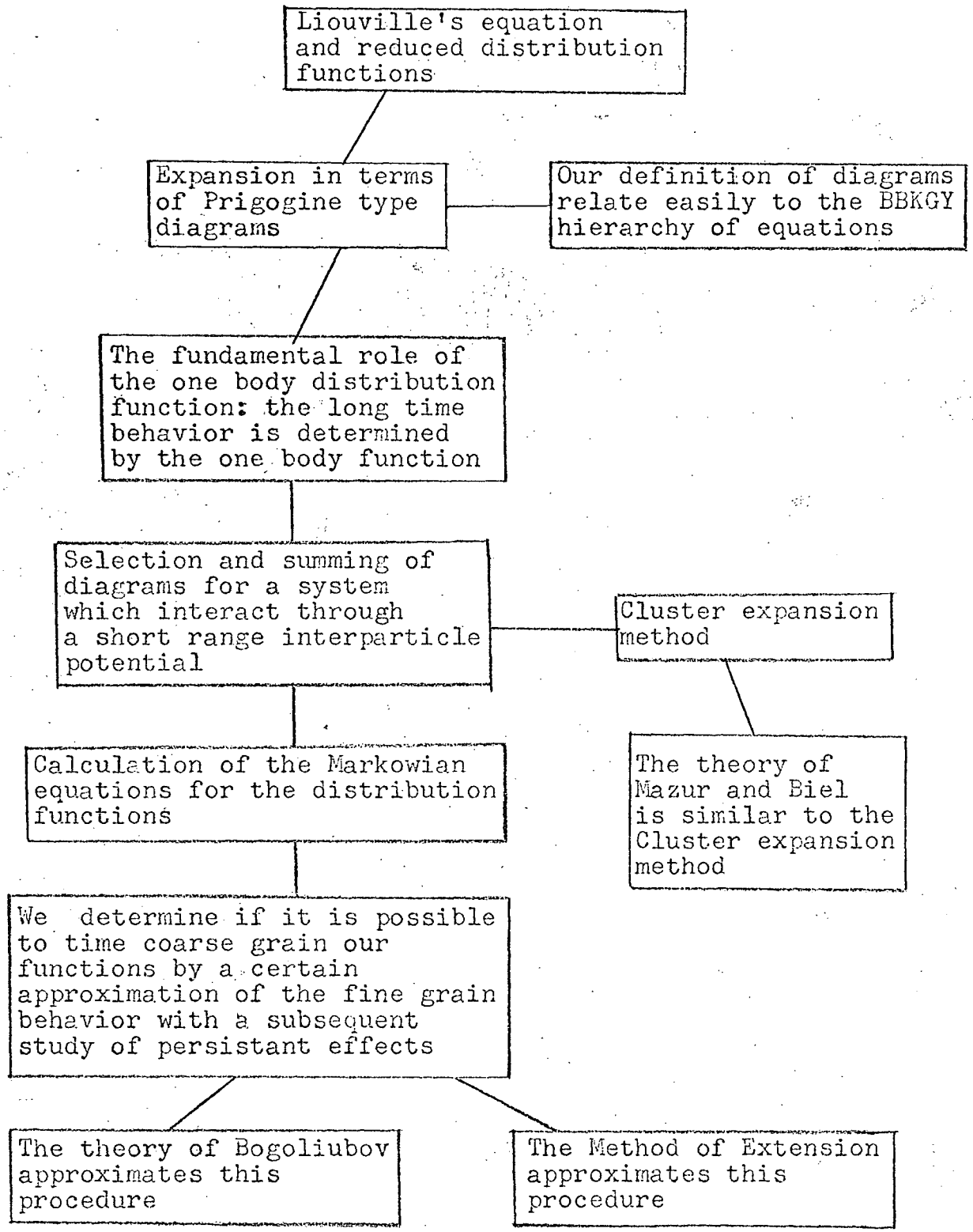

Liouville's equation and reduced distribution functions
Expansion in terms of Prigogine type diagrams
Our definition of diagrams relate easily to the BBKGY hierarchy of equations
The fundamental role of the one body distribution function: the long time behavior is determined by the one body function
Selection and summing of diagrams for a system which interact through a short range interparticle potential
Cluster expansion method
Calculation of the Markowian equations for the distribution functions
The theory of Mazur and Biel is similar to the Cluster expansion method
We determine if it is possible to time coarse grain our functions by a certain approximation of the fine grain behavior with a subsequent study of persistant effects
The theory of Bogoliubov approximates this procedure
The Method of Extension approximates this procedure

Figure. I.

II. THE LIOUVILLE EQUATION AND REDUCED DISTRIBUTION FUNCTIONS.

The starting point of this work is the basic equation of classical statistical mechanics, the Liouville equation. Consider a system, of volume V, formed by N identical particles with known interactions. The statistical state of the system is described by a distribution function $F^N(\underline{x}_1, \underline{v}_1, \underline{x}_2, \underline{v}_2, \ldots, \underline{x}_N \underline{v}_N; t)$ where $\underline{x}_i, \underline{v}_i$ are the respective position and velocity of particle i. The distribution function is normalized by

$$(2.1) \quad \int \cdots \int \frac{d\underline{x}_1}{V} d\underline{v}_1 \frac{d\underline{x}_2}{V} d\underline{v}_2 \cdots \frac{d\underline{x}_N}{V} d\underline{v}_N \; F^N = 1$$

and, for a system of identical particles, F^N must be a symmetric function of $(\underline{x}_1, \underline{v}_1), (\underline{x}_2, \underline{v}_2) \ldots (\underline{x}_N, \underline{v}_N)$. The evolution of F^N in time is governed by the Liouville equation

$$(2.2) \quad \frac{\partial F^N}{\partial t} = -H^N F^N = -(K^N - I^N) F^N$$

where K^N and I^N are operators defined by

$$(2.3) \quad K^N = \sum_{i=1}^{N} K_i = \sum_{i=1}^{N} \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i}$$

$$(2.4) \quad I^N = \sum_{i<j} I_{ij} = \sum_{i<j} \frac{1}{m} \frac{\partial U_{ij}(|\underline{x}_i - \underline{x}_j|)}{\partial \underline{x}_i} \cdot \left(\frac{\partial}{\partial \underline{v}_i} - \frac{\partial}{\partial \underline{v}_j} \right)$$

here m is the mass of a particle. We have presupposed that the particles interact through a central two body potential $U_{ij}(|\underline{x}_i - \underline{x}_j|)$ and that there are no external forces acting on the system. And, since we are interested only in the bulk properties of the system, the wall or container

potential has been neglected. The formal solution of Liouville's equation is

$$(2.5) \qquad F^N = e^{-(K^N - I^N)t} F^N(0)$$

We find that a more useful form of the solution is the perturbation series expansion

$$(2.6) \qquad F^N = e^{-K^N t} F^N(0) + e^{-K^N t}\int_0^t dt_1\, e^{K^N t_1} I^N e^{-K^N t_1} F^N(0)$$
$$+ e^{-K^N t}\int_0^t dt_1\, e^{K^N t_1} I^N e^{-K^N t_1}\int_0^{t_1} dt_2\, e^{K^N t_2} I^N e^{-K^N t_2} F^N(0)$$
$$+ \cdots$$

The reduced s-particle distribution functions

$$(2.7) \qquad F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; t) = \int\cdots\int \frac{d\underline{x}_{s+1}}{V} d\underline{v}_{s+1} \cdots \frac{d\underline{x}_N}{V} d\underline{v}_N\, F^N$$

are also introduced. In (2.7) the position and velocity integrals are to be always understood to extend over the full range of the integration variables. These functions give the probability density for the dynamic states of the s particles considered being located, respectively, in the infinitesimal phase volume elements $d\underline{x}_1 d\underline{v}_1 \ldots d\underline{x}_s d\underline{v}_s$ around the points $\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s$ at the time t. Using the definition (2.7) and the perturbation series (2.6), together with (2.4) we have

(2.8) ..(continued)

$$(2.8)\quad F^s = \int \frac{d\underline{x}_{s+1}}{V} d\underline{v}_{s+1} \cdots \frac{d\underline{x}_N}{V} d\underline{v}_N$$

$$\Big\{ e^{-K^N t} F^N(0) + e^{-K^N t} \int_0^t dt_1\, e^{K^N t_1} \sum_{i<j} I_{ij}\, e^{-K^N t_1} F^N(0)$$

$$+ e^{-K^N t} \int_0^t dt_1\, e^{K^N t_1} \sum_{i<j} I_{ij}\, e^{-K^N t_1} \int_0^{t_1} dt_2\, e^{K^N t_2} \sum_{l<k} I_{lk}\, e^{-K^N t_2} F^N(0)$$

$$+ \cdots \Big\}$$

At this point it is convenient to introduce a simplifying relation. Liouville's equation (2.2) assumes the system to be insensitive to its boundaries and thus to the shifting of its boundaries. Under this condition we have

$$(2.9)\quad \int_V d\underline{x}_i\, e^{-K_i t} G(\underline{x}_i) = \int_V d\underline{x}_i\, G(\underline{x}_i) \qquad \textit{for any well behaved } G(\underline{x}_i)$$

$$(2.10)\quad \int_V d\underline{x}_j\, e^{-K_{ij} t} G(\underline{x}_i - \underline{x}_j) = \int_V d(\underline{x}_i - \underline{x}_j)\, G(\underline{x}_i - \underline{x}_j)$$

because

$$(2.11)\quad K_i = \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i} \quad , \quad K_{ij} = K_i + K_j$$

in the exponentials produce a Taylor expansion

$$(2.12)\quad e^{-K_i t} G(\underline{x}_i) = G(\underline{x}_i - \underline{v}_i t)$$

and the integrals simplify by shifting the boundaries of the system.

Note that

$$(2.13)\quad e^{K_N t} I_{ij}\, e^{-K_N t} = e^{K_{ij} t} I_{ij}\, e^{-K_{ij} t}$$

and that using (2.9) the perturbation series (2.8) may be written

(2.14) ...(continued)

$$(2.14)\quad F^s = \int \frac{d\underline{x}_{s+1}}{V} d\underline{v}_{s+1} \cdots \frac{d\underline{x}_N}{V} d\underline{v}_N$$
$$\Big\{ e^{-K^s t} F^N(0) + e^{-K^s t}\int_0^t dt_1 \sum_{i<j} e^{K_{ij}t_1} I_{ij}\, e^{-K_{ij}t_1} F^N(0)$$
$$+ e^{-K^s t}\int_0^t dt_1 \sum_{i<j} e^{K_{ij}t_1} I_{ij}\, e^{-K_{ij}t_1} \int_0^{t_1} dt_2 \sum_{\ell<k} e^{K_{\ell k}t_2} I_{\ell k}\, e^{-K_{\ell k}t_2} F^N(0)$$
$$+ \cdots \Big\}$$

where

$$(2.15)\qquad K^s = \sum_{i=1}^{s} \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i}$$

We will write the terms of the expansion (2.14) in a form convenient for the diagram technique to be introduced in the following section. This point will be illustrated by an example. Consider the contribution to F^2

$$(2.16)\quad \int \frac{d\underline{x}_3}{V} d\underline{v}_3 \cdots \frac{d\underline{x}_N}{V} d\underline{v}_N$$
$$e^{-K^2 t}\int_0^t dt_1\, e^{K_{12}t_1} I_{12}\, e^{-K_{12}t_1} \int_0^{t_1} dt_2\, e^{K_{18}t_2} I_{18}\, e^{-K_{18}t_2} \times$$
$$\int_0^{t_2} dt_3\, e^{K_{69}t_3} I_{69}\, e^{-K_{69}t_3} F^N(0)$$

The spatial integrations are commuted from left to right as far as possible and used to perform any reduction on the $F^N(0)$ thus our example (2.16) will be written

$$(2.17)\quad e^{-K^2 t}\int_0^t dt_1\, e^{K_{12}t_1} I_{12}\, e^{-K_{12}t_1} \int_0^{t_1} dt_2 \int \frac{d\underline{x}_8}{V} d\underline{v}_8\, e^{K_{18}t_2} I_{18}\, e^{-K_{18}t_2}$$
$$\int_0^{t_2} dt_3 \int \frac{d\underline{x}_6}{V} d\underline{v}_6 \int \frac{d\underline{x}_9}{V} d\underline{v}_9\, e^{K_{69}t_3} I_{69}\, e^{-K_{69}t_3}$$
$$F^5(\underline{x}_1, \underline{v}_1, \underline{x}_2, \underline{v}_2, \underline{x}_6, \underline{v}_6, \underline{x}_8, \underline{v}_8, \underline{x}_9, \underline{v}_9; 0)$$

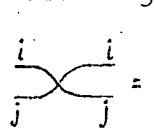
III. THE DIAGRAM TECHNIQUE.

As an aid in working with the series (2.14) the diagram technique of Prigogine and coworkers[2] will be used with some modification. First we write the terms of (2.14) in the form similar to (2.17). We see that each term starts with $e^{-K^s t}$ and we will write this first $e^{-K^s t}$ explicitly. For the s sets of particle coordinates of F^s we draw and label s lines running from left to right. For example F^2 is a function of the coordinates of two particles and, therefore, the diagram for each term contributing to F^2 starts on the left with

$$(3.1) \qquad e^{-K^2 t \frac{1}{2}}$$

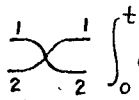
We find that the mathematical behavior of a general term can be broken down into three distinctive building blocks. Each of these contains an expression of the form $\int_0^{t_{m-1}} dt_m e^{K_{ij} t_m} I_{ij} e^{-K_{ij} t_m}$ which is made to correspond to a vertex. The three types of vertices corresponding to the three distinctive building blocks will be defined as follows:

(a). if to the left of the expression $\int_0^{t_{m-1}} dt_m e^{K_{ij} t_m} I_{ij} e^{-K_{ij} t_m}$ the labels i and j have already been used, lines labeled i and j are available and we cross them defining a vertex

(3.2) 

$$= \int_0^{t_{m-1}} dt_m e^{K_{ij} t_m} I_{ij} e^{-K_{ij} t_m}$$

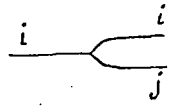
As an example, for the term (2.17), using the starting procedure (3.1), we draw

(3.3) $e^{-K^2 t}$  $\int_0^{t_1} dt_2 \int \frac{d\underline{\alpha}_8}{V} d\underline{\nu}_8 \, e^{K_{18} t_2} I_{18} e^{-K_{18} t_2}$

$$\int_0^{t_2} dt_3 \int \frac{d\underline{\alpha}_6}{V} d\underline{\nu}_6 \int \frac{d\underline{\alpha}_9}{V} d\underline{\nu}_9 \, e^{K_{69} t_3} I_{69} e^{-K_{69} t_3}$$

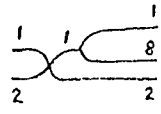
$$F^5_{12689}(0)$$

(b). if to the left of the expression $\int_0^{t_{m-1}} dt_m \, e^{K_{ij} t_m} I_{ij} \, e^{-K_{ij} t_m}$ only one of the labels i or j (say i) has appeared, we draw a branch on the available line (i) and define the vertex to include the integration over the new label

(3.4)  $= A \int \frac{d\underline{\alpha}_j}{V} d\underline{\nu}_j \int_0^{t_{m-1}} dt_m \, e^{K_{ij} t_m} I_{ij} \, e^{-K_{ij} t_m}$

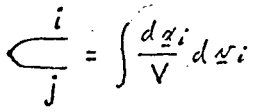
The symbol A will be explained shortly.

For example the second building block of (2.17) is of this type and we draw

(3.5) $e^{-K^2 t}$  $\int_0^{t_2} dt_3 \int \frac{d\underline{\alpha}_6}{V} d\underline{\nu}_6 \int \frac{d\underline{\alpha}_9}{V} d\underline{\nu}_9 \, e^{K_{69} t_3} I_{69} e^{-K_{69} t_3}$

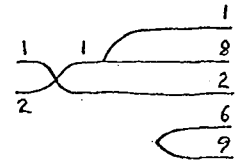
$$F^5_{12689}(0)$$

(c). if to the left of the expression $\int_0^{t_{m-1}} dt_m\, e^{K_{ij}t_m} I_{ij}\, e^{-K_{ij}t_m}$ neither i nor j has appeared, we introduce two new lines running to the right through a vertex defined by

(3.6) 

$$= \int \frac{d\underline{\alpha}_i}{V} d\underline{v}_i \int \frac{d\underline{\alpha}_j}{V} d\underline{v}_j \int_0^{t_{m-1}} dt_m\, e^{K_{ij}t_m} I_{ij}\, e^{-K_{ij}t_m}$$

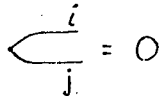
The example (2.17) can be represented now by

(3.7) $e^{-K^2 t}$ 

$F^{5}_{12689}(0)$

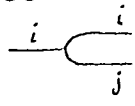
It is noted that time labels are not needed if the vertices are ordered from left to right to indicate the respective limits of the time integrations $t \geq t_1 \geq t_2 \geq t_3 \cdots \geq 0$

The expansion in terms of diagrams simplifies greatly because diagrams containing a type (c) vertex integrate to zero or one writes

(3.8) 

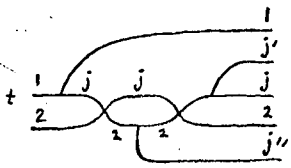
$= 0$

We have relegated this calculation to our Appendix I. Also in Appendix I we find that for a diagram with a (b) type vertex, where a particle label j first appears, the $\frac{\partial U_{ij}}{\partial \underline{\alpha}_i} \cdot \frac{\partial}{\partial \underline{v}_j}$ part of the I_{ij} in the vertex also integrates to zero, or one writes

(3.9) 

$$= A \int \frac{d\underline{\alpha}_j}{V} d\underline{v}_j \int_0^{t_{m-1}} dt_m \frac{1}{m} e^{K_{ij}t_m} \frac{\partial U_{ij}}{\partial \underline{\alpha}_i} \cdot \frac{\partial}{\partial \underline{v}_i} e^{-K_{ij}t_m}$$

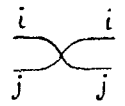
We will now explain the symbol A. Working from an example, let us consider all the contributions to F^2 that have the form

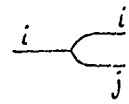
(3.10) $e^{-K^2 t}$  $F^5_{12jj'j''}(0)$

There are (N-2)(N-3)(N-4) diagrams of this form corresponding to the different ways of choosing the dummy labels j, j', j'' and we see that these diagrams are indistinguishable. In general, this type of redundance occurs wherever (b) type vertices appear. And, one sees that diagrams that differ only in their dummy particle labels can be summed by writing in the (b) type vertices

(3.11) A=N-r r= number of lines to the left of the vertex (b).

This concludes the definitions of our basic vertices which we summarize here,

(3.12) (a)  $= \int_0^{t_{m-1}} dt_m\, e^{K_{ij} t_m} I_{ij}\, e^{-K_{ij} t_m}$

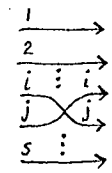
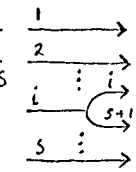
(3.13) (b)  $= \frac{N-r}{V} \int d\underline{x}_j\, d\underline{v}_j \int_0^{t_{m-1}} dt_m\, e^{K_{ij} t_m} I_{ij}\, e^{-K_{ij} t_m}$

$$= \frac{N-r}{V} \frac{1}{m} \int d\underline{x}_j\, d\underline{v}_j \int_0^{t_{m-1}} dt_m\, e^{K_{ij} t_m} \frac{\partial U_{ij}}{\partial \underline{x}_i} \cdot \frac{\partial}{\partial \underline{v}_i}\, e^{-K_{ij} t_m}$$

where r is the number of lines at the left of the vertex (b).

The BBKGY Hierarchy of Equations.

The aim of this work is to discuss the theories of Bogoliubov[1], Sandri & Frieman[4,5], and Mazur & Biel.[6] These authors use or derive the BBKGY chain of equations as a first step. It seems appropriate to derive this chain of equations at this point. It also supplies us a good example of a calculation using diagrams and diagram language. For a given F^s we separate out the first vertex only of the contributing diagrams. This gives, being careful to retain the leftmost $e^{-K^s t}$ for each term of the perturbation series (2.14),

(3.14) $F^s = e^{-K^s t} F^s(0) + e^{-K^s t} \sum_{i<j\leq s}$  $+ e^{-K^s t} \sum_{i \leq s}$ 

Here, the points indicate the lines make all possible vertex connections to the right including possible initial values. We recognize that in the second term, except for the operator $e^{-K^s t_1}$, all possible connections defines $F^s(t_1)$ and in the third term, except for the operator $e^{-K^{s+1} t_1}$ they define $F^{s+1}(t_1)$. Therefore, if the first vertex is written in detail one has

(3.15) ...(continued)

$$(3.15)\quad F^s = e^{-K^s t} F^s(0) + e^{-K^s t} \sum_{i<j\le s} \int_0^t dt_1\, e^{K_{ij} t_1} I_{ij}\, e^{-K_{ij} t_1} \left[e^{K^s t_1} F^s(t_1) \right]$$
$$+ e^{-K^s t} \sum_{i \le s} \frac{N-s}{V} \int d\underline{x}_{s+1}\, d\underline{v}_{s+1} \int_0^t dt_1\, e^{K_{i,s+1} t_1} I_{i,s+1}\, e^{-K_{i,s+1} t_1}$$
$$\left[e^{K^{s+1} t_1} F^{s+1}(t_1) \right]$$

By writing $e^{K_{ij} t_1} I_{ij}\, e^{-K_{ij} t_1} = e^{K^s t_1} I_{ij}\, e^{-K^s t_1}$ and $e^{K_{i,s+1} t_1} I_{i,s+1}\, e^{-K_{i,s+1} t_1} = e^{K^{s+1} t_1} I_{i,s+1}\, e^{-K^{s+1} t_1}$ and using the relation (2.9) we obtain

$$(3.16)\quad F^s = e^{-K^s t} F^s(0) + e^{-K^s t} \int_0^t dt_1\, e^{K^s t_1} \Big\{ \sum_{i<j\le s} I_{ij} F^s(t_1)$$
$$+ \sum_{i \le s} \frac{N-s}{V} \int d\underline{x}_{s+1}\, d\underline{v}_{s+1}\, I_{i,s+1} F^{s+1}(t_1) \Big\}$$

This is an integral form of the BBKGY chain

$$(3.17)\quad \frac{\partial F^s}{\partial t} + K^s F^s = \sum_{i<j\le s} I_{ij} F^s + \frac{N-s}{V} \sum_{i \le s} \int d\underline{x}_{s+1}\, d\underline{v}_{s+1}\, I_{i,s+1} F^{s+1}$$

Often a shorter notation will be used in following chapters

$$(3.18)\quad \frac{\partial F^s}{\partial t} + H^s F^{s+1} = L^s F^{s+1} \qquad H^s = K^s - I^s$$

where

$$(3.19)\quad I^s = \sum_{i<j\le s} I_{ij}$$

$$(3.20)\quad L^s = \sum_{i \le s} L_{i,s+1} \qquad L_{i,s+1} = \frac{N-s}{V} \frac{1}{m} \int d\underline{x}_{s+1}\, d\underline{v}_{s+1} \frac{\partial U_{i,s+1}}{\partial \underline{x}_i} \cdot \frac{\partial}{\partial \underline{v}_i}$$

Return now to the general perturbation expansion. We find that one key to making the expansion useful is to introduce the cluster expansion[11]

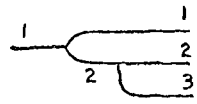
$$(3.21)\quad F^1 = F^1(\underline{x}_1, \underline{v}_1)$$

$$(3.22)\quad F^2 = F_1^1(\underline{x}_1, \underline{v}_1) F_2^1(\underline{x}_2, \underline{v}_2) + G_{12}^2(\underline{x}_1, \underline{v}_1, \underline{x}_2, \underline{v}_2)$$

$$(3.23)\quad F^3 = F_1^1(\underline{x}_1,\underline{v}_1)F_2^1(\underline{x}_2,\underline{v}_2)F_3^1(\underline{x}_3,\underline{v}_3) + F_1^1(\underline{x}_1,\underline{v}_1)G_{23}^2(\underline{x}_2,\underline{v}_2,\underline{x}_3,\underline{v}_3)$$
$$+ F_2^1(\underline{x}_2,\underline{v}_2)G_{13}^2(\underline{x}_1,\underline{v}_1,\underline{x}_3,\underline{v}_3) + F_3^1(\underline{x}_3,\underline{v}_3)G_{12}^2(\underline{x}_1,\underline{v}_1,\underline{x}_2,\underline{v}_2)$$
$$+ G_{123}^3(\underline{x}_1,\underline{v}_1,\underline{x}_2,\underline{v}_2,\underline{x}_3,\underline{v}_3)$$

$$F^4 = \cdots$$

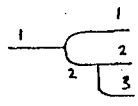
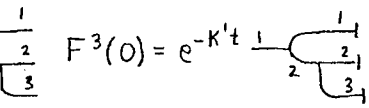
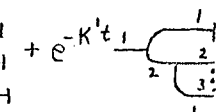
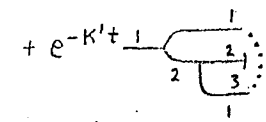
The G^s are interpreted as depending on interparticle distances and are called correlations. The cluster expansion is used here to expand the various $F^r(0)$ that appear of the right of each term in the general expansion of $F^s(t)$. Consider for example the contribution to F^1

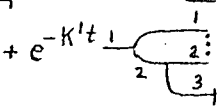
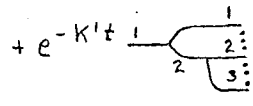
(3.24) $e^{-K't}$  $F^3(0)$

A cluster expansion of $F^3(0)$ is made and the initial correlations are represented by dotted lines at the right of the diagrams. Defining

(3.25) $F^1(0) =$ 

for the initial value of the one body function the example (3.24) may be written following the decomposition (3.23)

(3.26) $e^{-K't}$  $F^3(0) = e^{-K't}$  $+ e^{-K't}$  $+ e^{-K't}$ 

$+ e^{-K't}$  $+ e^{-K't}$ 

Our method of representing the general perturbation series in terms of diagrams is now complete.

In all the following sections of this work the so-called thermodynamic limit will be taken

(3.27) $N \to \infty, V \to \infty$ such that $\frac{N}{V} = n$ remains constant.

This has the effect that in each (b) type vertex

(3.28) $\frac{A}{V} = \frac{N-r}{V} \longrightarrow n$

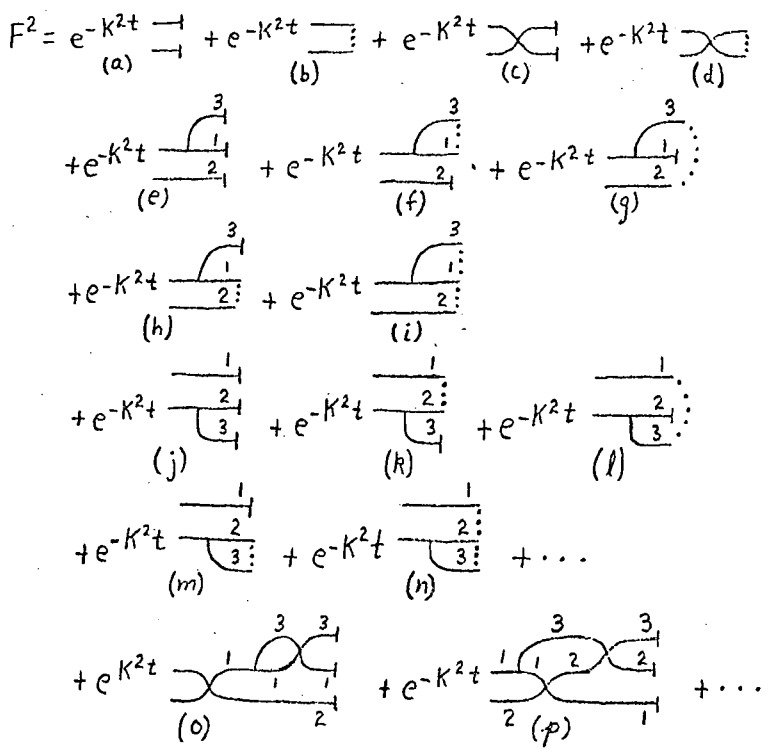
The thermodynamic limit should not affect the bulk properties of the system which allows us to assume convergence under this limit.

IV. THE DEPENDENCE OF THE DISTRIBUTION FUNCTIONS UPON THE ONE BODY FUNCTION.

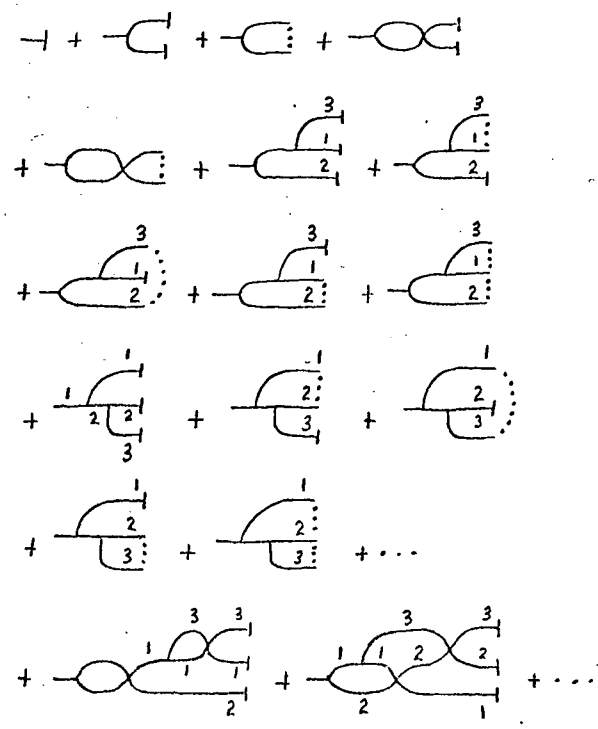
In the successful theories of irreversible statistical mechanics the dependence of the distribution functions $F^1, F^2, F^3, \ldots$ upon the one body distribution function F^1 has played a dominant role. In this chapter we work out the dependence of the distribution functions F^s upon F^1 in detail. The only departure from a general theory will be that the thermodynamic limit (3.27) will be assumed valid and taken. We find the dependence on F^1 by performing a particular sum of diagrams and in the later part of this chapter we point out that this summation is necessary to determine the long time behavior of a physical system. That is, the long time behavior of a physical system is determined through the one body function.

Consider the expansion of the two body function

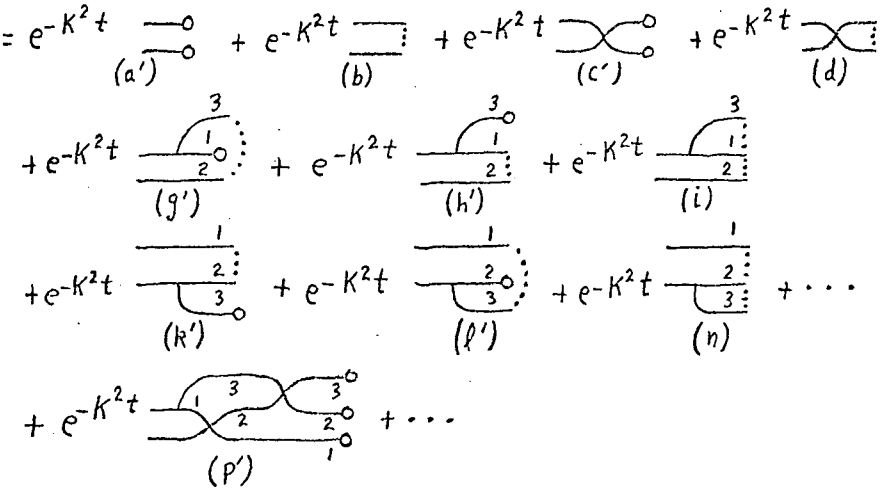
(4.1)



For convenience we define a diagram —o for the one body function

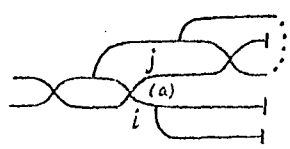
(4.2) $e^{K't}F' =$ 

It will be proved presently that the two body function may be written

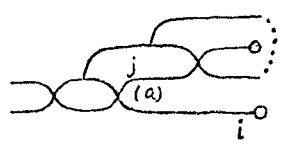
(4.3) $F^2 = e^{-K^2t}$ 

where it is understood that if a —o connects to a vertex it is a function of time through the integrated time variable of that vertex. In (4.1) the terms (a,e,f,j,m,...) have gone to contribute to the term (a') above and the term (o) has gone to contribute to (c') above. In the next paragraph we give a systematic procedure for writing out the expansion (4.3), and for the similar expansions of higher order distribution functions.

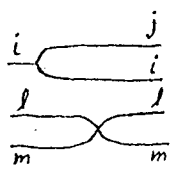
The systematic procedure is as follows. The diagrams are drawn as before replacing —| by —o where the series expansion for —o is taken into account by omitting diagrams with fragments that connect in by only one line. For example the pattern

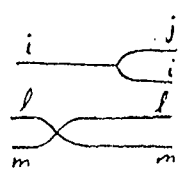
(4.4) $e^{-K^2 t}$ 

is not kept because we find it contributes to

(4.5) $e^{-K^2 t}$ 

This method of expansion can be proved valid by use of the "factorization" theorem. For a general proof see Resibois.[12] The factorization theorem deals with diagrams that are identical except for the left to right or "time" ordering of their vertices. The set of all such diagrams is called a permutation class. For example

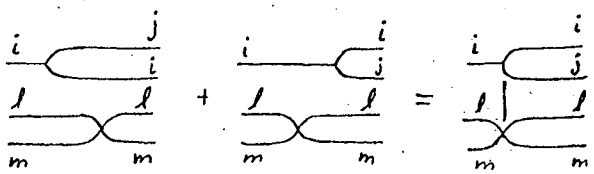
(4.6) 

and 

is a permutation class. The factorization theorem reads:

(4.7) The sum of a complete permutation class is equal to the product of the contributions represented by the component structures.

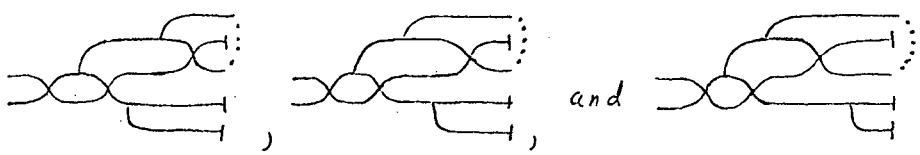
For our example (4.6) we write

(4.8) 

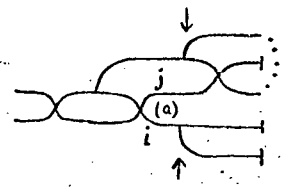
where the vertical bar indicates the vertices have the same limits on their time integrations. In detail (4.8) is written

$$
\begin{aligned}
(4.9)\quad & n\int d\underline{x}_j\, d\underline{v}_j \int_0^t dt_1\, e^{K_{ij}t_1} I_{ij}\, e^{-K_{ij}t_1} \int_0^{t_1} dt_2\, e^{K_{lm}t_2}\, I_{lm}\, e^{-K_{lm}t_2} \\
& + \int_0^t dt_1\, e^{K_{lm}t_1} I_{lm}\, e^{-K_{lm}t_1}\, n\int d\underline{x}_j\, d\underline{v}_j \int_0^{t_1} dt_2\, e^{K_{ij}t_2} I_{ij}\, e^{-K_{ij}t_2} \\
& = \int_0^t dt_1\, e^{K_{lm}t_1} I_{lm}\, e^{-K_{lm}t_1}\, n\int d\underline{x}_j\, d\underline{v}_j \int_0^t dt_1'\, e^{K_{ij}t_1'} I_{ij}\, e^{-K_{ij}t_1'}
\end{aligned}
$$

and since operators with labels i and j commute with those with labels l and m, the component structures factor. To get (4.3) from (4.1) we consider all diagrams of (4.1) that have fragments that connect in by one line, for example (4.4). We take the permutation class formed by these fragments with the other structures in the diagram, for the example (4.4) we consider

(4.10) 

When we sum over the permutation classes the fragments factor, for the example (4.10) the sum of the diagrams give

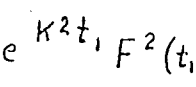
(4.11) 

where the arrows indicate the vertices are functions of the same time variable. The infinity of diagrams identical to (4.4) except for different fragments that connect to the vertex (a) on the branch i gives, by summing over the permutation classes, all possible ways of drawing at (a) diagrams that begin with one line. The sum of these defines —o and the expansion scheme outlined above is justified.

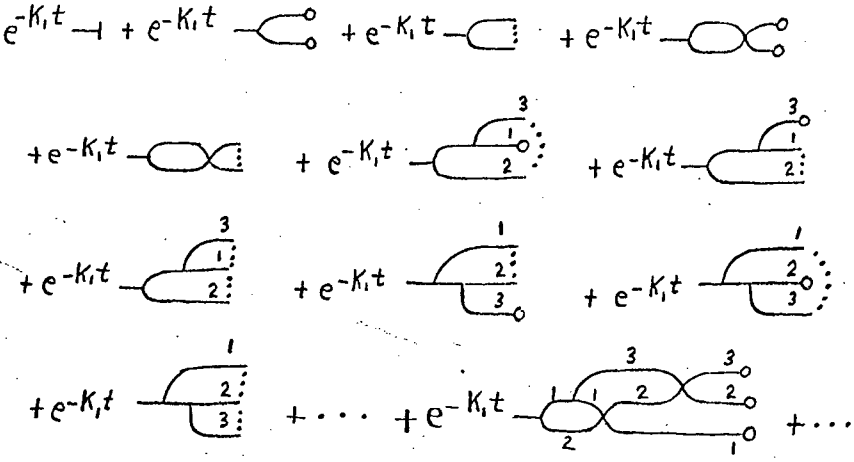
With an alteration we can use this expansion scheme to obtain, except for initial correlations, a closed equation for the one body distribution function. It is instructive to recall the coupling of the one body function to the two body function through the BBKGY chain (3.18)

$$(4.12) \qquad \frac{\partial F^1}{\partial t} + K^1 F^1 = L^1 F^2$$

Using (3.14 or 3.15) we find that the solution to (4.12) can be written as follows

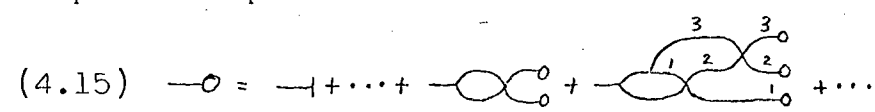
(4.13) $F^1 = e^{-K^1 t}$ —| $+ e^{-K^1 t}$  $e^{K^2 t_1} F^2(t_1)$

Except for initial correlations a closed equation for F^1 is obtained by substituting the expansion (4.3) for F^2 into (4.13), one has

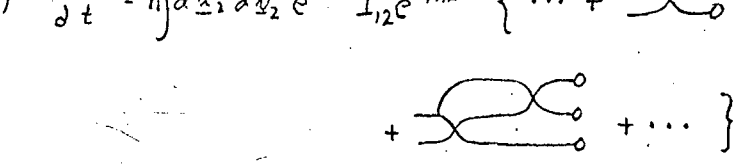
(4.14) $F' = e^{-K_1 t}$ 

It is recognized that the expansion here in terms of the one body function follows the same scheme as for the many particle functions except we allow the leftmost (b) type vertex, the one in equation (4.13) to be retained. An expression equivalent to (4.14) has formerly been obtained by Severne.[3] His approach to the problem is very similar to ours. A slight difference is found in his summation of terms to obtain the dependence of the distribution function upon the one body function. The answers differ only in the term with initial correlations. Where we have a diagram that terminates on the right with some product of initial correlation with one or more —o, Severne has an infinite series of terms where the —o's are expanded as in (4.2).

In the foregoing paragraph we rid ourselves of diagrams with fragments that connect in by one line, by summing them into the various —O. Through some approximations we will "indicate" that this summation of diagrams is necessary to determine the long time behavior of the system. We will neglect terms with initial correlations, assume the system forgets its past history and we will take the asymptotic behavior. From (4.14), by neglecting initial correlations, we have a closed equation for —O; and here we consider a couple of representative terms

(4.15) 

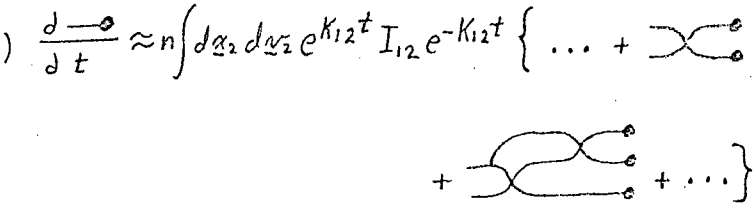
By taking the time derivative, one finds

(4.16) $\frac{\partial}{\partial t}$ 
$= n\int d\underline{x}_2\, d\underline{v}_2\, e^{K_{12}t} I_{12} e^{-K_{12}t} \{ \cdots +$
$+ \cdots \}$

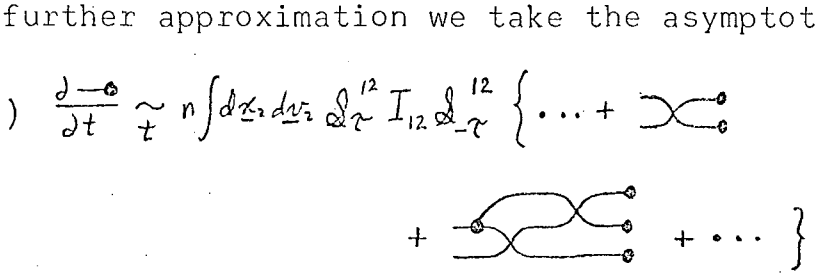
Equation (4.16) is said to be non-Markowian because the evolution of the one body distribution at time t depends on its values for all times $\tau < t$. For our purposes here we will assume the system "forgets its past history" by making a crude Markowian approximation

(4.17) $\cdots \!\!-\!\!\circ = e^{K_i t_m} F_i'(t_m) \Rightarrow e^{K_i t} F_i'(t) = \cdots \!\!-\!\!\circ$

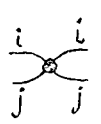
so that (4.16) is approximated by

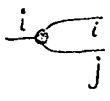
(4.18) $\frac{\partial}{\partial t}$ 
$\approx n\int d\underline{x}_2\, d\underline{v}_2\, e^{K_{12}t} I_{12} e^{-K_{12}t} \{ \cdots +$
$+ \cdots \}$

As a further approximation we take the asymptotic behavior

(4.19) $\frac{\partial}{\partial t}$ 
$\underset{t}{\sim} n\int d\underline{x}_2\, d\underline{v}_2\, \mathcal{D}_{\tau}^{12} I_{12} \mathcal{D}_{-\tau}^{12} \{ \cdots +$
$+ \cdots \}$

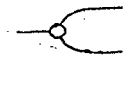
where

(4.20) 
$= \int_0^\infty dt_m\, e^{K_{ij}t_m} I_{ij}\, e^{-K_{ij}t_m}$

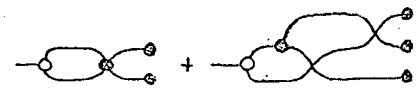
(4.21) 
$= n\int_0^\infty dt_m \int d\underline{x}_j\, d\underline{v}_j\, e^{K_{ij}t_m} I_{ij}\, e^{-K_{ij}t_m}$

(4.22) $$\mathcal{D}_{\tau}^{ij} = \lim_{\tau \to \infty} e^{K_{ij}\tau}$$

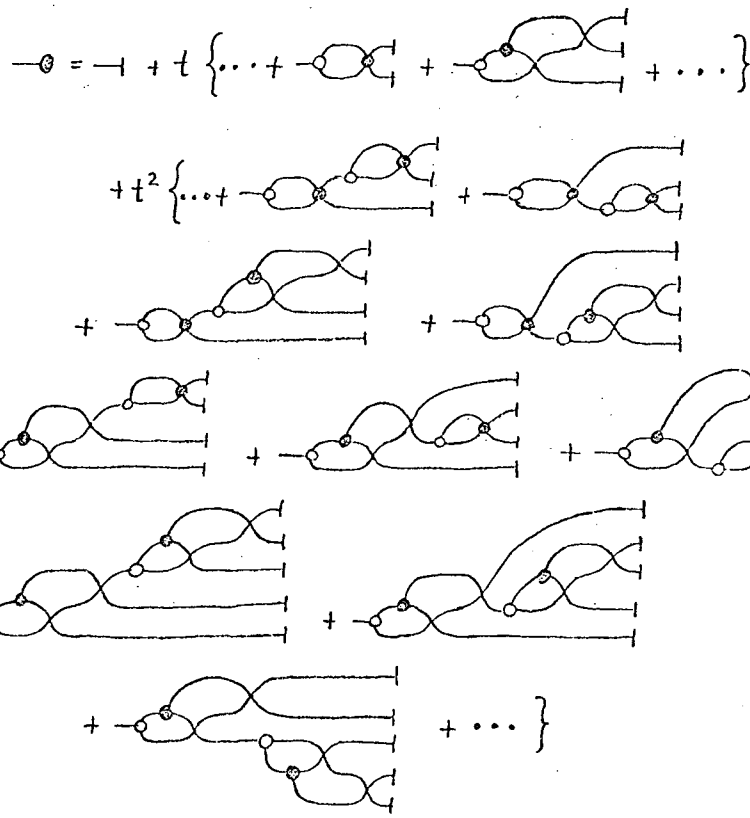
For convenience we also define

(4.23)  $$= n \int d\underline{x}_j \, d\underline{v}_j \; \mathcal{D}_{\tau}^{ij} \, I_{ij} \, \mathcal{D}_{-\tau}^{ij}$$

so that we can write (4.19) as follows

(4.24) $\frac{\partial}{\partial t}$ 

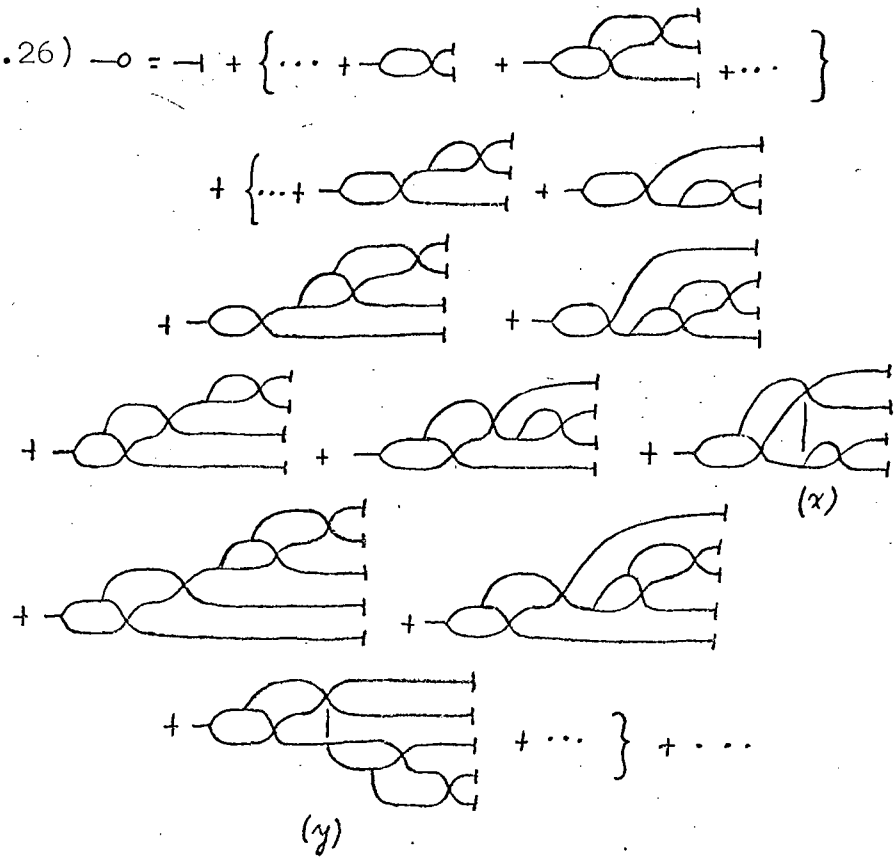
Finally we take the Taylor expansion of

(4.25) 

$$+ t^3 \{ \cdots \} + \cdots$$

(4.25) has replaced the expansion of (4.15) which is by iteration

(4.26)



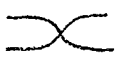
where in the terms (x) and (y) the vertical line indicates a complete permutation class. By comparing (4.25) with (4.26) it is found that each fragment of (4.26) that connects in by one line gives a time divergence or order t. (We should recall that terms with initial correlations have been neglected and the same may not be true for those terms.)

In order to discuss the long time behavior we must sum over the divergences that we observed in the former paragraph. And we see that this is done by separating out

and summing, where it appears, the infinite series $\longrightarrow\!\!\circ = e^{-K't}F'$ This illustrates, that the long time behavior is determined by the one particle distribution function. It is not known now if an arbitrary selection, say (4.15), of terms converges in time. This has only been verified for special cases through an H type theorem.

We will discuss the Markowian approximation in more detail later.

This brings us to our next topic which is an order of magnitude calculation. We roughly approximate the strength and range of the interparticle potential. Each vertex contains the interparticle potential and thus gives a measure ε of the strength of the potential. Each (b) type vertex contains an integration over the interparticle potential, which is limited by range of the range of the potential, and also since the density n is a factor each (b) type vertex gives a measure λ of the number of particles within the interaction sphere. For the vertices we have the orders of magnitude

(4.27)  $\sim O(\varepsilon)$  $\sim O(\varepsilon\lambda)$

For the remainder of this thesis we will be working with the expansion in small λ which we call the short-range theory.

V. THE SHORT-RANGE EXPANSION

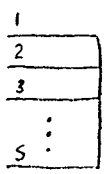
In this chapter we specialize to consider those systems for which only small clusters of particles interact simultaneously. Such a situation occurs for dilute systems or for systems in which the particles interact through short-range forces. From the order of magnitude calculation (4.27) we will be working with the expansion in small λ

$$\lambda \ll 1 \qquad \varepsilon \approx 1 \tag{5.1}$$

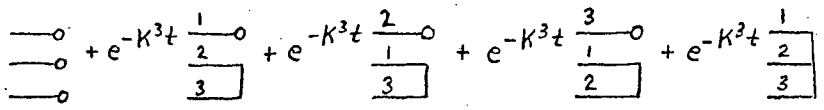
The task of this chapter is to select diagrams for the expansion in small λ, and to obtain reasonably compact answers we will sum the various infinite series that appear. We demonstrate the caluclations for the expansion of F^2; and we carry out the calculations to include all two and three particle collision, or correlation, effects.

The Hierarchy of Equations for the Cluster Expansion

We find that a valuable guide for selecting and summing diagrams is the hierarchy of equations, similar to the BBKGY hierarchy, that couple the cluster coefficients (3.21 to 3.23). Our purpose in this paragraph is to derive this hierarchy of equations. We will identify by diagrams the various cluster coefficients G^s

(5.2) $G^s = e^{-K^s t}$ 

where the vertical bar indicates the sum of all diagrams that have the s lines connected in some way. We see that this is a possible way to write the G^s, for example for F^3 we write

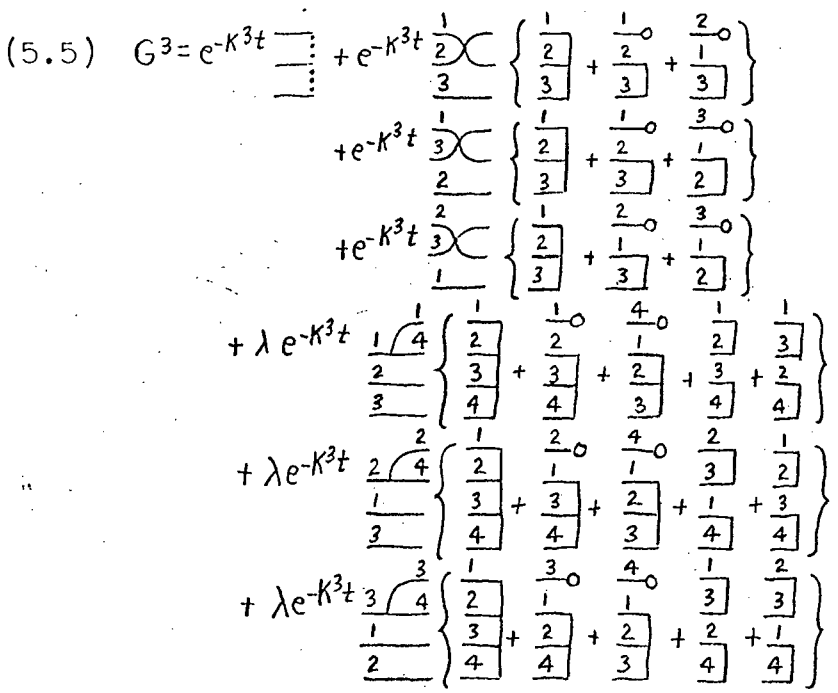
(5.3) $F^3 = e^{-K^3 t}$  $+ e^{-K^3 t}$ $+ e^{-K^3 t}$ $+ e^{-K^3 t}$ $+ e^{-K^3 t}$

The factorization theorem (4.7) has been used extensively here. Further, (5.2) is the only selection of diagrams for G^s because the system of equations (3.21 to 3.23) yields a unique solution for the G^s in terms of the F^s. A word of caution here; the expression (3.11) will not allow the identification (5.2) unless the thermodynamic limit (3.27) has been taken. It is convenient here to point out an important property of the G^s. We term as factorable any function J^s of s particle coordinates that can be written in a form

$$(5.4)\quad J^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s) = J_1^r(\underline{x}_i, \underline{v}_i, \underline{x}_j, \underline{v}_j, \ldots)\, J_2^{s-r}(\underline{x}_{i'}, \underline{v}_{i'}, \underline{x}_{j'}, \underline{v}_{j'}, \ldots)$$
$$\{i, j, \ldots\} \neq \{i', j', \ldots\}$$

We find that the diagrams that contribute to G^s are <u>not</u> in general factorable in this form; since the s starting lines, being connected in some way, always have an overlap of the interparticle potentials and initial correlations. We proceed to derive the hierarchy of equations for the G^s; we do this by example for the case of G^3. We separate out in the expansion for G^3 the first vertex only of the contributing diagrams to obtain

(5.5)



Where a product of diagrams means the diagrams formed by connecting the lines as indicated by their labels. After slight rearrangement we substitute in (5.5) the definitions of the diagrams to obtain

$$
\begin{aligned}
(5.6)\quad G^3_{123} = {} & e^{-K^3 t} G^3(0) + e^{-K^3 t}\int_0^t dt_1\, e^{K^3 t_1}\, I^3 G^3(t_1) \\
& + e^{-K^3 t}\int_0^t dt_1\, e^{K^3 t_1} \Big\{ I_{12}\left[F_1^1(t_1)\, G^2_{23}(t_1) + F_2^1(t_1)\, G^2_{13}(t_1)\right] \\
& \qquad + I_{13}\left[F_1^1(t_1)\, G^2_{23}(t_1) + F_3^1(t_1)\, G^2_{12}(t_1)\right] \\
& \qquad + I_{23}\left[F_2^1(t_1)\, G^2_{13}(t_1) + F_3^1(t_1)\, G^2_{12}(t_1)\right] \\
& + \lambda\, L_{14}\left[F_1^1(t_1)\, G^3_{234}(t_1) + F_4^1(t_1)\, G^3_{123}(t_1) + G^2_{12}(t_1)\, G^2_{34}(t_1) + G^2_{13}(t_1)\, G^2_{24}(t_1)\right] \\
& + \lambda\, L_{24}\left[F_2^1(t_1)\, G^3_{134}(t_1) + F_4^1(t_1)\, G^3_{123}(t_1) + G^2_{23}(t_1)\, G^2_{14}(t_1) + G^2_{12}(t_1)\, G_{34}(t_1)\right] \\
& + \lambda\, L_{34}\left[F_3^1(t_1)\, G^3_{124}(t_1) + F_4^1(t_1)\, G^3_{123}(t_1) + G^2_{13}(t_1)\, G^2_{24}(t_1) + G^2_{23}(t_1)\, G^2_{14}(t_1)\right] \\
& + \lambda\, L^3\, G^4(t_1) \Big\}
\end{aligned}
$$

Or by taking the time derivative one has

$$(5.7)\quad \frac{\partial G^3}{\partial t} + K^3 G^3 - I^3 G^3 = I_{12}\left[F_1^1 G_{23}^2 + F_2^1 G_{13}^2\right] + I_{13}\left[F_1^1 G_{23}^2 + F_3^1 G_{12}^2\right] + I_{23}\left[F_2^1 G_{13}^2 + F_3^1 G_{12}^2\right] + \lambda L_{14}\left[F_1^1 G_{234}^3 + F_4^1 G_{123}^3 + G_{12}^2 G_{34}^2 + G_{13}^2 G_{24}^2\right] + \lambda L_{24}\left[F_2^1 G_{134}^3 + F_4^1 G_{123}^3 + G_{23}^2 G_{14}^2 + G_{12}^2 G_{34}^2\right] + \lambda L_{34}\left[F_3^1 G_{124}^3 + F_4^1 G_{123}^3 + G_{13}^2 G_{24}^2 + G_{23}^2 G_{14}^2\right] + \lambda L^3 G^4$$

And this may be written in short hand as

$$(5.8)\quad \frac{\partial G^3}{\partial t} + K^3 G^3 - I^3 G^3 = \overline{I^3 F^3} + \lambda \overline{L^3 F^4}$$

where $\overline{I^3 F^3}$ is the produce of $I^3 = \sum_{i<j\leq 3} I_{ij}$ and the cluster expansion of F^3 from which we retain only the non-factorable, in the sense (5.4), terms excepting $I^3 G^3$ which is written separately on the left hand side of the equation. Similarly $\overline{L^3 F^4}$ is the product of $L^3 = \sum_{i\leq 3} L_{i4}$ and the cluster expansion of F^4 retaining only the non-factorable terms. Our derivation of (5.8) reveals the generalization

$$(5.9)\quad \frac{\partial G^s}{\partial t} + K^s G^s - I^s G^s = \overline{I^s F^s} + \lambda \overline{L^s F^{s+1}}$$

Though these equations are more complicated in the way they are written than the BBKGY hierarchy (3.18),

$$(5.10)\quad \frac{\partial F^s}{\partial t} + K^s F^s - I^s F^s = \lambda L^s F^{s+1}$$

the equations (5.9) are actually much simpler because we see that they may be obtained from the BBKGY hierarchy by cancelling the redundant factorable behavior. The equations (5.9) have formerly been obtained by Green.[11] For convenient reference we tabulate here the first three of these equations,

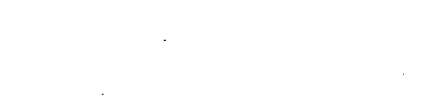
$$(5.11)\qquad \frac{\partial F^1}{\partial t} + K^1 F^1 = \lambda L_{12}\left(F_1^1 F_2^1 + G^2\right) = \lambda L_{12} F^2$$

$$(5.12)\qquad \frac{\partial G^2}{\partial t} + K^2 G^2 - I^2 G^2 = I^2 F_1^1 F_2^1 + \lambda L_{13}\left(F_1^1 G_{23}^2 + F_3^1 G_{12}^2\right) + \lambda L_{23}\left(F_2^1 G_{13}^2 + F_3^1 G_{12}^2\right) + \lambda L^2 G^3$$

$$(5.13)\qquad \frac{\partial G^3}{\partial t} + K^3 G^3 - I^3 G^3 = I_{12}\left[F_1^1 G_{23}^2 + F_2^1 G_{13}^2\right] + I_{13}\left[F_1^1 G_{23}^2 + F_3^1 G_{12}^2\right] + I_{23}\left[F_2^1 G_{13}^2 + F_3^1 G_{12}^2\right] + \lambda \overline{L_3} F^4$$

Let us begin our selection and summing of diagrams for the short-range theory. We will demonstrate the calculations for the expansion of F^2 to include all two and three particle collision, or correlation, effects. By cluster expansion of F^2 one has

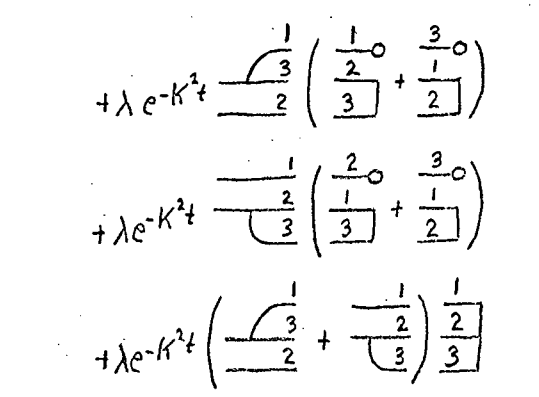
$$(5.14)\qquad F^2 = F_1^1 F_2^1 + G^2$$

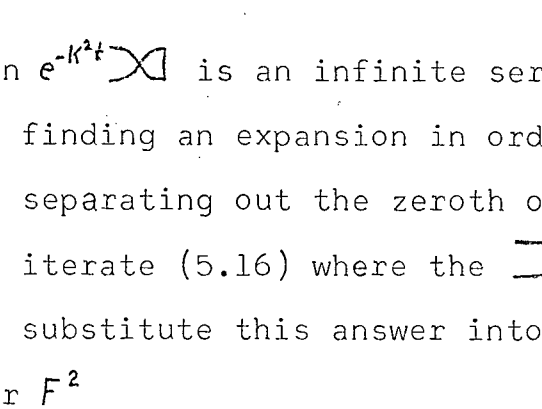
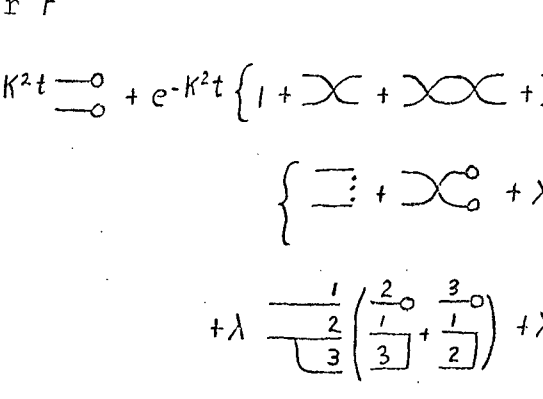


Our problem has reduced to expanding G^2; we have from (5.12) the solution

$$(5.15)\qquad G^2 = e^{-K^2 t} G^2(0) + e^{-K^2 t}\int_0^t dt_1\, e^{K^2 t_1}\Big\{\big[I^2 G^2(t_1) + I^2 F_1^1(t_1) F_2^1(t_1)\big]$$
$$+\lambda L_{13}\big[F_1^1(t_1)\, G_{23}^2(t_1) + F_3^1(t_1) G_{12}^2(t_1)\big]$$
$$+\lambda L_{23}\big[F_2^1(t_1)\, G_{13}^2(t_1) + F_3^1(t_1)\, G_{12}^2(t_1)\big]$$
$$+\lambda L^2 G^3(t_1)\Big\}$$

Or in terms of diagrams one has

(5.16) $e^{-K^2 t}$ 

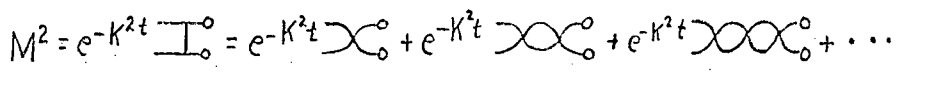
The expression $e^{-K^2 t}$  is an infinite series of terms; as a first step in finding an expansion in orders of λ we are interested in separating out the zeroth order contributions. To do this we iterate (5.16) where the  appears in zeroth order, and we substitute this answer into (5.14) to obtain an expression for F^2

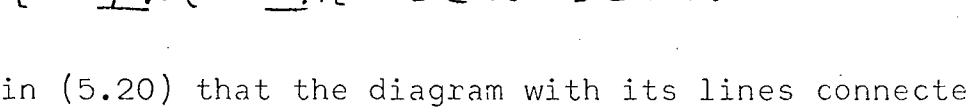
(5.17) $F^2 = e^{-K^2 t}$

We recognize that this expansion of F^2 follows the recipe of Chapter IV for expanding a general F^s in terms of the —o. In (5.17) one sees that the zeroth order terms give all the possible behavior where two particles feel the influence of each other only. To obtain the effect of a third particle upon these particles we will need to separate out all terms of first order in λ. To this end we define diagrams of the type

(5.18) $M^3 = e^{-K^3 t}$ 

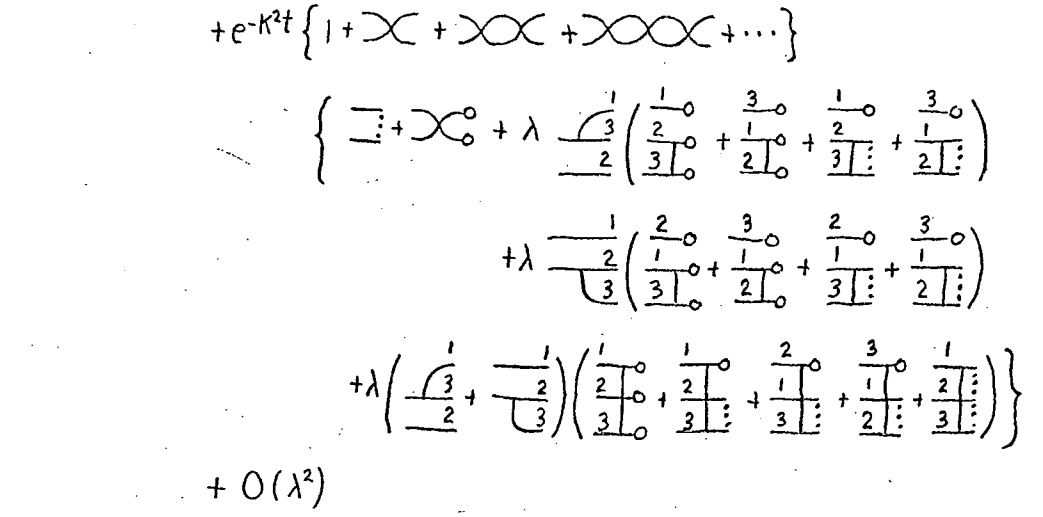
where the vertical line indicates a sum of all diagrams each having all the lines connected in some way and terminating on the right as indicated. This will always mean that there are no (b) type vertices in the contributing diagrams; for example we write

(5.19) $M^2 = e^{-K^2 t}$ 

(5.20) $e^{-K^2 t}$ 

Notice in (5.20) that the diagram with its lines connected by initial correlations alone is included in the sum. With these definitions we can write F^2 to first order in λ as follows

(5.21) $F^2 = e^{-K^2 t}$



$+ O(\lambda^2)$

Our task now is to sum the infinite series that appear in (5.21). The hierarchy of equations (5.9) makes this task an easy one. In particular we will use the equations (5.9) in the integral form

$$(5.22) \qquad G^s = e^{H^s t} G^s(0) + e^{-H^s t} \int_0^t dt_1 e^{H^s t_1} \left\{ \overline{I^s F^s}(t_1) + \lambda \overline{L^s F^{s+1}}(t_1) \right\} \quad ; \quad H^s = K^s - I^s$$

By substituting this equation for s=2,

$$(5.23) \quad G^2 = e^{-H^2 t} G^2(0) + e^{-H^2 t} \int_0^t dt_1 \, e^{H^2 t_1} I^2 F_1^1(t_1) F_2^1(t_1)$$
$$+ \lambda e^{-H^2 t} \int_0^t dt_1 e^{H^2 t_1} \Big\{ L_{13} \left[F_1^1(t_1) G_{23}^2(t_1) + F_3^1(t_1) G_{12}^2(t_1) \right]$$
$$+ L_{23} \left[F_2^1(t_1) G_{13}^2(t_1) + F_3^1(t_1) G_{12}^2(t_1) \right] + L^2 G^3(t_1) \Big] \Big\}$$

into (5.14); we sum the infinite series structure of the equation (5.17), or one has

$$(5.24)\quad F^2 = e^{-K^2 t}\,\overline{}\!\!\circ\!\!\circ + e^{-H^2 t}\,\overline{}\!\!\vdots + e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1}\, I^2\, F_1'(t_1)\, F_2'(t_1)$$

$$+\lambda e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1}\Big\{ L_{13} e^{-K^3 t_1}\Big(\overset{1}{\underset{\underset{3}{\square}}{\overset{2}{\circ}}} + \overset{3}{\underset{\underset{2}{\square}}{\overset{1}{\circ}}}\Big)_{t_1}$$

$$+ L_{23} e^{-K^3 t_1}\Big(\overset{2}{\underset{\underset{3}{\square}}{\overset{1}{\circ}}} + \overset{3}{\underset{\underset{2}{\square}}{\overset{1}{\circ}}}\Big)_{t_1}$$

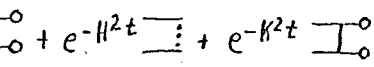
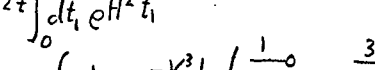
$$+ (L_{13} + L_{23})\, e^{-K^3 t_1}\, \overset{1}{\underset{\underset{3}{\square}}{\overset{2}{\square}}}\Big\}$$

where a subscript on a parenthesis means the included functions or operations yields a function of that variable. The expression (5.25) gives us the sum of the zeroth order terms, or by comparison with (5.17) one has with the definitions (5.19 and 5.20)

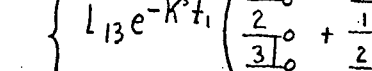
$$(5.25)\quad M^2 = e^{-K^2 t}\,\overline{}\!\!\circ\!\!\circ = e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1}\, I^2\, F_1'(t_1) F_2'(t_1)$$

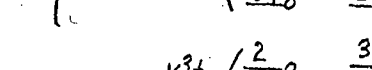
$$(5.26)\quad e^{-K^2 t}\,\overline{}\!\!\vdots = e^{-H^2 t}\,\overline{}\!\!\vdots$$

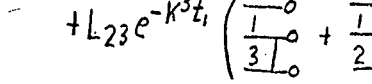
And, by retaining from (5.24) only the first order terms we have in place of (5.21) the expression

(5.27) $F^2 = e^{-K^2 t}$  $+ e^{-H^2 t}$  $+ e^{-K^2 t}$ 

$+ \lambda e^{-H^2 t} \int_0^t dt_1 \, e^{H^2 t_1}$

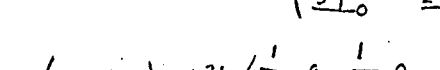
$\Big\{ L_{13} e^{-K^3 t_1} \Big($  $\Big)_{t_1}$

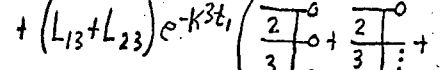
$+ L_{23} e^{-K^3 t_1} \Big($  $\Big)_{t_1}$

$+ (L_{13} + L_{23}) e^{-K^3 t_1} \Big($  $\Big)_{t_1} \Big\}$

$+ O(\lambda^2)$

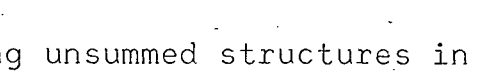
The remaining unsummed structures in (5.27) are the zeroth order contributions to G^3. To sum these we use the expression (5.22) for G^3 and retain only the zeroth order terms; and, after some further iteration with the expression (5.22) for G^2, we obtain the following sums of diagrams.

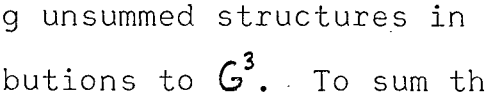
(5.28) $M^3 = e^{-K^3 t}$  $= e^{-H^3 t} \int_0^t dt_1 \, e^{H^3 t_1} \times$

$\Big\{ I_{12} e^{-K^3 t_1} \Big($  $\Big)_{t_1}$

$+ I_{13} e^{-K^3 t_1} \Big($  $\Big)_{t_1}$

$+ I_{23} e^{-K^3 t_1} \Big($  $\Big)_{t_1} \Big\}$

(5.29) $e^{-K^3 t}$  $= e^{-H^3 t} \int_0^t dt_1 \, e^{H^3 t_1} \times$

$(I_{12} + I_{13}) \, e^{-K^3 t_1} \Big($  $\Big)_{t_1}$, and cyclic

(5.30) $e^{-K^3 t}$  $= e^{-H^3 t}$ 

This concludes our discussion for the selection and summing of diagrams for the short-range theory. The meaning of our equations will become more clear in the following chapter.

VI. THE MARKOWIAN APPROXIMATION

To examine if the functions of the former chapters describe an approach to equilibrium we must consider their asymptotic behavior. Any asymptotic consideration is complicated because in Chapter IV we showed that the long time behavior was determined through the one body distribution function and this function is itself very complicated. In this chapter, we will discuss the complication due to the fact that the distribution functions, including the one body function, at a time t depends on the one body function through various times t_m, $t \geq t_m \geq 0$ of the past. In the literature this difficulty has to some extent been overcome by seeking approximations to the two particle and higher order distribution functions which depend on time only through the one particle function.

$$(6.1) \qquad F^s \approx F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; F'(t))$$

and with these functions the evolution of the one body function is determined, through the BBKGY chain, to be approximated by

$$(6.2) \qquad \frac{\partial F'}{\partial t} + K'F' \approx \lambda L F^2(\underline{x}_1, \underline{v}_1, \underline{x}_2, \underline{v}_2; F'(t))$$

These approximations, if they exist, define a Markowian process because the behavior at a time t is completely determined by F' and $\frac{\partial F'}{\partial t}$ at the time t; that is, the system "forgets its past history". A method for finding well behaved Markowian approximations has not to our knowledge been satisfactorily determined. In this chapter we produce a Markowian approximation procedure that we find relates most easily to those found in the

literature. At the end of the chapter we point out some asymptotic divergence difficulties of this method.

The Markowian approximation procedure we use to relate our theory to those of the literature involves two steps. First we illustrate a way for writing without making any approximations, the distribution functions in a form (for $s>1$)

$$(6.3) \qquad F^s = F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; t \mid F'(t))$$

And second we will assume the explicit, ie: other than through $F'(t)$, time behavior to be short lived so that we can obtain Markowian equations by taking the asymptotic limit.

$$(6.4) \quad F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; F'(t)) = \lim_{\tau \to \infty} F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; \tau \mid F'(t))$$

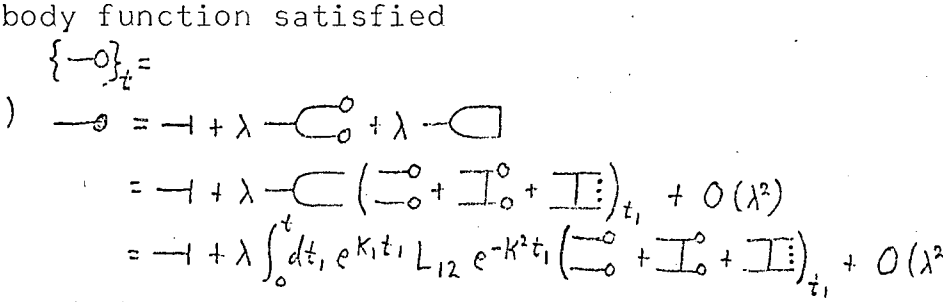
To cast the distribution functions into the form (6.3) we consider more carefully the replacement (4.17)

$$(6.5) \quad \cdots \text{—o} = e^{K_i' t_m} F_i'(t_m) \Rightarrow e^{K_i' t} F_i'(t) = \cdots \text{—o}$$

One has from (4.14) and definitions (5.2), (5.18) that the one body function satisfied

$$\{\text{—o}\}_t =$$

(6.6)



And; it follows that for a $\{\text{—o}\}_{t_m}$ which depends on time through $t_m, t \geq t_m \geq 0$ we can write

(6.7) $\{-o\}_{t_m} = -\!\!|\!\!- + \lambda\int_0^{t_m} dt_1\, e^{K_1 t_1} L_{12} e^{-K^2 t_1} \left(\begin{smallmatrix} -o \\ -o \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} \right)_{t_1} + O(\lambda^2)$

By combining the equations (6.6 & 6.7) we find a connection between $\{-o\}_{t_m}$ and $-\!\!\bullet$

(6.8) $\{-o\}_{t_m} = -\!\!\bullet - \lambda\int_{t_m}^{t} dt_1\, e^{K_1 t_1} L_{12} e^{-K^2 t_1} \left(\begin{smallmatrix} -o \\ -o \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} \right)_{t_1} + O(\lambda^2)$

Then by iteration we obtain $\{-o\}_{t_m}$ as an expansion in terms of $-\!\!\bullet$, one has

(6.9) $\{-o\}_{t_m} = -\!\!\bullet - \lambda\int_{t_m}^{t} dt_1\, e^{K_1 t_1} L_{12} e^{-K^2 t_1} \left(\begin{smallmatrix} -o \\ -\bullet \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} \right) + O(\lambda^2)$

$= -\!\!\bullet - \lambda\int_{t_m}^{t} dt_1\, e^{K_1 t_1} L_{12} e^{-H^2 t_1} \left(\begin{smallmatrix} -o \\ -\bullet \end{smallmatrix} + \begin{smallmatrix} -o \\ -o \end{smallmatrix} \right) + O(\lambda^2)$

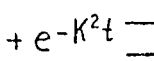
With this relation we can write the general F^s of the former chapters in the form (6.3).

Let us work with the example for F^2; one has by substitution of (6.9) into (5.27) the following expression for F^2

(6.10) ...(continued)

(6.10) $F^2 = e^{-K^2 t}$  $+ e^{-K^2 t}$  $+ e^{-K^2 t}$ 

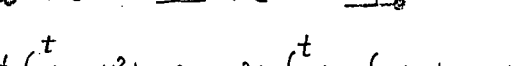
$$-\lambda e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} I^2 e^{-K^2 t_1}\int_{t_1}^t dt_2 \Big\{ e^{K_1 t_2} L_{13} e^{-H_{13}^2 t_2}$$



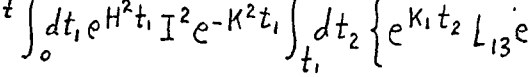
$$+ e^{K_2 t_2} L_{23} e^{-H_{23}^2 t_2}$$

$$+\lambda e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} \chi$$

$$\Big\{ L_{13} e^{-K^3 t_1}$$



$$+ L_{23} e^{-K^3 t_1}$$



$$+ (L_{13}+L_{23}) e^{-K^3 t_1}$$

$$+ O(\lambda^2)$$

The terms with a minus sign in (6.10) are new and we will call these and similar terms, that arise through the use of the equation (6.9), Markowian correction terms. We are now in a position to consider the asymptotic limit (6.4). We consider first the zeroth order contributions to F^2

$$(6.11) \qquad F^2 \approx \lim_{\tau\to\infty} \left\{ e^{-H^2\tau} e^{K^2\tau} F_1^1(t) F_2^1(t) + e^{-H^2\tau} G^2(0) \right\} + O(\lambda)$$

And for the evolution of the one body function we have from (6.2)

$$(6.12) \qquad \frac{\partial F^1}{\partial t} + K^1 F^1 \approx \lambda \lim_{\tau\to\infty} L_{12} \left\{ e^{-H^2\tau} e^{K^2\tau} F_1^1(t) F_2^1(t) + e^{-H^2\tau} G^2(0) \right\} + O(\lambda^2)$$

Bogoliubov[1] has formerly obtained the first term on the right hand side and he proves, for a homogeneous system, that this term is the Boltzman collision integral. The Boltzman collision integral takes into account all the two particle collision effects and it is hoped that (6.10) with the limit (6.4) will generalize Boltzman's collision integral to take into account three particle and higher order collision effects. We find, however, that with the limit (6.4) the Markowian correction terms diverge.

Let us consider for example from (6.10) the correction term

$$(6.13)\qquad -\lambda e^{-H^2 t}\int_0^t dt_1 e^{H^2 t_1} I^2 e^{-K^2 t_1}\int_{t_1}^t dt_2\, e^{K_1 t_2} L_{13} e^{-H_{13} t_3} e^{K^3 t} F_1'(t) F_2'(t) F_3'(t)$$

To see the divergence more easily let us specialize and consider a homogeneous system where in (6.13) the $e^{-K^s t_m}$ operations have no effect

$$(6.14)\qquad -\lambda e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} I^2 \int_{t_1}^t dt_2\, L_{13} e^{-H_{13}^2 t_2}\, F_1'(t) F_2'(t) F_3'(t)$$

From this let us consider the t_2 integration, the behavior which came directly from (6.9)

$$(6.15)\qquad \int_{t_1}^t dt_2 \frac{h}{m}\int d\underline{x}_3\, d\underline{v}_3\, \frac{\partial U(\underline{x}_{13})}{\partial \underline{x}_1}\cdot\frac{\partial}{\partial \underline{v}_1} e^{-H_{13}^2 t_2}\, F_1'(t) F_2'(t) F_3'(t)$$

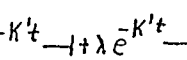
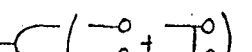
The operator $e^{-H_{13}^2 t}$ describes the evolution of any function under the mutual influence of the particles one and three, the other particles remaining stationary. One sees that the integral (6.15) vanishes except where the operator

$e^{-H_{13}t_2}$ moves from the probability densities $F_1'(t)\ F_2'(t)\ F_3'(t)$ the particles one and three within range of their interparticle potential $U(x_{13})$. When t_2 is large enough so that these interactions have taken place, the t_2 integrand is a constant; and under the limit (6.4) gives rise to the divergence

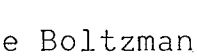
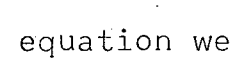
$$(6.16)\quad \int_{t_1}^{t} dt_2\, L_{13}\, e^{-H_{13}^2 t_2} F_1'(t)\, F_2'(t)\, F_3'(t) \sim \lim_{\tau\to\infty} \tau\, L_{13}\, e^{-H_{13}\tau} F_1'(t)\, F_2'(t)\, F_3'(t)$$

More generally, it has become apparent to us that the equation (6.9) is entirely similar to the ordinary and divergent perturbation expansion (4.2) for $\{-o\}_{t_m}$. In (4.2) we have a perturbation expansion which connects $\{-o\}_{t_m}$ to its initial value $-\!\!\dashv$; and this expansion is similar to the expansion (6.9) which connects $\{-o\}_{t_m}$ to its valve $-\!\!\bullet$ of the future. In Chapter IV we summed the series $-o$ in order to get rid of the asymptotic divergences of the form (4.25). In this chapter we have effectively destroyed this work because the use of the expansion (6.9) for $\{-o\}_{t_m}$ with the limit (6.4) reintroduces divergences similar to (4.25), in the second and higher order distribution functions, in the entirely similar positions. This difficulty prevents us from obtaining physically interesting results.

To avoid some confusion we should discuss a certain point about the way the Boltzman collision term in (6.12) was obtained. The Boltzman equation should be an approximation to the first order contribution to F' (neglecting terms with initial correlations)

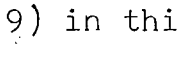
(6.17) $F'(t) = e^{-K't}$  $+ \lambda e^{-K't}$  $+ \; O(\lambda^2)$

To obtain the Boltzman equation we did "not" use the expansion (6.9) in this integral equations to write F' in a form

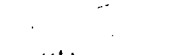
(6.18) $F'(t) = e^{-K't}$  $+ \lambda e^{-K't}$  $+ \; O(\lambda^2)$

$$= e^{-K^2 t} \dashv + \lambda e^{-K_1 t} \int_0^t dt_1 \, e^{K_1 t_1} L_{12} e^{-H^2 t_1} e^{K^2 t} F_1'(t) F_2'(t) + O(\lambda^2)$$

which diverges in exactly the same way as (6.15) or (6.9) if we tried to take an asymptotic limit. Rather, we worked from the differential equations for the one body function

(6.19) $\frac{\partial F'}{\partial t} + K'F' = \lambda L_{12} e^{-K^2 t}$  $+ \; O(\lambda^2)$

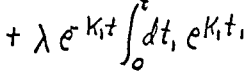
and in this equation we used the expansion (6.9) to obtain

(6.20) $\frac{\partial F'}{\partial t} + K'F' = \lambda L_{12} e^{-K^2 t}$  $+ \; O(\lambda^2)$

$$= \lambda L_{12} e^{-H^2 t} e^{K^2 t} F_1'(t) F_2'(t) + O(\lambda^2)$$

Or, by integration we have rather than (6.18) the behavior

(6.21) $F' = e^{-K't} \dashv + \lambda e^{-K^2 t} \int_0^t dt_1 \, e^{K^2 t_1} L_{12} e^{-H^2 t_1} e^{K^2 t_1} F_1'(t_1) F_2'(t_1) + O(\lambda^2)$

$= e^{-K't} \dashv + \lambda e^{-K't}$ 

where $\underset{\rightarrow}{i}\!\times = e^{K_i t_1} F_i'(t_1)$

And this expression is known to converge because it gives the Boltzman equation asymptotically. That is, working with the differential equation (6.19) rather than the integral equation (6.17) gives this one convergent term (6.21).

Sandri & Frieman[4,5], point out in their theory that

their solution for the three particle collision effects diverge. In Chapter VIII we show the connection of their theory to ours. In Chapter VII we find these same divergences in Bogoliubov's theory. Also we should mention that asymptotic divergences in Bogoliubov's of a different nature has been discussed by Cohen & Dorfman.[13] In (6.10) the terms which describe three particle collision effects contains an integration over the phase space of the particle 3; the four particle collision terms would contain an integration over the phase spaces of the particles 3 and 4; etc. Cohen & Dorfman make estimates of the amount of phase space available for these integrations. According to them the amount of phase space available for the four particle and higher order collision effects diverge asymptotically.

VII. THE THEORY OF BOGOLIUBOV

Since its introduction in (1946) the theory of Bogoliubov[1] has attracted considerable interest in the literature. We will give here a brief résumé of his theory. Then we develop from the knowledge of the former chapters an expansion method that we feel as nearly as possible follows Bogoliubov's expansion, and we solve our equations side by side with those of Bogoliubov. The connection between his theory and the divergent Markowian approximation procedure of Chapter VI, becomes apparent.

As a starting point Bogoliubov derives the BBKGY hierarchy (3.18) which for the short-range theory, with the thermodynamic limit (3.27), we write

$$(7.1) \quad \frac{\partial F^s}{\partial t} + H^s F^s = \lambda L^s F^{s+1}$$

Of particular interest is the temporal change of the one body distribution function

$$(7.2) \quad \frac{\partial F^1}{\partial t} = -K^1 F^1 + \lambda L F^2 \qquad L = L^1$$

Bogoliubov's first major assumption is that for a time scale coarser than a collision time the equation (7.2) can be approximated by

$$(7.3) \quad \frac{\partial F^1}{\partial t} = A(\underline{x}_1, \underline{v}_1, F^1(t))$$

where A depends functionally on $F^1(t)$ but does not depend on time explicitly. His second major assumption is that for the coarse grained time scale all the F^s depend on time only through F^1, so that one can write

$$(7.4) \quad F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; t) = F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1)$$

Bogoliubov tries to obtain (7.3) by succesive approximations in the form

$$(7.5) \quad \frac{\partial F^1}{\partial t} = A^0(\underline{x}_1, \underline{v}_1, F^1) + \lambda A^1(\underline{x}_1, \underline{v}_1, F^1) + \lambda^2 A^2(\underline{x}_1, \underline{v}_1, F^1) + \cdots$$

and for the many particle function (7.4) he tries a perturbation expansion

$$(7.6) \quad F^s = F^{s0}(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1) + \lambda F^{s1}(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1) + \lambda^2 F^{s2}(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1) + \cdots$$

Bogoliubov uses the following notation for writing the time derivative of a function $\psi(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1)$ which depends on time only through F^1

$$(7.7) \quad \frac{\partial}{\partial t}\psi(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s | F^1) = \mathcal{D}^0\psi + \lambda \mathcal{D}^1\psi + \lambda^2 \mathcal{D}^2\psi + \cdots$$

where the operator $\mathcal{D}^r$ denotes differentiation with respect to t (ψ depends on t through F^1) with subsequent substitution of $A^r(F^1)$ for $\frac{\partial F^1}{\partial t}$. He substitutes the expansions (7.5) and (7.6) with the operations (7.7) into the BBKGY hierarchy (7.1) to obtain by equating equal orders in λ the system of equations

(7.8) $A^0(\underline{x}_1, \underline{v}_1, F^1) = -K^1 F^1$

(7.9) $A^1(\underline{x}_1, \underline{v}_1, F^1) = L F^{20}$

(7.10) $A^2(\underline{x}_1, \underline{v}_1, F^1) = L F^{21}$

$\vdots$

(7.11) $\mathcal{D}^0 F^{20} + H^2 F^{20} = 0$

(7.12) $\mathcal{D}^0 F^{21} + H^2 F^{21} = L^2 F^{30} - \mathcal{D}^1 F^{20}$

$\vdots$

(7.13) $\mathcal{D}^0 F^{s0} + H^s F^{s0} = 0$

(7.14) $\mathcal{D}^0 F^{si} + H^s F^{si} = \psi^{si} = L^s F^{s+1, i-1} - \sum_{\ell+k=i} \mathcal{D}^\ell F^{s,k}$

The problem is to find the solution to this system of equations. One notices that the variable t does not appear explicitly in these equations, and for this reason Bogoliubov says that the problem has been reduced to the determination of the expressions F^{sr} and A^r as functionals of the "arbitrary" function F^1. This allows him to replace everywhere F^1 by $e^{-K^1\tau}F^1$ where τ is some parameter independent of t. One notices the property

(7.15) $\frac{\partial}{\partial\tau} e^{-K^1\tau}F^1 = -K^1 e^{-K^1\tau}F^1 = A^0(\underline{x}_1, \underline{v}_1, e^{-K^1\tau}F^1)$

Hence from the definition of the operator $\mathcal{D}^0$ it follows that

(7.16) $\mathcal{D}^0 F^{si}(\ \ |e^{-K^1\tau}F^1) = \frac{\partial}{\partial\tau} F^{si}(\ \ |e^{-K^1\tau}F^1)$

Substituting these results into the equations for the $F^{si}(\ \ |e^{-K^1\tau}F^1)$ one obtains

(7.17) $\frac{\partial}{\partial\tau} F^{si}(\ \ |e^{-K^1\tau}F^1) + H^s F^{si}(\ \ |e^{-K^1\tau}F^1) = \psi^{si}(\ \ |e^{-K^1\tau}F^1)$

where $\psi^{s0} = 0$

For the solution of (7.17) one has

$$(7.18)\quad F^{si}(\ |e^{-K'\tau}F') = e^{-H^s\tau}F^{si}(\ |F') + e^{-H^s\tau}\int_0^\tau d\tau'\, e^{H^s\tau'}\psi^{si}(\ |e^{-K'\tau'}F')$$

Following Bogoliubov we replace the arbitrary functional argument F' by $e^{K'\tau}F'$ to obtain (with a change in the τ' variable of integration)

$$(7.19)\quad F^{si}(\ |F') = e^{-H^s\tau}F^{si}(\ |e^{K'\tau}F') + \int_0^\tau d\tau'\, e^{-H^s\tau'}\psi^{si}(\ |e^{K'\tau'}F')$$

Since these equations (7.19) hold for arbitrary τ, and since the left-hand side does not depend on τ the limit $\tau\to\infty$ can be taken. For this limit Bogoliubov uses the boundary conditions

$$(7.20)\quad \lim_{\tau\to\infty} e^{-H^s\tau}F^{so}(\ |e^{K'\tau}F') = \lim_{\tau\to\infty} e^{-H^s\tau}\prod^{s} e^{K'\tau}F'$$

$$(7.21)\quad \lim_{\tau\to\infty} e^{-H^s\tau}F^{si}(\ |e^{K'\tau}F') = 0 \qquad i>0$$

These conditions are very far reaching assumptions, and we will discuss them later. With these boundary conditions in (7.19) one has

$$(7.22)\quad F^{so}(\ |F') = \lim_{\tau\to\infty} e^{-H^s\tau}\prod^{s} e^{K'\tau}F'$$

$$(7.23)\quad F^{si}(\ |F') = \int_0^\infty d\tau'\, e^{-H^s\tau'}\psi^{si}(\ |e^{K'\tau'}F')$$

By combining (7.22 & 7.23) with the definitions of the A^r's and ψ^{si}'s Bogoliubov's expansion can be written out to any

order in λ. We should mention that, as Bogoliubov proves, the solution for A' for a homogeneous system gives Boltzman's equation

$$(7.24)\quad \frac{\partial F'}{\partial t} = \lim_{\tau \to \infty} L\, e^{-H^2 \tau} F_1' F_2' \quad \text{for a homogeneous system.}$$

To explain Bogoliubov's theory we find it easier to go back and work from our more general theory of the former chapters.

We will develop an expansion method that we feel as nearly as possible resembles Bogoliubov's expansion. This expansion will be nothing more than an alternate method for finding or writing out the general F^s in the form (6.3) that we derived for the Markowian approximation procedure in Chapter VI. We know already that these expressions diverge but let us ignore this for now. We consider the expressions (6.3) written in the slightly different form

$$(7.25)\quad F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; t \,|\, F'[t]) = F^s(e^{K't} F'[t] \,|\, t_0 + \eta; \underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s)$$
$$\equiv F^s(e^{K't} F' \,|\, t_0 + \eta) \qquad t = t_0 + \eta \qquad t_0 = a \text{ constant}$$

where the last identity is a short hand we often use. It seems that the explicit time behavior η describes the fine grained evolution in time, and we will try to coarse grain our equations by performing a certain approximation of the explicit time behavior. And, we have included in (7.25) the constant t_0 so that our coarse graining procedure is not restricted to the origin in time t. We find it convenient to define the functions

$$(7.26)\quad \bar{F}^s = \bar{F}^s\left(e^{K't}F' \middle| t_0+\sigma\right)$$

which have the same form as (7.25) but here we treat, through a parameter σ independent of t, the explicit time behavior as though we could ignore the dependence upon $e^{K't}F'$. With these functions (7.26) the BBKGY hierarchy (7.1) can be written as follows

$$(7.27)\quad \left[\left(\frac{\partial \bar{F}^s}{\partial \sigma}\right)_t + \left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t} + H^s F^s\left(e^{K't}F' \middle| t\right) = \lambda L^s F^{s+1}\left(e^{K't}F' \middle| t\right)$$

or one has

$$(7.28)\quad \left[\left(\frac{\partial \bar{F}^s}{\partial \sigma}\right)_t\right]_{t_0+\sigma=t} + H^s F^s\left(e^{K't}F' \middle| t\right) = \lambda L^s F^{s+1}\left(e^{K't}F' \middle| t\right) - \left[\left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t}$$

From our work of Chapter VI we could in principle determine the function $\left[\left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t}$ *in a form*

$$(7.29)\quad J^s = \left[\left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t} = J^s\left(e^{K't}F[t] \middle| t_0+\eta;\ \underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s\right) \equiv J^s\left(e^{K't}F' \middle| t_0+\eta\right)$$

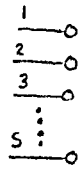
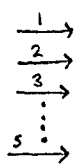
With this function J^s we can deduce an equation for $\left(\frac{\partial \bar{F}^s}{\partial \sigma}\right)_t$

$$(7.30)\quad \left(\frac{\partial \bar{F}^s}{\partial \sigma}\right)_t + H^s \bar{F}^s = \lambda L^s \bar{F}^{s+1} - \bar{J}^s$$

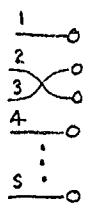
where $\bar{J}^s$ has the functional form

$$(7.31)\quad \bar{J}^s = \bar{J}^s\left(e^{K't}F' \middle| t_0+\sigma\right) = \overline{\left[\left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t}}$$

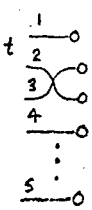
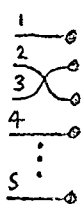
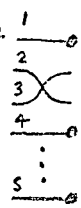
The chain of equations (7.30) we will try to solve by a perturbation expansion similar to Bogoliubov's, but first we must determine proper boundary conditions. To determine them, we write the F^s in terms of diagrams as follows

(7.32) $F^s(t) = e^{-K^s t}$  $+ e^{-K^s t}$ 

where the arrows indicate the sum of diagrams that have not already been used to produce the first term. From our general procedure of Chapter IV we know that a possible contribution to the second term must have at least two of its s lines connected; otherwise, the diagram contributes to the first term. As an example contribution to the second term we consider

(7.33) $e^{-K^s t}$ 

We use the relation (6.9) in (7.33) in order to write this term in the form (7.25)

(7.34) $e^{-K^s t}$  $= e^{-K^s t}$  $+ e^{-K^s t}$  $\times$ { some series expansion in  }

One sees in (7.34) that each term describes some correlation between the particles 2 and 3. By a similar calculation for any contribution to the second term in (7.32) one always finds that all describe some correlation among the s particles. For convenience we define a function for these correlations

$$(7.35)\qquad F^s(e^{K't}F'|t) = e^{-K^s t}\prod^s e^{K't}F' + C^s(e^{K't}F'|t)$$

where C^s is the second term in (7.32). For our functions (7.26) with the independent variables σ and t we would have from (7.35) the corresponding functions

$$(7.36)\qquad \bar{F}^s(e^{K't}F'|t_0+\sigma) = e^{-K'(t_0+\sigma)}\prod^s e^{K't}F' + C^s(e^{K't}F'|t_0+\sigma)$$

When σ is set equal to zero, one has

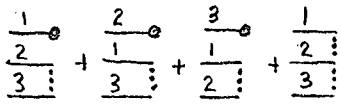
$$(7.37)\qquad \bar{F}^s(e^{K't}F'|t_0) = e^{-K^s t_0}\prod^s e^{K't}F' + C^s(e^{K't}F'|t_0)$$

We have in (7.37) the functional form of $\bar{F}^s$ at the origin of σ; this gives us a boundary condition with which we could in principle solve the equations (7.30). As a special case of (7.37) we will sometimes consider the case where σ and t have the same origin, or where $t_0=0$. To bring out what happens when $t_0=0$ let us consider again the example (7.33 & 7.34) from which we deduce the corresponding contributions to $\bar{C}^s(e^{K't}F'|t_0+\sigma)$

$$(7.38)\qquad e^{-K^s(t_0+\sigma)}\int_0^{t_0+\sigma} dt_1\, e^{K_{23}t_1} I_{23} e^{-K_{23}t_1}\prod^s e^{K't}F'(t) + e^{-K^s(t_0+\sigma)}\int_0^{t_0+\sigma} dt_1\, e^{K_{23}t_1} I_{23} e^{-K_{23}t_1} \times \{\text{some series expansion in } \sigma\}$$

One sees that (7.38) vanishes as a contribution to $\bar{C}^s(e^{K't}F'|t_0)$ for $t_0=0$. In general we find that the only contributions to the second term in (7.32) that lead to corresponding contributions to $C^s(e^{K't}F'|0)$ are those that do not contain any vertices, one has

(7.39) $\bar{C}^2(e^{K^2 t}F^1|0) =$  $= G^2(0) = G_{12}(0)$

(7.40) $\bar{C}^3(e^{K^1 t}F^1|0) =$ 

etc.

To solve the equations (7.30) we try a perturbation expansion for the various $\bar{F}^s$

$$(7.41)\quad \bar{F}^s = \bar{F}^{s0}(e^{K^1 t}F^1|t_0+\sigma) + \lambda \bar{F}^{s1}(e^{K^1 t}F^1|t_0+\sigma) + \lambda^2 \bar{F}^{s2}(e^{K^1 t}F^1|t_0+\sigma) + \cdots$$

If we are able to solve for the $\bar{F}^{si}$, they will give us in ordinary time a series expansion for F^s

$$(7.42)\quad F^s = F^{s0}(e^{K^1 t}F^1|t) + \lambda F^{s1}(e^{K^1 t}F^1|t) + \lambda^2 F^{s2}(e^{K^1 t}F^1|t) + \cdots$$

In order to solve the equations (7.31) we also need some way to find or expand the J^s. For this we write, from the BBKGY hierarchy, the evolution equation for the one particle function in the form

$$(7.43)\quad \frac{\partial e^{K^1 t}F^1}{\partial t} = \lambda e^{K^1 t} L F^2(e^{K^1 t}F^1|t) = e^{K^1 t} A(e^{K^1 t}F^1|t; \underline{x}_1, \underline{v}_1)$$

Further, with the expansion (7.42) for F^2 we can write (7.43) in successive approximations

$$(7.44)\quad \frac{\partial e^{K^1 t}F^1}{\partial t} = \lambda e^{K^1 t} A^1(e^{K^1 t}F^1|t) + \lambda^2 e^{K^1 t} A^2(e^{K^1 t}F^1|t) + \lambda^3 e^{K^1 t} A^3(e^{K^1 t}F^1|t)$$

where we have no zeroth order term. In (7.29) we can perform the operations $\left[\left(\frac{\partial \bar{F}^s}{\partial t}\right)_\sigma\right]_{t_0+\sigma=t}$ as follows; for each $\bar{F}^{si}$ one can

write

$$(7.45)\quad \left(\frac{\partial \bar{F}^{si}}{\partial t}\right)_\sigma = \lambda \underline{\mathfrak{D}}^1 \bar{F}^{si} + \lambda^2 \underline{\mathfrak{D}}^2 \bar{F}^{si} + \lambda^3 \underline{\mathfrak{D}}^3 \bar{F}^{si} + \cdots$$

where the operator $\underline{\mathfrak{D}}^r$ denotes differentiation with regard to t (F^{si} depends on t only in the combination $e^{K't}F'$) with subsequent substitution of $e^{K't}A^r(e^{K't}F'|t)$ for $\frac{\partial}{\partial t}\, e^{K't}F'$. For use in equation (7.30) we must rewrite these $e^{K't}A^r$'s in the form $e^{K'(t_0+\sigma)}A^r(e^{K't}F'|t_0+\sigma)$ and we denote this by $\mathfrak{D}^r$ over bars

$$(7.46)\quad \overline{\left[\left(\frac{\partial \bar{F}^{si}}{\partial t}\right)\right]}_{t_0+\sigma=t} = \lambda^1 \bar{\mathfrak{D}}^1 \bar{F}^{si} + \lambda^2 \bar{\mathfrak{D}}^2 \bar{F}^{si} + \lambda^3 \bar{\mathfrak{D}}^3 \bar{F}^{si} + \cdots$$

where $\bar{\mathfrak{D}}^n$ denotes differentiation with regard to t with subsequent substitution of $e^{K'(t_0+\sigma)}A^r(e^{K't}F'|t_0+\sigma)$ for $\frac{\partial}{\partial t}\, e^{K't}F'$.

Let us try our perturbation expansion in the following way. For the one particle function we try an ordinary expansion (7.42) for F^2 in equation (7.43 or 7.44) and for the many particle function we try the expansion (7.41) with (7.46) in (7.30) to obtain by equating equal orders in λ the set of equations

$$(7.47)\quad A^1 = L F^{20}(e^{K't}F'|t)$$

$$(7.48)\quad A^2 = L F^{21}(e^{K't}F'|t)$$

$$\vdots$$

$$(7.49)\quad \frac{\partial \bar{F}^{20}}{\partial \sigma} + H^2 \bar{F}^{20} = 0$$

(7.50) $$\frac{\partial \bar{F}^{21}}{\partial \sigma} + H^2 \bar{F}^{20} = L^2 \bar{F}^{30} - \bar{\mathcal{D}}^1 \bar{F}^{20}$$

$$\vdots$$

(7.51) $$\frac{\partial \bar{F}^{s0}}{\partial \sigma} + H^s \bar{F}^{s0} = 0$$

(7.52) $$\frac{\partial \bar{F}^{si}}{\partial t} + H^s \bar{F}^{si} = \bar{\psi}^{si} = L^s \bar{F}^{s+1,i-1} - \sum_{l+k=i} \bar{\mathcal{D}}^l \bar{F}^{s,k}$$

We are to solve this system of equations subject to the boundary condition (7.37) which for the perturbation expansion we can write as follows

(7.53) $$\bar{F}^{s0}(\sigma=0) = e^{-K^s t_0} \overset{s}{\prod} e^{K^1 t} F^1(t) + \bar{C}^{s0}(e^{K^1 t} F^1 | t_0)$$

(7.54) $$\bar{F}^{si}(\sigma=0) = \bar{C}^{si}(e^{K^1 t} F^1 | t_0)$$

where we have introduced for $\bar{C}^s(e^{K^1} F^1 | t_0)$ the expansion

(7.55) $$\bar{C}^s(e^{K^1 t} F^1 | t_0) = \bar{C}^{s0}(e^{K^1 t} F^1 | t_0) + \lambda \bar{C}^{s1}(e^{K^1 t} F^1 | t_0) + \lambda^2 \bar{C}^{s2}(e^{K^1 t} F^1 | t_0)$$

And, let us keep in mind the special case where σ and t have the same origin, or where $t_0 = 0$; for this case we find from our relations (7.39), (7.40), etc. the following conditions

(7.56) $$\bar{C}^{s0}(e^{K^1 t} F^1 | 0) = \bar{C}^s(e^{K^1 t} F^1 | 0)$$

(7.57) $$\bar{C}^{si}(e^{K^1 t} F^1 | 0) = 0 \quad \text{for} \quad i > 0$$

We find that our system of equations (7.47 to 7.52) with the boundary conditions (7.53 & 7.54) decouple and we can solve them to any order.

As is the plan of this chapter, let us solve our

system of equations side by side with Bogoliubov's system (7.8 to 7.14): we denote Bogoliubov's solution by B's in the equation numbers. The calculations go smoothly until we compute the $F^{21)}_{2}$: at that point is where the first Markowian correction term appears. To solve our system of equations we start with (7.51) for $\bar{F}^{so}$ or in Bogoliubov's case (7.13) for his $F^{so}(\ |e^{-K'\tau}F')$

$$(7.58)\quad \frac{\partial \bar{F}^{so}(e^{K't}F'|t_0+\sigma)}{\partial\sigma} + H^s\,\bar{F}^{so}(e^{K^2t}F'|t_0+\sigma) = 0$$

$$(7.58B)\quad \frac{\partial F^{so}(\ |e^{-K'\tau}F')}{\partial\tau} + H^s F^{so}(\ |e^{-K'\tau}F') = 0$$

We solve (7.58) subject to the boundary condition (7.53) and solve (7.58B) subject to the boundary condition (7.20) to obtain

$$(7.59)\quad \bar{F}^{so}(e^{K't}F'|t_0+\sigma) = e^{-H^s\sigma}e^{-K^st_0}\prod^{s} e^{K't}F'(t) + e^{-H^s\sigma}\,\bar{C}^{so}(e^{K't}F'|t_0)$$

$$(7.59B)\quad F^{so}(\ |F') = \lim_{\tau\to\infty} e^{-H^s\tau}\prod^{s} e^{K^2\tau}F'(t)$$

(7.59B) gives Bogoliubov's A'; to get our A' we must deduce in ordinary time our F^{20} from (7.59). This is easy when we consider the special case of (7.59) where σ and t have the same origin. Taking into account (7.56 and 7.39) one has for $t_0 = 0$

$$(7.60)\quad \bar{F}^{20}(e^{K't}F'|\sigma) = e^{-H^2\sigma}\prod^{2} e^{K't}F'(t) + e^{-H^2\sigma}\,G^2(0)$$

and for the corresponding $F^{20}(e^{K't}F'|t)$ one has

(7.61) $$F^{20}(e^{K't}F'|t) = e^{-H^2t}\prod^{2} e^{K't}F'(t) + e^{-H^2t}G^2(0)$$

This of course agrees with the zeroth order term in (6.10). With (7.61) our A' follows from (7.47) and we obtain Bogoliubov's A' from (7.59B) with (7.9)

(7.62) $$A'(e^{K't}F'|t) = Le^{-H^2t}e^{K_1t}F_1'(t)e^{K_2t}F_2'(t) + Le^{-H^2t}G^2(0)$$

(7.62B) $$A'(x_1, x_1, F') = \lim_{\tau\to\infty} Le^{-H^2\tau}e^{K_1\tau}F_1'(t)\,e^{K_2\tau}F_2'(t)$$

We are in a position to solve for $\bar{F}^{s1}$ and Bogoliubov's F^{s1}; however, we will only work out $\bar{F}^{21}$ and Bogoliubov's F^{21}. For $\bar{F}^{21}$ we use (7.50) taking into account (7.59) and in Bogoliubov's case we use (7.12) taking into account (7.59B)

(7.63) $$\frac{\partial\bar{F}^{21}}{\partial\sigma} + H^2F^{21} = L^2e^{-H^3\sigma}e^{-K^3t_0}\prod^{3} e^{K't}F'(t) + L^2e^{-H^3\sigma}\bar{C}^{30}(e^{K't}F'|t) - \bar{\mathcal{D}}'\left\{e^{-H^2\sigma}e^{-K^2t_0}\prod^{2} e^{K't}F'(t) + e^{-H^2\sigma}\bar{C}^{20}(e^{K't}F'|t_0)\right\}$$

(7.63B) $$\mathcal{D}^{\circ}F^{21} + H^2F^{21} = \lim_{\mu\to\infty}\left\{L^2e^{-H^3\mu}\prod^{3} e^{K'\mu}F' - \mathcal{D}'e^{-H^2\mu}\prod^{2} e^{K'\mu}F'(t)\right\}$$

Since we have the A''s, we can perform the $\bar{\mathcal{D}}'$ and $\mathcal{D}'$ operations; and for Bogoliubov's equation (7.63B) we replace the "arbitrary functional argument" F' by $e^{-K'\tau}F'$

(7.64) ...(continued)

$$(7.64)\quad \frac{\partial \bar{F}^{21}}{\partial \sigma} + H^2 \bar{F}^{21} = L^2 e^{-H^3\sigma} e^{-K^3 t_0} \prod^{3} e^{K^1 t} F^1(t) + L^2 e^{-H^3\sigma} \bar{C}^{30}(e^{K^1 t} F^1 | t_0)$$

$$- e^{-H^2\sigma} e^{-K^2 t_0}\left[e^{K_1(t_0+\sigma)} L_{13} e^{-H_{13}(t_0+\sigma)} + e^{K_2(t_0+\sigma)} L_{23} e^{-H_{23}(t_0+\sigma)}\right] \prod^{3} e^{K^1 t} F^1(t)$$

$$- e^{-H^2\sigma} e^{-K^2 t_0}\left[e^{K_1(t_0+\sigma)} L_{13} e^{-H_{13}(t_0+\sigma)} e^{K_2 t} F_2^1(t)\, G_{13}(0) + e^{K_2(t_0+\sigma)} L_{23} e^{-H_{23}(t_0+\sigma)} e^{K_1 t} F_1^1(t)\, G_{23}(0)\right]$$

$$- \bar{\mathfrak{D}}^1 e^{-H^2\sigma} \bar{C}^{20}(e^{K^1 t} F^1 | t_0)$$

$$(7.64B)\quad \frac{\partial F^{21}(\ | e^{-K^1\tau} F^1)}{\partial \tau} + H^2 F^{21}(\ | e^{-K^1\tau} F^1) =$$

$$\lim_{\mu\to\infty}\left\{ L^2 e^{-H^3\mu} - e^{-H^2\mu}\left[L_{13} e^{-H_{13}\mu} + L_{23} e^{-H_{23}\mu}\right] \prod^{3} e^{K^1(\mu-\tau)} F^1(0)\right.$$

And we solve (7.64) subject to the boundary conditions (7.54) and solve (7.64B) subject to the boundary condition (7.21), or use (7.23),

$$(7.65)\quad \bar{F}^{21}(e^{K^1 t} F^1 | t_0+\sigma) =$$

$$e^{-H^2\sigma} \bar{C}^{21}(e^{K^1 t} F^1 | t_0)$$

$$+ \int_0^\sigma dt_1\, e^{-H^2 t_1}\left\{ L^2 e^{-H^3(\sigma-t_1)} e^{-K^3 t_0} \prod^{3} e^{K^1 t} F^1(t) + L^2 e^{-H^3(\sigma-t_1)} \bar{C}^{30}(e^{K_1 t} F^1 | t_0)\right.$$

$$- \int_0^\sigma dt_1\, e^{-H^2\sigma} e^{-K^2 t_0}\left[e^{K_1(t_0+\sigma-t_1)} L_{13} e^{-H_{13}(t_0+\sigma-t_1)} + e^{K_2(t_0+\sigma-t_1)} L_{23} e^{-H_{23}(t_0+\sigma-t_1)}\right] \prod^{3} e^{K^1 t} F^1(t)$$

$$- \int_0^\sigma dt_1\, e^{-H^2\sigma} e^{-K^2 t_0}\left[e^{K_1(t_0+\sigma-t_1)} L_{13} e^{-H_{13}(t_0+\sigma-t_1)} e^{K_2 t} F_2^1(t)\, G_{13}(0) + e^{K_2(t_0+\sigma-t_1)} L_{23} e^{-H_{23}(t_0+\sigma-t_1)} e^{K_1 t} F_1^1(t)\, G_{23}(0)\right]$$

$$- e^{-H^2\sigma} \int_0^\sigma d\sigma'\, e^{-H^2\sigma'}\left[\bar{\mathfrak{D}}^1 e^{-H^3\sigma'} \bar{C}^{20}(e^{K^1 t} F^1 | t_0)\right]$$

(7.65B) $F^{21}(\quad|F') =$

$$\lim_{\mu\to\infty}\int_0^\infty dt_1\, e^{-H^2 t_1} L^2 e^{-H^3\mu} \prod^3 e^{K'(\mu+t_1)} F'(t)$$

$$-\lim_{\mu\to\infty}\int_0^\infty dt_1\, e^{H^2 t_1} e^{-H^2\mu}\left[L_{13} e^{-H_{13}\mu} + L_{23} e^{-H_{23}\mu}\right] \prod^3 e^{K'(\mu+t_1)} F'(t)$$

$$= \lim_{\mu\to\infty}\int dt_1\, e^{-H^2 t_1} L^2 e^{-H^3\mu} \prod^3 e^{K'\mu} F'(t)$$

$$-\lim_{\mu\to\infty}\int_0^\infty dt_1\, e^{-H^2\mu}\left[L_{13} e^{-H_{13}\mu} + L_{23} e^{-H_{23}\mu}\right] \prod^3 e^{K'\mu} F'(t)$$

We are not able to go further with Bogoliubov's theory because clearly the second term in (7.65B) diverges. To bring out a connection to our theory, let us first consider the general solution for our $\bar{F}^{so}$ and $\bar{F}^{si}$; from (7.51) and (7.52) using the boundary conditions (7.53) and (7.54) one has

(7.66) $\bar{F}^{so} = e^{-H^s\sigma} e^{-K^s t_0} \prod^s e^{K't} F'(t) + e^{-H^s\sigma}\, \bar{C}^{so}(e^{K't}F' | t_0)$

(7.67) $\bar{F}^{si} = e^{-H^s\sigma}\, \bar{C}^{si}(e^{K't}F' | t_0) + \int_0^\sigma dt_1\, e^{-H^s t_1}\, \bar{\psi}^{si}(e^{K't}F' | t_0 + t_1)$

We find that our expansion becomes almost identical to Bogoliubov's expansion if we make the following two assumptions:

(i). We assume our expansion is valid for asymptotic σ so that we can coarse grain our functions by taking the limits

(7.68) $\lim\limits_{\substack{\sigma\to\infty \\ \mu\to\infty}} \bar{F}^{so}\left(e^{K'\mu} F'[t] \,\middle|\, t_0 + \sigma\right)$

$$(7.69)\quad \lim_{\substack{\sigma\to\infty\\ \mu\to\infty}} \bar{F}^{si}\left(e^{K'\mu}F'[t]\,|\,t_0+\sigma\right)$$

where one notices that the t_0 is no longer important in comparison to σ.

(ii). We assume that the correlations which existed at the origin of σ vanish due to the natural motion of the system, or one has

$$(7.70)\quad \lim_{\substack{\sigma\to\infty\\ \mu\to\infty}} e^{-H^s\sigma}\,\bar{C}^s\left(e^{K'\mu}F'[t]\,|\,t_0\right) = 0$$

With these asymptotic conditions in (7.66 & 7.67) one has

$$(7.71)\quad \lim_{\substack{\sigma\to\infty\\ \mu\to\infty}} \bar{F}^{so} = \lim_{\mu\to\infty} e^{-H^s\mu}\prod^{s} e^{K'\mu}F'(t)$$

$$(7.72)\quad \lim_{\substack{\sigma\to\infty\\ \mu\to\infty}} \bar{F}^{si} = \lim_{\mu\to\infty}\int_0^{\mu} dt_1\, e^{-H^s t_1}\,\bar{\psi}^{si}\left(e^{K'\mu}F'\,|\,t_0+t_1\right)$$

Let us consider our solution for $\bar{F}^{21}$ (7.65) with these asymptotic conditions

$$(7.73)\quad \bar{F}^{21} \sim \lim_{\mu\to\infty}\int_0^{\mu} dt_1\, e^{-H^2 t_1}\left\{L^2 e^{-H^3\mu}\prod^{3} e^{K^3\mu}F'(t)\right\}$$
$$-\lim_{\mu\to\infty}\int_0^{\mu} dt_1\, e^{-H^2\mu}\left[e^{K_1\mu}L_{13}e^{-H_{13}\mu}+e^{K_2\mu}L_{23}e^{-H_{13}\mu}\right]\prod^{3} e^{K'\mu}F'(t)$$

And we compare (7.73) with Bogoliubov's solution for (7.65B) and we see they are the same except for some operators $e^{K'\mu}$. The important point is that $\bar{F}^{21}$ diverges if we take the asymptotic limit of the explicit time behavior. From our work in Chapter VI we of course expected a divergent $\bar{F}^{21}$ because, from (6.10), the first order term

of F^2 contains Markowian correction terms. It is not apparent that (7.65) will give us in ordinary time the same F^{21} as in (6.10); it can be shown that it does and we have relegated this caluclation to our Appendix II. Due to the strong resemblence of our σ to Bogoliubov's τ and since our σ describes, except for the $e^{K't}$ affixed to the F'^{1}_{2}, the explicit time behavior we feel justified in saying that Bogoliubov's τ describes the explicit time behavior in his theory. By comparison with our expansion we know that Bogoliubov's expansion is divergent, and in particular it is not valid to take the limit $\tau \to \infty$. If the limit of the explicit time behavior were valid, we feel justified in saying that Bogoliubov's boundary conditions (7.20) and (7.21) have the same meaning as the assumption (ii); that is, the correlations which existed at the 'arbitrary' origin of τ vanish for asymptotic τ.

This concludes our discussion of Bogoliubov's theory. In the next chapter we will discuss the method of extension due to Sandri & Frieman.[4,5] This method is similar to Bogoliubov's theory.

VIII. THE METHOD OF EXTENSION

The method of extension due to Sandri & Frieman[4,5] will now be discussed. We discuss their method for the short-range theory and for simplicity we assume the system treated to be homogeneous and initially uncorrelated. These authors use as a starting point the BBKGY chain (3.18) which for the short range theory we write

$$(8.1) \quad \frac{\partial F^s}{\partial t} + H^s F^s = \lambda L^s F^{s+1}$$

We find the method of extension is better understood if we work first from an ordinary perturbation expansion. Later we will follow Sandri & Frieman's work more closely. Let us introduce into (8.1) the expansions

$$(8.2) \quad F^1 = f^0 + \lambda f^1 + \lambda^2 f^2 + \cdots$$

$$(8.3) \quad F^2 = F^{20} + \lambda F^{21} + \lambda^2 F^{22} + \cdots$$

$$(8.4) \quad F^s = F^{s0} + \lambda F^{s1} + \lambda^2 F^{s2} + \cdots$$

We obtain by equating equal orders in λ the set of equations

$$(8.5) \quad \frac{\partial f^0}{\partial t} = 0$$

$$(8.6) \quad \frac{\partial f^i}{\partial t} = L F^{2,i-1} \qquad i > 0 \qquad L = L'$$

$$(8.7) \quad \frac{\partial F^{s0}}{\partial t} + H^s F^{s0} = 0$$

$$(8.8) \quad \frac{\partial F^{si}}{\partial t} + H^s F^{si} = L^s F^{s+1,i-1} \qquad i > 0$$

Since the system is assumed initially uncorrelated, for initial conditions one has

(8.9) $f^0(0) = \text{given} =$

(8.10) $f^i(0) = 0 \qquad i > 0$

(8.11) $F^{s0}(0) = \prod^{s} f^0(0)$

(8.12) $F^{si}(0) = 0$

We proceed to solve the set of equations (8.5) to (8.8) starting with the zeroth order and working to higher order. From (8.5 with 8.9) we find that f^0 is time independent

(8.13) $f^0(t) = f^0(0) = f^0 =$

And, for the many particle function we obtain from (8.7)

(8.14) $F^{s0}(t) = e^{-H^s t} \prod^{s} f^0$

To solve (8.6) for f^1 we will be interested in the two body behavior

(8.15) $F^{20} = e^{-H^2 t} f_1^0 f_2^0 = e^{-K^2 t} \{$ $+$ $+$ $+$ $+ \cdots \}$

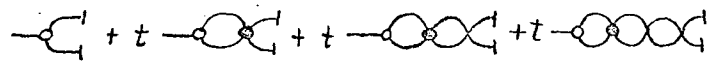
By substitution of (8.15) into (8.6) one finds the solution

(8.16) $f^1 =$ $+$ $+$ $+$ $+ \cdots$

$$= \int_0^t dt_1\, n \int d\underline{x}_2\, d\underline{v}_2\, I_{12}\, e^{-H^2 t_1} f_1^0 f_2^0$$

For asymptotic time we find that (8.16) diverges, or we have

(8.17) $f' \sim t \lim_{\eta \to \infty} L e^{-H^2 \eta} f_1^o f_2^o$

$= t$ 

where we have recalled the diagram definitions (4.20) and (4.23). For the asymptotic behavior of the one body function we now have

(8.18) $F' = f^o + \lambda t \lim_{\eta \to \infty} L e^{-H^2 \eta} f_1^o f_2^o + O(\lambda^2)$

Sandri & Frieman use a trick to take care of these divergent or secular terms. For this case (8.18) we find that they redefine the zeroth order approximation by the following relations

(8.19) $F' = \bar{f}^o + O + \text{order}(\lambda^2)$

(8.20) $\frac{\partial \bar{f}^o}{\partial \sigma_1} = \lim_{\eta \to \infty} L e^{-H^2 \eta} \bar{f}_1^o \bar{f}_2^o$ (Boltzmann's equation)

(8.21) $\sigma_1 = \lambda t$

One sees that the terms of (8.18) appear now in the Taylor expansion of $\bar{f}^o$

(8.22) $\bar{f}^o = f^o + \sigma_1 \lim_{\eta \to \infty} L e^{-H^2 \eta} f_1^o f_2^o + \sigma_1^2 \frac{\partial^2 \bar{f}^o(0)}{\partial \sigma_1^2} + \cdots$

Sandri & Frieman assume that the general expansion contains series of the type (8.22) and that these are the significant ones. From our calculation (4.15) through (4.25) we know that the general expansion does contain series of the type

(8.22) and this is the reason their method seems to work. The series (8.22) comes from the behavior

(8.23) $\frac{\partial F'}{\partial t} \approx \lambda -$  $+ \lambda -$  $+ \lambda -$  $+ \cdots$

Although (8.20) is Boltzman's equation, the way it was found was no more than a guess. We will now follow Sandri & Fireman's method more closely and find they make other assumptions and, as they do, divergence difficulties.

In the last paragraph we presented what we consider the basic reason the method of Sandri & Frieman works. We will have to go much, much deeper however, to bring out all the assumptions and meanings of their theory. Let us start by writing the general F^s in the form

(8.24) $F^s = F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s \mid \sigma_0, \sigma_1, \sigma_2, \sigma_3 \ldots)$

where we have introduced the parameters

(8.25) $\sigma_0 = t + C_0\,,\ \sigma_1 = \lambda t + C_1\,,\ \sigma_2 = \lambda^2 t + C_2\,,\ \sigma_3 = \lambda^3 t + C_3\,, \ldots$

$C_0, C_1, C_2, C_3, \ldots$ are constants.

We have done nothing in (8.24) but assert that we can write, in yet some undetermined way, the various F^s in terms of the parameters (8.25). At this point we begin to follow Sandri & Frieman's method of extension. Following them, we imagine now a function that has the same form as (8.24)

(8.26) $\bar{F}^s = \bar{F}^s(x_1, v_1, \ldots, x_s, v_s \mid \tau_0, \tau_1, \tau_2, \tau_3, \ldots)$

but here $\tau_0, \tau_1, \tau_2, \tau_3, \ldots$ are independent variables. With this function (8.26) the BBKGY chain (8.1) can be written as follows

(8.27) $$\left[\left(\frac{\partial \bar{F}^s}{\partial \tau_0}\right) + \lambda\left(\frac{\partial \bar{F}^s}{\partial \tau_1}\right) + \lambda^2\left(\frac{\partial \bar{F}^s}{\partial \tau_2}\right) + \cdots\right]_{\tau_i = \sigma_i} + H^s F^s = \lambda L^s F^{s+1}$$

Let us assume, as Sandri & Frieman do, that the following equation is also true

(8.28) $$\left[\left(\frac{\partial \bar{F}^s}{\partial \tau_1}\right) + \lambda\left(\frac{\partial \bar{F}^s}{\partial \tau_1}\right) + \lambda^2\left(\frac{\partial \bar{F}^s}{\partial \tau_2}\right) + \cdots\right] + H^s \bar{F}^s = \lambda L^s \bar{F}^{s+1}$$

The transition from (8.27) to (8.28) clearly puts some restrictions on the possible specifications of the $\tau_0, \tau_1, \tau_2, \tau_3 \ldots$ and we should check this whenever a specification is made. Following Sandri & Frieman we introduce into (8.28) the perturbation expansions

(8.28) $\bar{F}^1 = \bar{f}^0 + \lambda \bar{f}^1 + \lambda^2 \bar{f}^2 + \cdots$

(8.29) $\bar{F}^2 = \bar{F}^{20} + \lambda \bar{F}^{21} + \lambda^2 \bar{F}^{22} + \ldots$

(8.30) $\bar{F}^s = \bar{F}^{s0} + \lambda \bar{F}^{s1} + \lambda^2 \bar{F}^{s2} + \ldots$

And we obtain by equating equal orders in λ the set of equations

(8.31) $\frac{\partial \bar{f}^0}{\partial \tau_0} = 0$

(8.32) $\frac{\partial \bar{f}^1}{\partial \tau_0} + \frac{\partial \bar{f}^0}{\partial \tau_1} = L\,\bar{F}^{20}$

(8.33) $\frac{\partial \bar{f}^2}{\partial \tau_0} + \frac{\partial \bar{f}^1}{\partial \tau_1} + \frac{\partial \bar{f}^0}{\partial \tau_2} = L\,\bar{F}^{21}$

$\vdots$

(8.34) $\frac{\partial \bar{F}^{20}}{\partial \tau_0} + H^2 \bar{F}^{20} = 0$

(8.35) $\frac{\partial \bar{F}^{21}}{\partial \tau_0} + H^2 \bar{F}^{21} = L^2 \bar{F}^{30} - \frac{\partial \bar{F}^{30}}{\partial \tau_1}$

$\vdots$

(8.36) $\frac{\partial \bar{F}^{s0}}{\partial \tau_0} + H^s \bar{F}^{s0} = 0$

(8.37) $\frac{\partial \bar{F}^{si}}{\partial \tau_0} + H^s \bar{F}^{si} = L^s \bar{F}^{s+1,i-1} - \sum_{i=l+k} \frac{\partial \bar{F}^{sk}}{\partial \tau_l}$

Sandri & Frieman often use the initial conditions

(8.38) $\bar{f}^0(\tau_0 = 0) =$ arbitrary function of $\tau_1, \tau_2, \tau_3, \ldots$

(8.39) $\bar{f}^i(\tau_0 = 0) = 0 \qquad i > 0$

(8.40) $\bar{F}^{s0}(\tau_0 = 0) = \prod^s \bar{f}^0(\tau_0 = 0)$

(8.41) $\bar{F}^{si}(\tau_0 = 0) = 0$

These conditions are meaningless at this point because the dependence of $\bar{F}^s$ upon $\tau_0, \tau_1, \tau_2, \ldots$ has not yet been specified. We will have to study the initial conditions later. The solution to the zeroth order equations are the same as before, or one has

(8.42) $\bar{f}^0(\tau_0, \tau_1, \tau_2, \ldots) = \bar{f}^0(\tau_0 = 0, \tau_1, \tau_2, \ldots) = \bar{f}^0$

(8.43) $\bar{F}^{s0} = e^{-H^s \tau_0} \prod^s \bar{f}^0$

From (8.32) with (8.43) $\bar{f}^1$ satisfies

$$(8.44)\quad \frac{\partial \bar{f}^1}{\partial \tau_0} = L e^{-H^2\tau_0} \bar{f}_1^{\,0} \bar{f}_1^{\,0} - \frac{\partial \bar{f}^0}{\partial \tau_0}$$

or, for the solution of (8.44), considering only the asymptotic behavior, one has

$$(8.45)\quad \bar{f}^1 \sim \tau_0 \lim_{\eta\to\infty} L e^{-H^2\eta} \bar{f}_1^{\,0} \bar{f}_1^{\,0} - \tau_0 \frac{\partial \bar{f}^0}{\partial \tau_1}$$

To obtain the ordinary perturbation expansion, where the τ_1 is never introduced, one would put

$$(8.46)\quad \frac{\partial \bar{f}^0}{\partial \tau_1} = 0 \qquad \text{(ordinary perturbation expansion)}$$

in which case $\bar{f}^0$ is simply the initial value of the one body function. However; it is convenient to assume, and this is what Sandri & Frieman do, that the general expansion contains the series (8.22) by specifying

$$(8.47)\quad \frac{\partial \bar{f}^0}{\partial \tau_1} = \lim_{\eta\to\infty} L e^{-H^2\eta} \bar{f}_1^{\,0} \bar{f}_2^{\,0}$$

which cancels the divergence in (8.45). Without the support of a more general theory, (8.47) is no more than a guess. Let us compute $\bar{F}^{21}$; from (8.35) taking into account (8.43 and 8.47) one has

$$(8.48)\quad \frac{\partial \bar{F}^{21}}{\partial \tau_0} + H^2 \bar{F}^{21} = L^2 e^{-H^3\tau_0} \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0} + \lim_{\eta\to\infty} e^{-H^2\tau_0}\left[L_{13} e^{-H_{13}\eta} + L_{23} e^{-H_{23}\eta}\right] \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0}$$

or, with the initial value (8.91) one has the solution

$$(8.49)\quad \bar{F}^{21} = \int_0^{\tau_0} dt_1\, e^{-H^2 t_1} L^2 e^{-H^3(\tau_0 - t_1)}\, \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0}$$
$$- \lim_{\eta \to \infty} e^{-H^2 \tau_0} \int_0^{\tau_0} dt_1 \left[L_{13} e^{-H_{13}\eta} + L_{23} e^{-H_{23}\eta} \right] \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0}$$

When we consider the asymptotic behavior, $\bar{F}^{21}$ diverges

$$(8.50)\quad \bar{F}^{21} \sim \lim_{\eta \to \infty} \int_0^{\eta} dt_1\, e^{-H^2 t_1} L^2 e^{-H^3 \eta} \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0}$$
$$- \tau_0 \lim_{\eta \to \infty} e^{-H^2 \eta} \left[L_{13} e^{-H_{13}\eta} + L_{23} e^{-H_{23}\eta} \right] \bar{f}_1^{\,0} \bar{f}_2^{\,0} \bar{f}_3^{\,0}$$

And this is the same behavior (7.73) we obtain in Chapter VII. Let us suppose that we could go further with the method of extension. In that case repeated identifications of the type (8.47), or summing of series of the type (8.22) into $\bar{f}^{\,0}$, would yield an $\bar{f}^{\,0}$ that we can identify as the asymptotic one body function. With this understanding that $\bar{f}^{\,0}$ is the one body function (written in terms of the parameters $\tau_1, \tau_2, \tau_3 \ldots$) and by comparing the method of extension with our perturbation expansion of Chapter VII, in particular comparing τ_0 with σ there; we find that the method of extension is just another approximation that can be obtained from our coarse graining procedure. And, we know that these expansions diverge quite badly. To terminate this Chapter we will discuss the boundary conditions (8.38 to 8.41) of the method of extension. Due to the arbitrary constants c_0 in σ_0 (8.25) and thus an arbitrary constant in the corresponding τ_0, the point or origin from which the perturbation expansion is attempted, is arbitrary. In order to satisfy

the boundary conditions (8.38 to 8.41) and to agree with the assumption that the particles are initially uncorrelated one must state that $\sigma_0, \sigma_1, \sigma_2, \ldots$ or rather the corresponding $\tau_0, \tau_1, \tau_2, \ldots$ have the same origin. Otherwise, these boundary conditions (8.38 to 8.41) state that regardless of where the origin of τ_0 is the particles are uncorrelated and this doesn't make sense. In order to make the origin of τ_0 arbitrary, which is a more meaningful way to try to coarse grain the equations by a perturbation expansion, we must introduce the correlations that existed at the choice of origin of τ_0

$$(8.51) \qquad \bar{F}^s(\tau_0 = 0) = \prod^s \bar{f}^0 + \bar{C}^s(\tau_1, \tau_2, \tau_3 \ldots)$$

or by cluster expansion we can write

$$(8.52) \qquad \bar{C}^2(\tau_1, \tau_2, \tau_3, \ldots) = g^2(\tau_1, \tau_2, \tau_3, \ldots)$$

$$(8.53) \qquad \bar{C}^3(\tau_1, \tau_2, \tau_3, \ldots) = \bar{f}_1^0 g_{23}^2(\tau_1, \tau_2, \tau_3, \ldots) + \bar{f}_2^0 g_{13}^2(\tau_1, \tau_2, \tau_3, \ldots) + \bar{f}_3^0 g_{12}^2(\tau_1, \tau_2, \tau_3, \ldots) + g^3(\tau_1, \tau_2, \tau_3, \ldots)$$

$$\vdots$$

Sandri & Fireman, see Sandri[4], discuss their expansion method with boundary conditions similar to (8.52), (8.53), etc. We would like to stress that these correlations are not initial correlations and in general a given g^s depends upon the one body function $\bar{f}^0$.

IX. THE THEORY OF MAZUR AND BIEL

Mazur and Biel,[6] MB for short, work from the BBKGY chain (3.18) for the short-range system

$$(9.1) \quad \frac{\partial F^s}{\partial t} + H^s F^s = \lambda L^s F^{s+1}$$

where

$$(9.2) \quad L^s = \sum_{i=1}^{s} L_{i,s+1} \qquad L_{i,s+1} = \frac{N-s}{mV} \int d\underline{x}_{s+1}\, d\underline{v}_{s+1}\, \frac{\partial U_{i,s+1}}{\partial \underline{x}_i} \cdot \frac{\partial}{\partial \underline{v}_i}$$

At this stage; as shown in the $L_{i,s+1}$; the thermodynamic limit (3.27) has not been taken. Let us introduce MB's reduced momentum (velocity) distribution functions

$$(9.3) \quad f^s(\underline{v}_1, \ldots, \underline{v}_s; t) = \frac{1}{V^s} \int \cdots \int d\underline{x}_1 \ldots d\underline{x}_s \; F^s(\underline{x}_1, \underline{v}_1, \ldots, \underline{x}_s, \underline{v}_s; t)$$

and to simplify notation MB defines the operators

$$(9.4) \quad P^s = \frac{1}{V^s} \int \cdots \int d\underline{x}_1 \ldots d\underline{x}_s \; (\ldots)$$

so that the f^s may be written

$$(9.5) \quad f^s = P^s F^s$$

The distribution functions F^s can now be written

$$(9.6) \quad F^s = P^s F^s + (1-P^s) F^s = f^s + h^s$$

where

$$(9.7) \quad h^s = (1-P^s) F^s = F^s - f^s$$

Following MB we apply the operators P^s and $(1-P^s)$ respectively to the BBKGY chain (9.1) to obtain the coupled sets of equations

$$(9.8)\quad \frac{\partial f^s}{\partial t} + P^s H^s f^s + P^s H^s h^s = \lambda P^s L^s f^{s+1} + \lambda P^s L^s h^{s+1}$$

$$(9.9)\quad \frac{\partial h^s}{\partial t} + (1-P^s) H^s f^s + (1-P^s) H^s h^s = \lambda (1-P^s) L^s f^{s+1} + \lambda (1-P^s) L^s h^{s+1}$$

At this point the thermodynamic limit ($N \to \infty, V \to \infty, \frac{N}{V} = n$ finite) is taken. Under this limit MB claim that, due to the finite range of the interparticle potential, the following expression vanishes

$$(9.10)\quad P^s H^s F^s = \frac{1}{V^s} \int \cdots \int d\underline{x}_1 \cdots d\underline{x}_s \, H^s F^s \underset{N,V \to \infty}{\Rightarrow} 0$$

One has also; since the f^s do not depend on $\underline{x}_1, \ldots, x_s$;

$$(9.11)\quad K^s f^s = 0 \quad , \quad L^s f^{s+1} = 0$$

in the second of these we have assumed the system is insensitive to the walls of the container. With (9.11), and the thermodynamic limit the coupled equations (9.8 & 9.9) reduce to

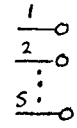
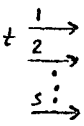
$$(9.12)\quad \frac{\partial f^s}{\partial t} = \lambda \lim_{V \to \infty} P^s L^s h^{s+1}$$

$$(9.13)\quad \frac{\partial h^s}{\partial t} + H^s h^s = I^s f^s + \lambda \lim_{V \to \infty} (1-P^s) L^s h^{s+1}$$

This separation of the BBKGY chain into these coupled equations is MB's major result and here we begin our discuss-

ion of the thoery.

Let us begin by writing the general F^s in terms of diagrams. For small s, in comparison to N, it is a good approximation to write the F^s in the form

(9.14) $F^s = e^{-K^s t}$  $+ e^{-K^2 t}$ 

here the arrows indicate the sum of diagrams where at least two of the s lines are connected: (9.14) is good enough for our purposes because soon we will consider the thermodynamic limit and we know that the general F^s approaches the form (9.14) under that limit. If we assume that initial correlations are of finite range, each diagram in the second term of (9.14) depends on interparticle distance through an overlap of the interparticle potentials and initial correlations. Under the operation P^s with the thermodynamic limit the second term in (9.14) vanishes and one has for f^s the limit

$$(9.15) \qquad f^s = \frac{1}{V^s} \int \cdots \int d\underline{x}_1 \ldots d\underline{x}_s \, F^s \Rightarrow \prod^s f'$$

This limit, rather identification, is made by MB but at a fairly advanced stage of their work. Let us check the simplifying limit (9.10); we find a non-vanishing answer

$$(9.16) \qquad P^s H^s F^s \Rightarrow \lim_{V\to\infty} P^s K^s \prod^s F' = \lim_{V\to\infty} P^s K^s \prod^s (f'+h')$$
$$= \lim_{V\to\infty} P^s K^s \prod^s h'$$

Since this limit vanishes for a homogeneous system, MB's coupled equations (9.12 & 9.13) are valid only for homogeneous systems. For an inhomogeneous system one should have the coupled equations

$$(9.17)\quad \frac{\partial f^1}{\partial t} = -\lim_{V\to\infty} P^1 K^1 h^1 + \lambda \lim_{V\to\infty} P^1 L^1 h^2$$

$$(9.18)\quad \frac{\partial h^1}{\partial t} + K^1 h^1 = \lim_{V\to\infty} P^1 K^1 h^1 + \lambda \lim_{V\to\infty} (1-P^1) L^1 h^2$$

$$(9.19)\quad \frac{\partial h^s}{\partial t} + H^s h^s = \lim_{V\to\infty} P^s K^s \prod^s h^1 + I^s \prod^s f^1 + \lambda \lim_{V\to\infty} (1-P^s) L^s h^{s+1}$$

because of the redundance (9.15) we need no longer write out the formula for f^s. The extra complication that appears in the coupled equations (9.17, 9.18 & 9.19) for an inhomogeneous system restricts their usefulness for that case. We prefer to write out an alternate to MB's theory which is simpler for an inhomogeneous system and interchangeable with their theory for a homogeneous system. From this point on we assume the thermodynamic limit is valid and has been taken in the general F^s. Our basic separation of the will be (9.14) for which we write

$$(9.20)\quad F^s = \mathcal{F}^s + C^s$$

where

$$(9.21)\quad \mathcal{F}^s = \prod^s F^1$$

We substitute (9.20) into the BBKGY chain (9.1) to obtain

$$(9.22)\quad \frac{\partial \mathcal{F}^s}{\partial t} + \frac{\partial C^s}{\partial t} + K^s \mathcal{F}^s + K^s C^s - I^s \mathcal{F}^s - I^s C^s = \lambda L^s \mathcal{F}^{s+1} + \lambda L^s C^{s+1}$$

and separate this into two equations; one where each term is free of correlations

$$(9.23)\quad \frac{\partial \mathcal{F}^s}{\partial t} + K^s \mathcal{F}^s = \lambda L^s \mathcal{F}^{s+1} + \lambda L^s_u C^{s+1}$$

and one where each term contains a correlation

$$(9.24)\quad \frac{\partial C^s}{\partial t} + K^s C^s - I^s C^s = I^s \mathcal{F}^s + \lambda L^s_c C^{s+1}$$

Here, we have split $L^s C^{s+1}$ into two terms

$$(9.25)\quad L^s C^{s+1} = L^s_u C^{s+1} + L^s_c C^{s+1}$$

one term that is free of correlations and one term that contains correlations. It is easily seen, when we draw on the cluster expansion (3.21 to 3.23) to expand C^s, that this separation (9.23 & 9.24) is valid. First of all C^2 and G^2 have the same definition

$$(9.26)\quad G^2 = C^2 = C_{12}$$

and one can show by the cluster expansion of C^{s+1} that

$$(9.27) \qquad L_U^s C^{s+1} = \sum_{i=1}^{s} L_{i,s+1}\, C_{i,s+1} \prod_{j \le s}^{j \ne i} F_j^1(\underline{v}_j, \underline{x}_j, t)$$

With (9.27) and the definition of $\mathcal{F}^s$ (9.21) one finds that (9.23) is simply an s fold redundance of the equation for $\mathcal{F}^1 = F^1$

$$(9.28) \qquad \frac{\partial F^1}{\partial t} + K^1 F^1 = \lambda L_{12} \left(F_1^1 F_2^1 + C^2 \right)$$

For comparison to MB's theory let us write our coupled equations (9.23 & 9.24) for the special case of a homogeneous system

$$(9.29) \qquad \frac{\partial \mathcal{F}^s}{\partial t} = \lambda L_U^s C^{s+1}$$

$$(9.30) \qquad \frac{\partial C^s}{\partial t} + H^s C^s = I^s \mathcal{F}^s + \lambda L_C^s C^{s+1}$$

We compare these equations with MB's (9.12 & 9.13) and we recall the effect of the operators P^s. Our equations are slightly more general because we can without loss of generality remove the restrictions that the interparticle potential and initial correlations are of finite range. For an inhomogeneous system our method is simpler than MB's because our $C^1 = 0$: in the MB equations the need for the h^1 causes excessive complication. We will now compare our equations here with the cluster expansion method we used in Chapter V to select and sum diagrams. To begin let us write down the equations for F^1, C^2, and C^3

$$(9.31)\quad \frac{\partial F^1}{\partial t} + K^1 F^1 = \lambda L_{12}\left(F_1^1 F_2^1 + C^2\right) = \lambda L_{12} F^2$$

$$(9.32)\quad \frac{\partial C^2}{\partial t} + K^2 C^2 - I^2 C^2 = I^2 F_1^1 F_2^1 + \lambda L_c^2 C^3$$

$$(9.33)\quad \frac{\partial C^3}{\partial t} + K^3 C^3 - I^3 C^3 = I^3 F_1^1 F_2^1 F_3^1 + \lambda L_c^3 C^4$$

These equations are to be compared with the "simpler" equations (5.11, 5.12 & 5.13). We obtain here the two particle collision effects without difficulty by substitution of the solution for C^2 into (9.31)

$$(9.34)\quad \frac{\partial F^1}{\partial t} + K^1 F^1 = \lambda L_{12} F^2$$
$$= \lambda L_{12}\Big[F_1^1 F_2^1 + e^{-H^2 t} C^2(0) + e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} I^2 F_1^1(t_1) F_2^1(t_1)$$
$$+ \lambda^2 L_{12}\, e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} L_c^2 C^3(t)$$

This equation is to be compared with the way we obtained our former equation (5.24). Let us write out the corresponding MB result for (9.34) for the special case of a homogeneous system.

$$(9.35)\quad \frac{\partial f^1}{\partial t} = \lambda L_{12}\Big[e^{-H^2 t} h^2(0) + e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1} I^2 f_1^1(t_1) f_2^1(t_1)\Big]$$
$$+ \lambda^2 L_{12}\, e^{-H^2 t}\int_0^t dt_2\, e^{H^2 t_1}\Big[\lim_{V\to\infty} (1 - P^s)\, L^2 h^3(t_1)\Big]$$

We could extend the solution of (9.34) or (9.35) to any order in λ. Though these solutions are correct we find them inconvenient due to the special operators L_c^s or the

corresponding $\lim_{V \to \infty} (1 - P^s)$ which appear in the solutions. Working from the cluster expansion equations (5.9) gives a more transparent answer. This concludes our remarks about Mazur & Biel's theory.

X. CONCLUSION

The aim of this thesis was to discuss Bogoliubov's theory of classical irreversible statistical mechanics. To do this we developed a theory that stems from the diagram techniques of Pigogine and coworkers. We have found our theory sufficiently general for us to obtain the theory of Bogoliubov as a special case. We have shown that Bogoliubov's expansion diverges quite badly. Even to obtain the Boltzman equation Markowian correction terms must be introduced, and these terms diverge. This evidence gives us sufficient doubt if Bogoliubov's derivation of the Boltzman equation is significant. These results and doubts carry over to our discussion of the theory of Sandri & Frieman; their theory is similar to Bogoliubov's. To show the versatility of our expansion techniques we have discussed the theory of Mazur & Biel; a theory that has little resemblance to Bogoliubov's.

BIBLIOGRAPGY

1. N.N. Bogoliubov, Stud. Stat. Mech., 1, 11 (1962).

2. I. Prigogine, "Non-Equilibrium Statistical Mechanics", Interscience, New York, (1962).

3. G. Severne, Physica, 31, 877 (1965).

4. G. Sandri, Ann. Phys., 24, 332 (1963); 24, 380 (1963).

5. E.A. Frieman, J. Math. Phys., 4, 410 (1963).

6. P. Mazur & J. Biel, Physica, 32, 1633 (1966).

7. I. Prigogine & P. Resibois, Physica, 27, 629 (1961).

8. J. Stecki & H.S. Taylor, Rev. Mod. Phys., 37, 762 (1965).

9. J. Brocas & P. Resibois, Physica, 32, 1050 (1966).

10. E. Braun & L.S. Garcia-Colin, Phys. Let., 23, 460 (1966).

11. M.S. Green, J. Chem. Phys., 25, 836 (1956).

12. P. Resibois, Phys. Fluids, 6, 817 (1963).

13. E.G.D. Cohen & J.R. Dorfman, J. Math. Phys., 8, 282 (1967).

Appendix I.

In this appendix we show that diagrams with a type (c) vertex (3.6) integrate to zero. Let us consider a diagram with a type (b) or (c) vertex where the line labelled j first appears. Look at the expression $\frac{\partial U_{ij}}{\partial \underline{x}_j} \cdot \frac{\partial}{\partial \underline{v}_j}$ in I_{ij} and at the integral

$$\text{(A1.1)} \quad D = \cdots J(\{\underline{x}_r, \underline{v}_r\}_{r \neq j}) \int \frac{d\underline{x}_j}{V} d\underline{v}_j \, e^{K_{ij} t_m} \frac{\partial U_{ij}}{\partial \underline{x}_j} \cdot \frac{\partial}{\partial \underline{v}_j} G(\{\underline{x}, \underline{v}\})$$

Here, the set $\{r\}$ represents the particle labels used to the left of the vertex considered. This expression becomes, with the help of the relation (2.9)

$$\text{(A1.2)} \quad D = \cdots J(\{\underline{x}_r, \underline{v}_r\} e^{K_i t_m} \int \frac{d\underline{x}_j}{V} d\underline{v}_j \frac{\partial U_{ij}}{\partial \underline{x}_j} \cdot \frac{\partial}{\partial \underline{v}_j} G(\{\underline{x}, \underline{v}\})$$

Use of Green's theorem in the velocity integral gives

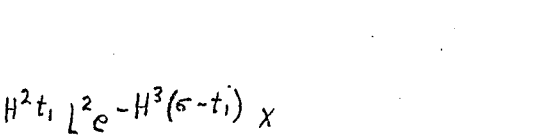
$$\text{(A1.3)} \quad \int \frac{\partial}{\partial \underline{v}} \phi \, d\underline{v} = \oint \phi \, d\vec{s}$$

The integral then vanishes because the velocity distribution vanishes sufficiently fast at infinity. We have thus a simplification of (b) type vertices and by performing the calculation twice we see that diagrams with a (c) type vertex vanish.

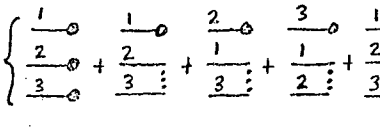
Appendix II

In this appendix we show that the $\bar{F}^{21}$ obtained in (7.65) gives in ordinary time the first order term obtained in (6.10). To obtain in ordinary time a solution for F^{21} from $\bar{F}^{21}$ we consider the special case of (7.65) where σ and t have the same origin, or where $t_0 = 0$. One has taking into account (7.56 & 7.57 with 7.39 & 7.40) for the functions $C^{si}(e^{K't}F'|0)$ and the definition of the operator $\bar{\mathfrak{D}}'$ the following expression for $\bar{F}^{21}(e^{K't}F'|\sigma)$

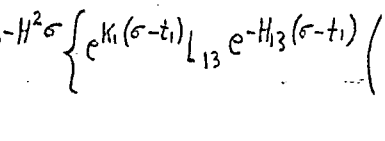
(A2.1) $$\bar{F}^{21}(e^{K't}F'|\sigma) = \int_0^\sigma dt_1\, e^{-H^2 t_1} L^2 e^{-H^3(\sigma - t_1)} \times$$



$$- \int_0^\sigma dt_1\, e^{-H^2\sigma} \Big\{ e^{K_1(\sigma - t_1)} L_{13}\, e^{-H_{13}(\sigma - t_1)} \Big($$

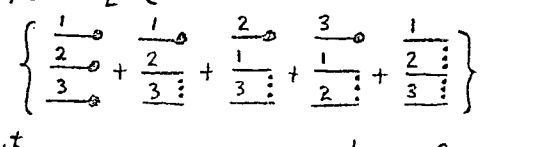


$$+ e^{K_2(\sigma - t_1)} L_{23}\, e^{-H_{23}(\sigma - t_1)} \Big($$

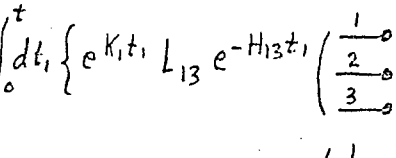


And for the corresponding F^{21} we have, with some changes in the variables of integration, the expression

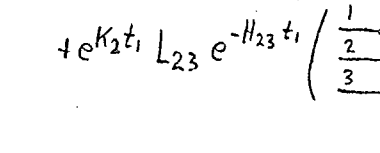
(A2.2) $$F^{21}(e^{K't}F'|t) = e^{-H^2 t} \int_0^t dt_1\, e^{H^2 t_1} L^2\, e^{-H^3 t_1}$$



$$- e^{-H^2 t} \int_0^t dt_1 \Big\{ e^{K_1 t_1} L_{13}\, e^{-H_{13} t_1} \Big($$

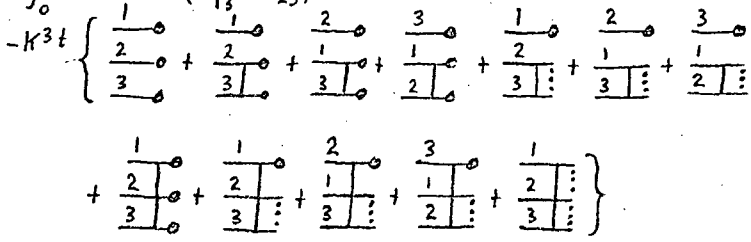


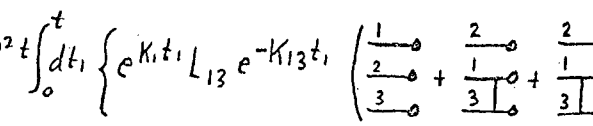
$$+ e^{K_2 t_1} L_{23}\, e^{-H_{23} t_1} \Big($$

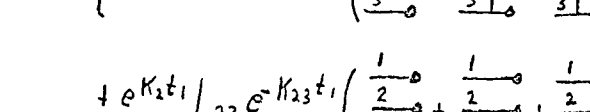


With notation of the type (5.18, 5.19, 5.20, etc.) we can write (A2.2)as follows

(A2.3) $F^{21} = e^{-H^2 t}\int_0^t dt_1\, e^{H^2 t_1}\left(L_{13}+L_{23}\right) \times$

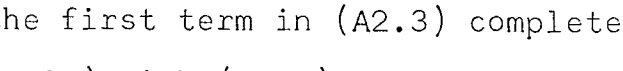
$e^{-K^3 t}\Big\{$ 

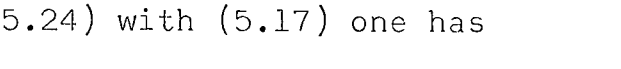
$-\,e^{-H^2 t}\int_0^t dt_1 \Big\{ e^{K_1 t_1} L_{13}\, e^{-K_{13} t_1}\Big($ 

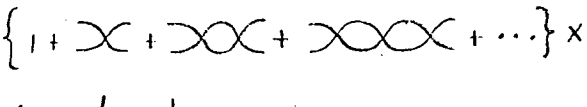
$+\, e^{K_2 t_1} L_{23}\, e^{-K_{23} t_1}\Big($ 

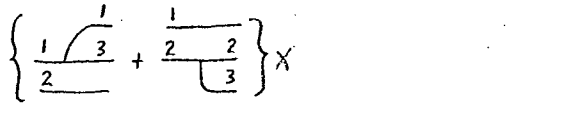
Let us expand the first term in (A2.3) completely, or by comparison of (5.24) with (5.17) one has

(A2.4) $F^{21} = e^{-K^2 t}\Big\{1 +$  $\Big\} \times$

$\Big\{$  $\Big\} \times$

$\Big\{$ 

$-\,e^{-H^2 t}\int_0^t dt_1 \Big\{ e^{K_1 t_1} L_{13}\, e^{-K_{13} t_1}\Big($ 

$+\, e^{K_2 t_1} L_{23}\, e^{-K_{23} t_1}\Big($ 

One sees that (A2.4) contains diagrams with fragments that connect in by one line. We know from Chapter IV that such behavior always contributes to lower order terms; in this case to F^{20}. Thus we should, with the second term in (A2.4), be able to cancel diagrams with fragments that connect in by one line. Further, as a remainder in the second term we should obtain the Markowian correction terms shown in (6.10) that contribute to F^{21}. Let us introduce in the second term of (A2.3 or A2.4) the identity

$$\text{(A2.5)} \qquad 1 = e^{H^2 t_1} e^{-K^2 t_1} + \int_0^{t_1} dt_2\, e^{H^2 t_2}\, I^2\, e^{-K^2 t_2}$$

so that this second term may be written in the following way

$$\text{(A2.6)} \quad -e^{-H^2 t}\int_0^{t} dt_1\, e^{H^2 t_1}\Big\{ L_{13}\, e^{-K^3 t_1}\Big(\underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} \Big)$$

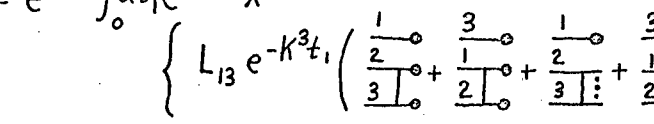
$$+ L_{23}\, e^{-K^3 t_1}\Big(\underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} \Big)\Big\}$$

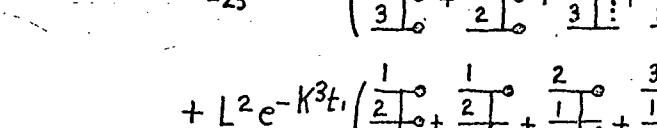
$$-e^{-H^2 t}\int_0^{t} dt_1 \int_0^{t_1} dt_2\, e^{H^2 t_2}\, I^2\, e^{-K^2 t_2}\Big\{ e^{K_1 t_1} L_{13}\, e^{-K_{13} t_1}\Big(\underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} \Big)$$

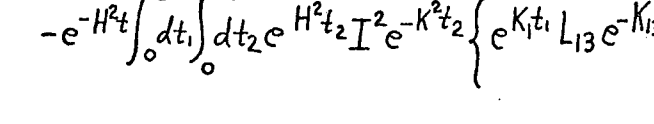
$$+ e^{K_2 t_1} L_{23}\, e^{-K_{23} t_1}\Big(\underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} + \underset{3}{\overset{1}{\overset{2}{\circ}}} \Big)\Big\}$$

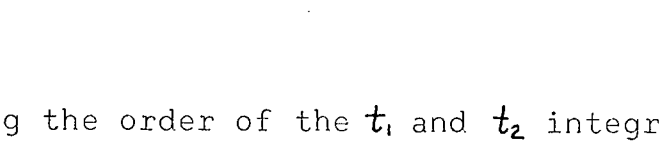
With this expression for the second term in (A2.3) or (A2.4) we obtain the desired cancellation of diagrams with fragments that connect in by one line; one has

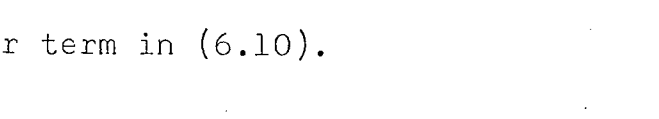
(A2.7) $F^{21} = e^{-H^2 t}\int_0^t dt_1 e^{H^2 t_1} \times$

$\Big\{ L_{13}\, e^{-K^3 t_1}\Big($  $\Big)$

$+ L_{23}\, e^{-K^3 t_1}\Big($  $\Big)$

$+ L^2 e^{-K^3 t_1}\Big($  $\Big)\Big\}$

$- e^{-H^2 t}\int_0^t dt_1 \int_0^{t_1} dt_2\, e^{H^2 t_2} I^2 e^{-K^2 t_2}\Big\{ e^{K_1 t_1} L_{13}\, e^{-K_{13} t_1}\Big($  $\Big)$

$+ e^{K_2 t_1} L_{23}\, e^{-K_{13} t_1}\Big($  $\Big)\Big\}$

By changing the order of the t_1 and t_2 integrations in the second term, we see that (A2.8) is the same expression as the first order term in (6.10).