T H E   U N I V E R S I T Y   O F   M I C H I G A N

COLLEGE OF ENGINEERING

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Technical Report

IRREVERSIBLE STATISTICAL MECHANICS OF MODERATELY DENSE FLUIDS

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ABSTRACT

Primary attention is given to the calculation of time-relaxed probability densities and associated correlation functions for particles moving through an equilibrium assembly of like particles.

An integro-differential equation describing the temporal evolution of the probability densities is obtained from the Liouville equation. In contrast to the BBGKY hierarchy, the derived equation contains all the information necessary for its solution; i.e., the kinetic equation for a reduced probability density does not contain integrals over unknown higher order densities.

The kinetic equation for the one-particle density is studied in detail. An expansion for the collision integral appearing in this equation is obtained such that effects of interparticle forces are represented by terms of increasingly higher order. Collision integral terms through the "fourth power of the forces" are obtained explicitly.

Solution of the kinetic equation is obtained by an iteration procedure in which the zeroth order terms are those which would be the only ones appearing were the assembly an ideal gas. Higher order terms are coupled with constants which are, effectively, increasingly higher powers of the ratio of potential to kinetic energy of the assembly.

The time-relaxed momentum density is obtained from the full probability density by integrating over spatial coordinates. Corresponding expansions are obtained, also, for some related correlation functions (e.g., the momentum auto-correlation function).

An expansion for the "self" part of the spatial two-time density $G_s(r,t)$, is also found in direct correspondence with the expansion obtained for the full μ-space density. The general functional form of this expression is derived and explicit evaluation is made of the low order terms of the expansion. By taking Fourier transforms with respect to space and time, expressions are obtained for the classical "scattering functions" for incoherent scattering of slow neutrons. Corrections for the purpose of obtaining the proper quantum mechanical scattering functions are discussed

Bogoliubov type equations are also investigated in order to obtain kinetic equations pertinent to a density expansion of the one particle probability function. Methods previously developed for model systems interacting solely through repulsive forces are extended to systems for which attractive terms are also present in the interparticle potentials. The asymptotic collision integrals present in the kinetic equation appear as coefficients of a <u>double</u> expansion in $\mathcal{C}$ and $\mathcal{EC}$, where $\mathcal{C}$ is the density, and $\mathcal{E}$ is a coupling constant

ABSTRACT (Concluded)

related to the ratio of potential to kinetic energies of the assembly. Approximate expressions for the two-particle probability density, consistent with the assumptions employed in the derivation of the kinetic equation for the one-particle density, are also derived.

Finally, investigation of the "distinct" part of the two-time spatial density, $G_d(r,t)$, is initiated. A relationship between the "convolution approximation" for $G_d(r,t)$ and the superposition approximation for the two-particle density is explicitly demonstrated.

CHAPTER I

INTRODUCTION

This investigation was undertaken with two goals in
mind. One was the expectation of obtaining a better under-
standing of the manner in which the cross section for
scattering of slow neutrons from matter is dependent upon
the detailed properties of the scattering medium. The other
was to study the possibilities of calculating, from first
principles, certain probablity densities arising in theories
of non-equilibrium statistical mechanics.. The emphasis in
this thesis probably falls upon the latter.

Specifically, major effort is directed towards the
derivation and subsequent solution of equations providing
the temporal evolution of conditional probability densitites
for locating particles moving within an equilibrium as-
sembly. A particular example of these functions is $G(r,t)$,
the probability density for finding a particle in the
neighborhood of a point of <u>configuration</u> space at time t,
conditioned upon the presence of a particle being located
at a different specified point at some specified earlier
time. This quantity is of particular interest and importance
because of its relation to the scattering cross-section.[1]

The work which follows is presented in subdivisions
of eight chapters. <u>Chapter</u> <u>two</u> is primarily a brief review
of various techniques employed in other studies of non-

equilibrium statistical mechanics where the goal is to obtain kinetic equations from the Liouville equation. Included in this section, also, is a statement of the relationship between the neutron scattering cross-section and the time-relaxed spatial density, $G(r,t)$.

In <u>chapter</u> <u>three</u>, kinetic equations are obtained from the Liouville equation to describe the temporal evolution of reduced time-relaxed probability densities. Although the work was inspired by a method used by Zwanzig[2] in his studies of the statistical mechanics of non-equilibrium systems, the equations obtained differ quite significantly from any which have previously appeared in the literature.

The kinetic equation for the one-particle time-relaxed density is further investigated in <u>chapter</u> <u>four</u>. Considerable effort is expended in obtaining pertinent expansions for the collision integral appearing in the equation.

An iteration scheme for the solution of this equation consistant with the expansion of the collision integral, is developed in <u>chapter</u> <u>five</u>. The resulting expressions have the form of expansions in terms related, roughly, to powers of the ratio of potential to kinetic energies of the assembly. From the full μ-space density, momentum densities and related time-relaxed expectations and correlation functions are obtained. Some brief remarks are made concerning the calculation of the dielectric constant for partially ionized gases.

In <u>chapter</u> <u>six</u>, major effort is expended in calculating the "self" part of the time-relaxed spatial density, $G_s(r,t)$. Corresponding expressions for the incoherent part of the neutron scattering cross-section are determined and comparison is made with some expressions based upon various proposed approximation schemes.[**] Relationships between $G_s(r\ t)$ (classical) and the exact quantum-mechanical cross-section are stated.

The work of chapters 4-6 provides expressions for conditional densities and related correlation functions which are, essentially, expansions in inverse powers of the temperature. As an alternative, in <u>chapter</u> <u>seven</u> Bogoliubov type kinetic equations[3] are developed to provide <u>density</u> expansions for these quantities. Equations pertinent to the study of the evolution of the time-relaxed densities are developed and, by employing a double expansion, the Bogoliubov methods originally developed for model systems interacting solely through repulsive forces are extended to systems for which attractive terms are also present in the interparticle potentials. An approximation for the two particle probability density is also obtained.

<u>Chapter</u> <u>eight</u> deals mainly with calculations of the distinct part of the conditional spatial density, $G_d(r,t)$,

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[**] e.g., the "Gaussian approximation" for determination of scattering cross-sections.

and associated contributions to the neutron scattering cross-section.

The main results of this study are summarized in <u>chapter nine</u>.

Much of the material appearing on the following pages is new, at least in detail, if not in basic concept The original Zwanzig kinetic equations have been modified and extended for the purpose of obtaining equations appropriate to this particular non-equilibrium problem. Expansions of the collision integrals appearing in these equations are also obtained for the first time. The kinetic equations have been developed without the imposition of frequently employed approximations such as time smoothing or termination of a hierarchy.

From the kinetic equations, expressions are obtained for various probability densities and correlation functions, These expressions are also new, although expansions for the dielectric constant and the resulting functions which are obtained from the correlation functions have already appeared in similar form elsewhere. However, particularly for the scattering functions it is felt that the discussion in this thesis more clearly demonstrates the effect of variation in temperature.

The studies of the Bogoliubov methods which appear in chapter 7 are somewhat of a deviation from the main pattern of this investigation. However, they are included because

they are an interesting continuation of the investigations
which have previously appeared in the literature. The ex-
tension of the theory to systems with attractive forces,
while requiring some new calculation, is quite straight-
forward. However, when one tries to obtain expressions for
the two particle densities, modifications are necessary be-
cause the usual BBGKY hierarchy (which underlies the theory)
does not apply here. After making necessary corrections,
expansions for the two particle time-relaxed density are
obtained consistent with assumptions used to obtain a kinetic
equation for the one-particle density .

A major problem in the field of non-equilibrium statisti-
cal mechanics is that there are almost as many approaches
to a problem as there are researchers investigating it. This
chaos is probably more apparent than real, and the equivalence
of various theories is being quite rapidly elucidated. [4]
The particular methods used in this thesis were chosen sim-
ply because they seemed best for the particular problem
at hand. This point is discussed at greated length in the next
chapter.

Note that most of the calculations of this report fall
within the context of classical statistical mechanics, In
many studies of phenomena investigated by statistical
mechanics, classical theory has preceded and suggested an-
alogous quantum theories. Although quantum theories already
exist, explicit calculations are few; perhaps, in this sense,

the studies appearing here can be considered preliminary to a more "basic" quantum calculation. However, it must be pointed out that many physical phenomena of macroscopic nature seem to be adequately represented by the classical theories, and the calculations appearing in this study certainly have meaning with relation to such investigations.

A limitation that should be acknowledged here is that, mainly for calculational convenience, in chapter four (and ff.) is imposed the requirement that the internal potential energy of the assembly is to be represented by purely additive pair potentials. Furthermore, at various points it is assumed that the medium is isotropic, As a result, the investigation is restricted to a study of fluid assemblies. These assumptions are commonly employed in non-equilibrium studies of statistical mechanics of course, it is to be expected that as our understanding develops, extensions of the theory will be made to somewhat more complicated systems.

CHAPTER II

REVIEW

It is well known that the scattering cross-section for neutrons is strongly dependent upon the dynamical behavior of the scattering medium. For low energy neutrons (for which s-wave scattering is predominant), for a system in which the directions of nuclear spins are uncorrelated and where the distribution of isotopic species is random, if one uses a Fermi-pseudopotential [5] to represent neutron-nuclei interactions, the first Born approximation provides the following expression for the differential scattering cross-section: [1,6,7]

$$\frac{\partial^2 \sigma}{\partial \Omega \partial \omega} = \frac{1}{4\pi\hbar} \frac{K'}{K_o} \left(a_{coh}^2 \, S_{coh}(\vec{k},\omega) + a_{inc}^2 \, S_{inc}(\vec{k},\omega) \right) \qquad \ldots \quad (2.1)$$

In the above,

$$\ldots \quad (2.2)$$

E_o = the energy of the incident neutron; E' = the energy of the scattered neutron; K_o and K' are the associated wave-numbers; $\omega = \hbar^{-1}(E_o - E')$; $\vec{k} = (\vec{K}_o - \vec{K}')$; and, a_{coh} and a_{inc} are the (energy independent) coherent and incoherent scattering lengths, respectively.

For monatomic systems, the "scattering functions" are defined by:

$$S_{coh}(\vec{k},\omega) \equiv \int d\vec{k} \, dt \, e^{-i[\omega t - \vec{k}\cdot\vec{r}]} G(r,t) \qquad \ldots \quad (2.3a)$$

and

$$S_{inc}(\vec{k},\omega) \equiv \int d\vec{k} \, dt \, e^{-i[\omega t - \vec{k}\cdot\vec{r}]} G_s(r,t) \qquad \ldots \quad (2.3b)$$

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$G(r,t)$ and $G_s(r,t)$ are defined by:

$$G(r,t) \equiv 1/n \quad < \sum_{j,k=1}^{n} \int \delta(\vec{r}+\vec{q}_k(0)-\vec{r}') \; \delta(\vec{r}'-\vec{q}_j(t)) \; d\vec{r}' > \qquad \text{.... (2.4a)}$$

and

$$G_s(r,t) \equiv 1/n \quad < \sum_{j=1}^{n} \int \delta(\vec{r}+\vec{q}_j(0)-\vec{r}') \; \delta(\vec{r}'-\vec{q}_j(t)) \; d\vec{r}' > \qquad \text{.... (2.4b)}$$

n = the number of particles in the scattering assembly.

$q_k(0)$ and $q_j(t)$ are the positions of the kth nucleus at $t = 0$, and of the jth nucleus at time t, respectively.

The expectation values denoted by $< \ldots >$ are to be taken with respect to the distribution of initial states of the scattering system.

Thus, it is seen that the dependence of the cross-section on the scattering medium is manifest through the G functions. It is also to be noted that the G functions are determined only by the properties of the scattering medium.

In the classical limit, these expressions have well understood meaning:

$$\text{.... (2.5a)}$$

$G(r,t)$ = the probability density for finding a particle in the neighborhood of r at time t, given that there was a particle at $r = 0$ at $t = 0$;

$$\text{.... (2.5b)}$$

$G_s(r,t)$ = the probability density for finding a particle at r at time t, given that the same particle was at $r = 0$ at $t = 0$.

It is quickly seen that, in the interpretation of classical mechanics, 2.5a follows from 2.4a. Viz., by definition,

$$G(r,t) \equiv 1/n \; < \sum_{k,j} \int d\vec{r}' \; [\; \delta(\vec{r}+\vec{q}_k(0)-\vec{r}') \; \delta(\vec{r}'-\vec{q}_j(t)) \;] \; >$$

$$= 1/n \; \sum_{k,j} \int d\vec{r}' \; < \delta(\vec{r}+\vec{q}_k(0)-\vec{r}') \; \delta(\vec{r}'-\vec{q}_j(t)) \; >$$

But, the classical joint expectation of any quantity,

$< J_1(X_t)J_2(X_0) > $, is defined by

$$< J_1(X_t)J_2(X_0) > \; = \int dX_0 \int dX \; J_1(X)J_2(X_0) \; f(X_0) \; f(X;t|X_0) \quad \ldots (2.6)$$

where $J(X)$ is a function of the phase variable $X \equiv (\vec{x}_1,..,\vec{x}_s)$. $f(X_0)$ is the probability density for X at $t = 0$; $f(X;t|X_0)$ is the conditional density for X @ t, given that at $t = 0, X_0$.

Thus,

$$G(r,t) = 1/n \; \sum_{k,j} \int d\vec{r}' \int d\vec{q}_{k_0} d\vec{q}_{j_t} \; \delta(\vec{r}+\vec{q}_k(0)-\vec{r}')\delta(\vec{r}'-\vec{q}_j(t)) \;)f(\vec{q}_j;t|\vec{q}_{k_0})f(\vec{q}_{k_0})$$

$$= 1/n \; \sum_{k,j} \int d\vec{r}' \int d\vec{q}_{k_0} \; \delta(\vec{r}+\vec{q}_k(0)-\vec{r}') \; f(\vec{r}'|\vec{q}_{k_0};t) \; 1/\Omega$$

where the integration has been performed over $q_j(t)$. It has been noticed that, because the scattering system is assumed to be in thermal equilibrium** $f_0(q_{k_0}) = 1/\Omega$, where Ω is the volume occupied by the assembly. Next, performing the integration over r':

**Here, we assume also that the scattering system is isotropic.

$$G(r,t) = 1/n \sum_j \sum_k \int d\vec{q}_{k_o} \; f_{j,k}(\; \vec{r}+\vec{q}_{k_o} \; | \vec{q}_{k_o} \; ; t \;) \; /\Omega$$

But, $f(\; \vec{r}+\vec{q}_{k_o} \; | \vec{q}_{k_o} \; ;t) = f(\; \vec{r} \; |0;t \;)$. Recognizing this, and summing over k and j after performing the integration over $\vec{q}_o$:

$$G(r,t) = f^{self}_{k,k}(\; r|0; \; t \;) + (n-1) \; f^{distinct}_{j,k}(\; r|0; \; t \;) \; ,$$

In the above equation, $f^{self}_{k,k} \; (r \; |0;t)$ is the probability density for finding the kth designated particle in the neighborhood of r, given that it was at $r = 0 \; @ \; t = 0$; $f_{j,k} \; (r|0;t)$ is the probability density for finding the jth particle at r @ time t, given that the kth designated particle (j $\neq$ k) was located at $r = 0 \; @ \; t = 0$.

Thus,

$$G_s(r,t) = f^{self}(\; r|0; \; t \;) \qquad \ldots\ldots \qquad (2.7a)$$

Frequently, there is also defined:

$$G_d(r,t) = (n-1) \; f^{dist\cdot}(\; r|0; \; t \;) \qquad \ldots\ldots \qquad \text{** } (2.7b)$$

**Anticipating, somewhat, we note that

$$G_d(r,0) = c \; g_2(r)$$

, with $g_2(r)$ defined by eqn. 4.19. c is the average density of the assembly:
$c = (n-1)/ \; \Omega$.

A number of investigators have considered the possibility
of expressing the neutron scattering cross-section in terms
of the classical G functions given by 2.5 and 2.7. Of course,
the actual cross-section requires calculation of the quantum
function defined by 2.4. However, theories have been devised[8-11]

for the purpose of relating the exact cross section to
scattering functions, $S(k, \omega)$, determined from the 'classi-
cal' G functions. Clearly, there is some advantage to pro-
ceeding in this way, if for no other reason than to provide
the investigator of eqn. 2.4 an opportunity to utilize some
of the results of the extensive inquiry already made into
similar problems which have been studied by the methods of
classical statistical mechanics.

However, the calculation of $G(r,t)$ is just a part of
a much larger program. The problem is basically as follows.
Given the initial positions and momenta of a group of
classical particles which are a subset of a collection of
like particles, we wish to know the probability density for
finding the subset in the neighborhood of a given point in
their phase space at some later time. Furthermore, let it
be postulated that the complete collection is at thermal
equilibrium and has a canonical distribution of positions
and momenta in Γ-space.

Thus, we wish to find some way of calculating $f_{s,s}$
$(X_s;t|X_{s_o})$ ** which, when multiplied by $dx_1 \ldots dx_s$, is the

**X_s is the six-s dimensional vector, $(x_1, \ldots, x_s)$. x_i is
the 6-dimensional vector, (q_i, p_i).

probability of finding particle #1 in a differential volume

element dx_1 about x_1, etc., at time t, given that at zero

time the particles were located at $x_{1_0}, \ldots, x_{s_0}$. $f_{s,s}(X_s; t| X_{s_0})$

is often referred to, in the following, as the conditional or

time-relaxed s-particle probability density.

But, how to calculate such quantities? All that is

really known is that the temporal dependence of the density

for the totality of particles in the assembly, n, is given

by the classical Liouville equation, viz.,

$$\frac{\partial f_{n,n}}{\partial t}(X_n; t|X_{s_0}) = [H_n(X_n); f_{n,n}] . \qquad \ldots\ldots \quad (2.8)$$

$H_n(X_n)$ is the total Hamiltonian for the system; $f_{n,n}(X_n; t| X_{s_0})$

is the n-particle probability density; the bracket notation

is the usual Poisson bracket, viz.,

$$[H ; f_{n,n}] = \sum_{1 \leq i \leq n} (\vec{\nabla}_{q_i} H \circ \vec{\nabla}_{p_i} f_{n,n} - \vec{\nabla}_{p_i} H \circ \vec{\nabla}_{q_i} f_{n,n}) .$$

One needs to obtain, from 2.8, a kinetic equation providing

the temporal evolution of the s-particle density of interest,

$f_{s,s}(X_s; t |X_{s_0})$. Then, one must solve the equation!

The deduction of appropriate kinetic equations for

reduced densities is a central problem in non-equilibrium

statistical mechanics. Although most efforts have been di-

rected towards obtaining kinetic equations for "distribution

fucntions" other than the conditional densities of interest

here, it is pertinent and instructive to review some of the

techniques employed in those studies as a prelude to calcu-
lations carried on later in this report.

A first advance in the general theory of non-equilibrium
statistical mechanics came with the deduction,[12-14] from the
Liouville equation, of a hierarchy of coupled integro-differ-
ential equations giving the evolution of many particle, reduced
distribution functions. This set of equations, often referred
to as the BBGKY hierarchy, provides the temporal evolution
of an $(s-1)$ particle distribution function in terms of the
next highest, i.e., (s) particle distribution. Frequently,**
the set may be written as follows:

$$\frac{\partial f}{\partial t}_{s,s} - [H_s ; f_{s,s}] = (n-s) \int d\vec{x}_{s+1} [\sum \phi(\vec{q}_j - \vec{q}_{s+1}); f_{s+1,s+1}]$$

$$\ldots\ldots\ldots \quad (2.9)$$

Unfortunately, this is an almost empty scheme, because to
determine the sth order distribution one must know, first,
higher order distributions which are themselves to be deter-
mined from similarly open equations.

Of course, one might try to find some way of terminating
the chain of kinetic equations at low order. Commonly em-
ployed is the "superposition approximation", which consists
of assuming that the $s+1^{st}$ order distribution is propor-
tional to products of s order distributions. E.g., to termi-
nate the BBGKY hierarchy at second order, it is assumed that[15]

_____

** ...but, not always; cf., appendix F.

$$f_3(x_1,x_2,x_3) = f_2(x_1,x_2)f_2(x_1,x_3)f_2(x_2,x_3)/f_1(x_1)f_1(x_2)f_1(x_3).$$

Unfortunately, the applicability of this approximation is still controversial[16] ; it is known that, for the equilibrium case, the superposition approximation fails to provide the correct virial coefficients for a gas beyond the third coefficient.[17] Also, there is lacking in this theory a logical prescription for demonstrating the progressively more important contributions of higher order collisions[18] , an effect which is demonstrated in certain other theories.**

For example, Bogoliubov[3,12] , using an elegant functional analysis, obtained a temporal equation for the one particle distribution which not only contains terms involving higher order collisions ad infinitum, but remarkably demonstrates that the higher order collision effects are associated with a power series expansion of the density. Unfortunately, the kinetic equation is provided in a functional form which, although formally correct, is in practise limiting in that many-body determanistic mechanical problems must first be solved before the theory is applicable to dense gases. However, the Bogoliubov theory is of considerable help in understanding the validity of commonly employed kinetic equations such as the Vlasov and Boltzmann gas equations.[3,20,21]   Although

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** On the other hand, it has been shown that the super-position approximation can be used to terminate the BBGKY hierarchy so long as one doesn't demand information about the distribution functions inconsistent with the order of the approximation used in the termination.[19]

kinetic equations obtained by other methods from the basis of the analysis of most of this report, Bogoliubov type equations are considered in some detail in chapter 7, below.**

Motivated by the success of theories of Brownian motion, in which the detailed motion of a particle is replaced by a sum of average motions over small periods of time, there have been developed various theories for "course grained" distribution functions. Notable among these are the theories of Kirkwood and his associates ## Important work has been performed, using these theories, in obtaining expressions for linear transport coefficients in dense fluids. The origins and validity of the Boltzmann equation have also been clarified to a great extent.

The distribution functions investigated by these methods are "time smoothed" functions,

$$\tilde{f}_{s,s}(X_s;t) \equiv 1/\tau \int_0^\tau d\rho \int dx_{s+1} \cdots dx_n \, f_{n,n}(X_n;t+\rho) \, ,$$

defined for small but finite τ . Unfortunately, when calculating the neutron scattering cross-sections the short time behavior of the G-functions (eqn. 2.5) is quite important and it is to be expected that course graining would introduce

**In addition to the great difficulty in obtaining solutions to equations of this type, their derivation requires the imposition of some restrictive assumptions concerning the functional dependence of the higher order distributions upon those of lower order. (Hollinger[22] has indicated that these assumptions imply a lack of correlations between particles before collision, an assumption akin the Strosszahlansatz of Boltzmann.[18]

##For an excellent review of Kirkwood's work and the subsequent work of Rice, et al., cf. Rice and Frisch.[23]

error. Also, the introduction of course-graining requires
approximation at the earliest step in the analysis; one would
prefer to defer making approximations until it is demonstrated
that no further progress is possible without them.

The same objections pertain to theories in which other
types of course graining (e.g., in phase space) are intro-
duced.

Prigogine and collaborators[24,25,26] have developed an
elegant scheme to obtain equations describing the temporal
behavior of systems close to equilibrium. Their scheme
involves a Fourier expansion in configuration space of the
general n-particle distribution function, after which the
temporal evolution of the expansion coefficients is investi-
gated. An elaborate diagram scheme, analogous to those used
in the quantum theory of fields, has been developed to expe-
dite evaluation of contributions to the kinetic equations
for coefficients; in effect, the BBGKY hierarchy is replaced
by a hierarchy in momentum space only. Unfortunately, this
work is not directly applicable to the study of short time
evolution of a distribution function differing significantly
from the equilibrium distribution. Although the Prigogine
methods could, undoubtedly, be modified so as to be applicable
to the study of such problems, the methods which are used
in this thesis for that purpose seem, at the outset, to be
somewhat simpler and are, for that reason, preferred.

It is interesting to note that the Prigogine methods

and the Bogoliubov methods, while seemingly very different and each involving a great deal of specialized difficult analysis, have both been used to obtain an identical equation for the evolution of the one particle distribution function for an ionized gas. [21,26]

The schemes for obtaining kinetic equations, described on the last few pages, have been applied to investigations other than the calculation of the conditional probability densities defined on p. [11]. Relatively little attention has been paid to the latter problem. An attempt to derive integro-differential equations giving the temporal evolution of, _specifically_, the _conditional_ densities was made by Vineyard. [27] Starting with the Liouville equation, he derived a double set of equations (which reduce to a single set for a stationary assembly) analogous to the BBGKY hierarchy of the usual non-equilibrium theory. But, as before, there remains the problem of terminating the chain.

A phenomenological probabilistic calculation of time-relaxed pair correlation functions has been performed for dilute gases by Christov. [28] However, there is little clue furnished concerning the actual calculation of the kernels appearing in this theory. A knowledge of the latter is necessary before application of the theory can be made.

Thus, the calculation of time-relaxed densities is still very much an open question. Each of the methods discussed above is in some way not appropriate to the task

of obtaining kinetic equations applicable to this study. But, we have not yet mentioned a procedure only relatively recently suggested. By defining the projection operator,

$Pr \equiv 1/\Omega^n \int dq_1 \ldots \int dq_n$, and manipulating the Liouville equation in a clever way, Zwanzig derived [2,29] the following equation for the one particle non-equilibrium momentum density:

$$\frac{\partial f}{\partial t}_{0,1}(p_1;t) = \int d\vec{p}_2 \ldots d\vec{p}_n \left(PrL \int ds \ e^{s(1-Pr)L} (1-Pr)L \ f_{0,n}(p_1,\ldots,p_n;t-s) \right. +$$

$$\left. + Pr \ L \ e^{t(1-Pr)L} (1-Pr) \ f_{n,n}(X_n;0)\right). ** $$

Although $f_{0,1}(p_1;t)$ is dependent upon the n-particle density, $f_{0,n}(p_1,\ldots,p_n;t)$, there is no dependence upon any unknown spatial probability density. As such, this equation is already an improvement over the BBGKY hierarchy. Also, the equation is valid for all times and does not require course graining.

We find that similar equations are very useful in the study of the conditional probability densities, $f_{s,s}(X_s;t|X_{s_0})$; Zwanzig's original suggestion for using projection operators is amended and extended in the next chapter, providing the equations we desire.

It is to be noted that $G_s(r,t)$ may be calculated once $f_{1,1}(X_1 ; t |X_{s_0})$ is known. $G_d(r,t)$ may be similarly obtained from $f_{2,2}(X_1,X_2;t |X_{1_0})$.

Although the major part of this report deals with the derivation and solution of equations for probability densities, considerable attention is paid, also, to obtaining expressions for the cross-sections. It is necessary to point out that

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** L is the Liouville operator. For definitions, see (3.4), below.

expansions for the latter, similar to the ones obtained in this report, have already been reported elsewhere.** Expressions for the scattering functions (and their inverse spatial fourier transforms) have been obtained in various forms of perturbation series. A notable characteristic of these expressions, however, is that they have been obtained without first performing calculations for G(r,t).

On the other hand, one of the reasons for performing both theoretical and experimental studies of neutron scattering is the hope of better understanding the functional form of the G-functions. Because we study these functions directly, it is felt that the calculations presented in this thesis contribute to such understanding beyond that afforded by the expressions for the <u>transforms</u> of G(r,t). In addition, the effects on the cross-section caused by varying the temperature are perhaps better demonstrated by this theory.

Finally, it should be pointed out that the conditional probability densities are of great significance if one wishes to calculate transport coefficients. It is well known[23,31,32] that the linear transport coefficients can be related to temporal integrals of appropriate time-relaxed correlation functions. An example is the proportionality of the dielectric constant to the Laplace transform of the momentum auto-correlation function. Since this point is elaborated upon in chapter five, we shall not discuss it further here.

**For a review, cf., Nelkin[30] or Schofield.[9]

CHAPTER 3

DERIVATION OF KINETIC EQUATIONS

A central problem of irreversible statistical mechanics
has been the derivation of kinetic equations necessary for
the description of the temporal behavior of pertinent re-
duced probability densities. Here, this question is discus-
sed in detail for the particular case of time-relaxed proba-
bility densities in equilibrium assemblies. Interest in
these functions is not only intrinsic; as has been indicated
in the previous chapter, various quantities of physical im-
portance such as the linear transport coefficients and the
slow neutron scattering cross-section may be related to
temporal integrals of appropriate densities and correlation
functions.

Whereas major concern in the following is the derivation
of equations for time-relaxed densities in equilibrium sys-
tems, it is indicated that under certain conditions closely
related equations may be derived for probability densities
of a more general nature.

The method employed in the following investigation is an
extension of a procedure originally suggested by R. W. Zwanzig[2]
in his studies of the approach to equilibrium.

Let it be agreed that

$$f_{n,n}(\vec{q}_1, \ldots, \vec{q}_n; \vec{p}_1, \ldots, \vec{p}_n; t | \vec{q}_{1_0}, \ldots, \vec{q}_{s_0}; \vec{p}_{1_0}, \ldots, \vec{p}_{s_0}) \equiv$$

$$\equiv f_{n,n}(X_n; t | X_{s_0}) \qquad \ldots(3.1)$$

will represent the <u>conditional</u> probability density for find-

ing a specified isolated n-particle system in the neighborhood

of a point $(\vec{q}_1,\dots,\vec{q}_n,\vec{p}_1,\dots,\vec{p}_n) \equiv X_n$ of Γ -space, at time t,

given that at t = 0, $X_s = X_{s_o}$. (X_s designates a

point in a pertinent 6s dimensional reduced phase space.)

Marginal densities** are obtained from $f_{n,n}(X_n;t|X_{s_o})$

in the following manner:

$$f_{a,b}(\vec{q}_1,\dots,\vec{q}_a;\vec{p}_1,\dots,\vec{p}_b;t|X_{s_o}) = \qquad \dots (3.2)$$

$$= \int \int d\vec{q}_{a+1}\dots d\vec{q}_n \, d\vec{p}_{b+1}\dots d\vec{p}_n \, f_{n,n}(X_n;t|X_{s_o})\dots$$

is the marginal conditional density, with respect to

$f_{n,n}(X_n;t|X_{s_o})$), for finding the set of position coor-

dinates $\{ \underline{q}_1,\dots, \underline{q}_a \}$ and momentum coordinates $\{ \underline{p}_1,\dots,\underline{p}_b \}$

in the neighborhood of the point $(\underline{q}_1,\dots,\underline{q}_a,\underline{p}_1,\dots,\underline{p}_b)$

of the appropriate reduced Γ -space, at time t, given

that at t = 0: $X_s = X_{s_o}$.

It is noted that $f_{a,b} \geq 0$ and that $\int d\vec{q}_1\dots d\vec{q}_a d\vec{p}_1\dots d\vec{p}_b \, f_{a,b}(\vec{q}_1,\dots\vec{p}_b;t| X_{s_o}) = 1$

for all a,b.

As is well known, once the initial state $f_{n,n}(X_n;0|X_{s_o})$

is specified, $f_{n,n}(X_n;t | X_{s_o})$ is determined for all time

by the Liouville equation. The latter may be written in

the following convenient form:

$$\frac{\partial f_{n,n}}{\partial t}(X_n;t|X_{s_o}) = L \, f_{n,n}(X_n;t|X_{s_o}) \qquad \dots (3.3)$$

** For a review of some of the concepts and terminology of
probability theory see appendix A, below.

The Liouville operator appearing in eqn. 3.3 may be expressed as the sum of three terms: $L = L_0 + L_1 + L_2$, with,

$$L_0 \equiv -\sum_{i=1}^{n} \frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} \qquad \ldots (3.4a)$$

$$L_1 \equiv \frac{1}{2} \sum_{j}^{n} \sum_{\neq k}^{n} \frac{\partial V(|\vec{q}_j - \vec{q}_k|)}{\partial q_j} \cdot (\vec{\nabla}_{p_j} - \vec{\nabla}_{p_k}) \qquad \ldots (3.4b)$$

$$L_2 \equiv \sum_{1}^{n} \frac{\partial U^{[i]}}{\partial \bar{q}_i} \cdot \vec{\nabla}_{p_i} \qquad \ldots (3.4c)$$

To obtain 3.4a-3.4c, it is required that all forces be assumed to be velocity independent. Also, the internal potential energy is assumed to be well represented as the sum of two-particle central force interactions.

In the above expressions, $V(|q_i - q_j|)$ is the potential between the ith and j^{th} particles and $U^{[i]}$ is the external potential acting upon the ith particle. It has been assumed that all particles are alike.

Kinetic equations for the lower order (marginal) probability densities are obtained directly from the Liouville equation. As has been mentioned in the previous chapters, a quantity of special interest to us is the one-particle time-relaxed function, $f_{1,1}(\underline{p}_1, \underline{q}_1; t \,|\, \underline{p}_{1_0}, \underline{q}_{1_0})$, defined as the probability density for finding particle # 1 in the neighborhood of the phase point $(\underline{q}_1, \underline{p}_1)$ at time t, given that it was at $(\underline{q}_{1_0}, \underline{p}_{1_0})$ at t = 0. Let us obtain an equation describing the temporal evolution of this function.

To obtain a kinetic equation for $f_{1,1}$ it is convenient

to introduce the following operator. Define:

$$\mathcal{P} \equiv f_{n|1}(x_2,\ldots,x_n;0|x_1) \int\cdots\int d^6x_2\cdots d^6x_n \qquad \ldots (3.5)$$

where $f_{n|1}(0)$ designates the probability density at
$t = 0$ for finding the n-1 particle subsystem in the neigh-
borhood of phase point ($\underline{x}_2,\ldots\ldots,\underline{x}_n$), given that the
coordinates of particle #1 are $\underline{x}_1 = (\underline{p}_1,\underline{q}_1)$.

Note that, once given $f_{n,n} (\underline{x}_1,\ldots\ldots,\underline{x}_n; 0)$, one
easily finds $f_{n|1}$ by the relationship $f_{n|1}(0) = f_{n,n}(0)/f_{1,1}(0)$

where $f_{1,1}(0) = \int\cdots\int dx_2\cdots dx_n \; f_{n,n}(0)$
(unconditioned one-particle density.) Note, also, that $\mathcal{P}$
is a projection operator; i.e.,

$$\mathcal{P}^2 \text{Fcn}(X_n;t) = \mathcal{P} \text{Fcn}(X_n;t) \text{ , since } \int\cdots\int dx_2\cdots dx_n \; f_{n|1}(x_2,\ldots,x_n;0|x_1)= 1.$$

Using 3.5, the following two identities are obtained
from the Liouville equation:

$$\mathcal{P} \frac{\partial f}{\partial t}_{n,n}(X_n;t|x_{1_0}) = \mathcal{P} L\left(\mathcal{P}f_{n,n} + (1-\mathcal{P}) f_{n,n}\right) \qquad \ldots (3.6)$$

$$(1-\mathcal{P}) \frac{\partial f}{\partial t}_{n,n} = (1-\mathcal{P}) L \left(\mathcal{P} f_{n,n} + (1-\mathcal{P}) f_{n,n}\right) \qquad \ldots(3.7)$$

The second of these equations is easily solved (formally)
to yield:

$$(1-\mathcal{P}) f_{n,n} = \int_0^t ds \; e^{s(1-\mathcal{P})L}(1-\mathcal{P})L \; f_{n|1}(0) \; f_{1,1}(x_1;t-s|x_{1_0}) +$$

$$+ e^{t(1-\mathcal{P})L}(1-\mathcal{P}) f_{n,n}(X_n;0|x_{1_0})$$

$$\ldots\ldots (3.8)$$

Placing (3.8) into (3.6), one obtains:

$$\frac{\partial[\theta f_{n,n}(X_n;t|x_{1o})]}{\partial t} = \theta L[\theta f_{n,n}] + \int_0^t d\tau \theta L e^{(1-\theta)L}(1-\theta)L f_{n,n}(t-\tau) +$$

$$+ \theta L e^{t(1-\theta)L}(1-\theta)f_{n,n}(X_n;0|x_{1o}) \quad ..(3.9)$$

Let us at this point assume that there are no external fields**

How are the initial conditions specified? For the case

of interest (viz., a set of particles moving through an equi-

librium assembly of like particles) the initial condition

for the full n - particle density, conditioned upon the posi-

tions of a designated subset of s particles, is given by:

$$f_{n,n}(X_n;0|X_{so}) =$$

$$= e^{-\beta V(\vec{q}_1^o,..,\vec{q}_s^o,\vec{q}_{s+1},..,\vec{q}_n)} e^{-\beta \sum_i^n p_i^2/2m} \frac{\prod_{i=1}^s \delta(\vec{q}_i-\vec{q}_{io})\delta(\vec{p}_i-\vec{p}_{io})}{Z_{q_n} \quad (2\pi mkT)^{3n/2} \quad f_{eq.}^{[s]}(q_{1o},..,p_{so})}$$

Here,
$$.......(3.10)$$

$$Z_{q_n} \equiv \int dq_1 ... dq_n \ e^{-\beta V(q_1,..,q_n)} \qquad .....(3.11)$$

and

$$f_{eq}^{[s]}(q_{1o},..,p_{so}) \equiv \int dq_{s+1}^o ... dq_n^o dp_{s+1}^o ... dp_n^o \ f_{eq}^{[n]}(X_{no}) =$$

$$.....(3.12)$$

$$= e^{-\beta \sum_{i=1}^s p_i^2/2m} \frac{1}{(2\pi mkT)^{3s/2}} \int dq_{s+1}...dq_n \ \frac{e^{-\beta V(q_1,..,q_n)}}{Z_{q_n}}$$

It is evident that we have assumed that the equilibrium

state of the assembly can be specified by a canonical

distribution.

The proof that (3.10) is correct is as follows.

Let $x_i = (\underline{q}_i, \underline{p}_i)$

** i.e., set $L_2 = 0$. This condition will be relaxed later.

It is certainly true that $f_{n,n}(X_n;0|X_{n_0}) = \prod_{i=1}^{n}\delta(\vec{x}_i-\vec{x}_{i_0})$.
But, the quantities of interest here are of the form:

$f_{n,n}(X_n;0|X_{s_0})$, i.e., the probability density for

finding the system in the neighborhood of X_n given the

exact position of the subset of particles #'s $(1 \rightarrow s)$

and no knowledge of the positions of the other particles

except that the probability density for the entire system

is a canonical distribution.

We recognize the following relationship for conditional

probability densities:**

$$f_{X|Y}(x|y) = \int_{-\infty}^{\infty} f_{X|Y,Z}(x|y,z') \, f_{Z|Y}(z'|y) \, dz' \qquad .$$

The generalization of this relationship leads us to the con-

clusion:

$$f_{n,n}(X_n;0|X_{s_0}) = \int_{x_{s+1}^0} dx_{s+1}^0 \cdots \int_{x_n^0} dx_n^0 \, f_{n,n}(X_n;0|X_{n_0}) \, f_{eq}(x_{s+1_0},\cdots,x_{n_0}|X_{s_0}) \quad .$$

But, because

$$f_{X|Y}(x|y) = f(X;Y)/f(X)$$

we have

$$f_{eq}(x_{s+1_0},\cdots,x_{n_0}|X_{s_0}) = f_{eq}^{[n]}(X_{n_0})/\, f_{eq}^{[s]}(X_{s_0})$$

Therefore:

$$f_{n,n}(X_n;0|X_{s_0}) =$$

$$= \int\int dx_{s+1_0}\cdots dx_{n_0} \, \delta(\vec{x}_1-\vec{x}_{1_0})\cdots\delta(\vec{x}_n-\vec{x}_{n_0}) \, \frac{f_{eq}^{[n]}(X_{n_0})}{f_{eq}^{[s]}(X_{s_0})}$$

$$= \frac{f_{eq}^{[n]}(x_{1_0},\cdots,x_{s_0},x_{s+1},\cdots,x_n)}{f_{eq}^{[s]}(x_{1_0},\cdots,x_{s_0})} \prod_{i=1}^{s}\delta(\vec{x}_i-\vec{x}_{i_0})$$

**For proof of this statement refer to appendix A.

In particular, as a special case of (3.10):

$$f_{n,n}(X_n;0|\underline{x}_{1_o}) = \frac{e^{-\beta V(q_1,\ldots,q_n)}}{Z_{q_n}/\Omega} \; \frac{e^{-\beta\sum_{i=2}^{n}p_i^2/2m}}{(2\pi mkT)^{3(n-1)/2}} \; \delta(\vec{q}_1-\vec{q}_{1_o}) \; \delta(\vec{p}_1-\vec{p}_{1_o}) \quad \ldots \quad (3.13)$$

Note how this differs from $f_{n|1}(0)$, the latter being given by:

$$f_{n|1}(x_2,\ldots,x_n;0|x_1) = \frac{e^{-\beta V(q_1,\ldots,q_n)}}{Z_{q_n}/\Omega} \; \frac{e^{-\beta\sum_{i}^{n}p_i^2/2m}}{(2\pi mkT)^{3(n-1)/2}} \quad \ldots \quad (3.14)$$

With these considerations in mind, however, the following relationship is noted:

$$\mathcal{P}f_{n,n}(X_n;0|\underline{x}_{1_o}) = f_{n|1}(x_2,\ldots,x_n;0|\underline{x}_{1_o}) \cdot f(\underline{x}_1;0|\underline{x}_{1_o}) =$$

$$= f_{n,n}(X_n;0|\underline{x}_{1_o}) \quad \ldots (3.15)$$

Thus, referring to equation 3.9, it is seen that the inhomogeneous term vanishes due to the fact that

$$(1-\mathcal{P}) f_{n,n}(X_n;0|x_{1_o}) = 0$$

. In this way, the simplification of the kinetic equation has been initiated.

Further simplification ensues upon noting that:

$$\mathcal{P}L\mathcal{P}f_{n,n} = f_{n|1} \{ \frac{-\vec{p}_1}{m} \cdot \vec{\nabla}_{q1} \} \; f_{1,1}(x_1;t|x_{1_o}) \cdot \quad \ldots \ldots (3.16)$$

This statement is true because

1) $\mathcal{P}_o L\mathcal{P} f_{n,n} = \mathcal{P}(-\frac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q1})\mathcal{P}f_{n,n} = f_{n|1}(-\frac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q1})f_{1,1}(x_1;t|x_o)$,

which follows due to the fact that, in the limit

$\Omega \to \infty$, $\int d\vec{q}_2 \ldots d\vec{q}_n \; \vec{\nabla}_{q_i}$ yields boundary terms which

$\to 0$ for $i \neq 1$;

2) $\mathcal{P}L_1\mathcal{P}f_{n,n} = 0$ if $f_{n|1}(\vec{x}_2,\ldots,\vec{x}_n;0|\vec{x}_{1_o})$

is an even function of the variables $(\vec{q}_i-\vec{q}_1)$, $i = 2,3,\ldots,n$.

This is due to the fact a typical contribution will be

proportional to $\int d\vec{q}_2 \ldots d\vec{q}_n \ \vec{F}_{1j}(\ |q_j-q_1| \ )\cdot \frac{\partial f}{\partial p_1}_{n|1} \ f_{1,1}$

which, in turn, will be equal to zero because the inter-

molecular potential, under the assumptions already stated,

is an even function of the intermolecular coordinates

(hence, the forces are odd functions and the integration

is over an odd function.)**

Of course, these arguments are valid for any isolated

system for which the initial n-particle density is symmetric

in the interparticle coordinates. We need not concern our-

selves only with particles moving through equilibrium assem-

blies. Other non-equilibrium problems might be attacked this

way (e.g., upon the assumption of binary isotropic interac-

tions, (cf. 3.4b), an approximate kinetic equation from which

hydrodynamical transport equations might be deduced could be

obtained were the local flow velocity of the fluid a slowly

varying function of the configurational coordinates.) In

**It is true that for some of the particles, the effective
configurational integration space will not be symmetric be-
cause of proximity to the boundaries of the system. However,
as the following argument demonstrates, these particles give
a vanishingly small contribution.

Notice that, for the case of specific interest here,

$$\int d\vec{q}_2 \ldots dq_n \ \vec{F}_{12}(q_1-q_2)\cdot\vec{\nabla}_{p_1} \ f_{n|1}(0) \ f_{1,1} \ = \ \frac{1}{\Omega}\int dq_2 \ \vec{F} \cdot \vec{\nabla}_{p_1} \ g_2(q_2-q_1) \ f_{1,1}$$

where Ω is the volume of the assembly. $g_2(q_2-q_1)$ (cf.,also,
eqn. 4.19 & ff.) depends on the density but is not
strongly volume dependent in the limit $\Omega \to \infty$. Thus, each
particle near the wall of the container contributes, at most,
a quantity of the order of $1/\Omega$. However, it seems clear
that the number of such particles will be proportional to
the surface area of the container. For this reason the to-
tal contribution from these terms will $\propto \frac{\Omega^{2/3}}{\Omega} = \Omega^{-1/3}$
Thus, in the limit $\Omega \to \infty$, $n \to \infty$, $n/\Omega = c$ = constant,
such contributions become vanishingly small.

general, the full knowledge of the initial probability density will be unknown. On the other hand, at least $f_{1,1}(\underline{x}_1;0)$ must be known for the problem to have a meaning. A good guess would have to be made for $f_{n|1}(\underline{x}_2,\ldots,\underline{x}_n;0|\underline{x}_1)$.

Let us remember that to obtain the simplifications 3.15 and 3.16 the absence of external fields was required (cf. p. 3-4). In the spirit of this derivation, non-zero external fields lead to difficulties: were we to choose the projection operator to include the full initial condition, $f_{n|1}(0)$ would not be symmetric in the interparticle coordinates and 3.16 would not hold; on the other hand, were we to retain the operator 3.5 with $f_{n|1}(0)$ given by 3.14, then 3.15 would not be valid.** In other words, 3.14 and 3.15 could not simultaneously be satisfied. This difficulty can be circumvented by deriving a different set of equations which, while satisfactorily describing systems with external fields, are not nearly as convenient for solution as the one we are here discussing (let us defer further examination of this point for the time being. cf. eqn. 3.28, below.)

As a result of 3.15 & 3.16, the kinetic equation for

**Although it is true that if the external fields are not rapidly varying functions of the configurational coordinates the full $f_{n|1}(0)$ could be used and 3.16:2 would be satisfied to a good degree of approximation. 3.15 would hold rigorously. 3.16 would read:

$$Q L Q f_{n,n} \simeq f_{n|1}(0)\left\{\frac{-\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1} + \frac{\partial U^{ext}}{\partial q_1}\cdot\vec{\nabla}_{p_1}\right\} f_{1,1}(\underline{x}_1;t|\underline{x}_{1_o})$$

$f_{1,1}(\ \underline{p}_1,\ \underline{q}_1;\ t|\ \underline{p}_{1_o},\ \underline{q}_{1_o}\ )$ may now be written

$$\ldots\ (3.18)$$

$$\frac{\partial f}{\partial t}_{1,1}(x_1;t|x_{1_o}) + \frac{\underline{p}}{m}_1 \cdot \vec{\nabla}_{q_1} f_{1,1} =$$

$$= \bar{\theta} \int_0^t d\tau\ L\ e^{\tau(1-\theta)L}\ (1-\theta)Lf_{n|1}(0)\ f_{1,1}(\vec{x}_1;t-\tau|\vec{x}_{1_o})$$

In the above equation,

$$(3.19) \qquad \bar{\theta} \equiv \int d\vec{x}_2 \ldots \ldots d\vec{x}_n$$

(In other words, $\bar{\theta} = f_{n|1}(0)\bar{\theta}$ and $f_{1,1}(\vec{x}_1;t|\vec{x}_{1_o}) = \bar{\theta}\ f_{n,n}(X_n;t|\vec{x}_{1_o})$

Further simplification of the terms appearing on the right hand side of equation 3.18 is deferred until the next chapter. We wish merely to demonstrate the structural form of the equation. Notice that the left hand side is the usual streaming operator, while on the r.h.s. there appears a complicated collision operator which contains a 'memory' of the evolution of the system from its initial state. In contrast to the BBGKY hierarchy this kinetic equation does not require integration over any unknown temporal correlation functions or densities of higher order. It will be seen later that $f_{1,1}$ can be expressed in terms of static correlation functions related to the initial full system density. Whereas in practise these correlations are not necessarily easily evaluated, in principle all the necessary information is provided.

****

The above derivation is easily extended to study the evolution of density functions for motion of groups of par-

ticles. Suppose one desires a kinetic equation for the s-
particle probability density. Define:

$$Q_s \equiv f_{n|s}(x_{s+1}, \ldots, x_n; 0 | x_1, \ldots, x_s) \int \ldots \int dx_{s+1} \cdots dx_n \qquad \ldots (3.20)$$

Then, as before, one obtains (cf. 3.15)

$$Q_s f_{n,n}(0) = f_{n,n}(0) \quad ; \quad \Rightarrow \quad (1 - Q_s) f_{n,n}(0) = 0 \ .$$

In anology to 3.16, we have:

$$Q_s L Q_s f_{n,n} = f_{n|s}(0)\{ -\sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} + \frac{1}{2} \sum_{i \neq k}^{s} \sum^{s} \vec{\nabla}_{q_i} \phi_{ij} \circ \vec{D}_{i,j} \} f_{s,s}(t)$$

$$\ldots (3.21)$$

where

$$\vec{D}_{i,j} \equiv \{ \vec{\nabla}_{p_i} - \vec{\nabla}_{p_j} \} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.22)$$

This follows because

$$Q_s L_1 Q_s f_{n,n} = f_{n|s} \int dx_{s+1} \cdots dx_n [\frac{1}{2} \sum_{i \neq j} \sum -\vec{F}_{ij} \cdot \vec{D}_{ij}] f_{n|s}(0) f_{s,s} =$$

$$= f_{n|s}(0) \int dx_{s+1} \cdots dx_n [\frac{1}{2} \sum_{i \neq k}^{s} \sum^{s} -\vec{F}_{ik} \cdot \vec{D}_{ik} + \sum_{i=1}^{s} \sum_{k=s+1}^{n} -\vec{F}_{ik} \cdot \vec{\nabla}_{p_i}]^{0} f_{n|s} f_{ss}$$

$$= f_{n|s}(0) [\frac{1}{2} \sum_{i \neq j}^{s} \sum^{s} \vec{\nabla}_{q_i} \phi_{ij} \circ \vec{D}_{ij}] f_{s,s}(t)$$

where $\int dx_{s+1} \cdots dx_n [\sum_{i}^{s} \sum_{k=s+1}^{n} -\vec{F}_{ik} \circ \frac{\partial}{\partial p_i}] f_{n|s} = 0$ by virtue of integra-
tion over an odd function. We have, in the above argument,

noticed that $\int dx_{s+1} \cdots dx_n f_{n|s}(x_{s+1}, \ldots, x_n; 0 | x_1, \ldots, x_s) = 1$

As a result, the kinetic equation describing the evolution

of the s-particle density in the absence of external forces

is given by $\qquad\qquad \ldots\ldots (3.23)$

$$\frac{\partial f}{\partial t}_{s,s}(X_s; t | X_{s_0}) + \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} f_{s,s} + \frac{1}{2} \sum_{i \neq j}^{s} \sum^{s} \vec{\nabla}_{q_i} \phi \cdot \vec{D}_{ij} f_{s,s} =$$

$$\equiv \frac{\partial f}{\partial t}_{s,s} - [H_s ; f_{s,s}] =$$

$$= Q_s \int_0^t d\tau \ L \ e^{\tau(1-Q_s)L} (1-Q_s) L f_{n|s}(0) f_{s,s}(X_s; t-\tau | X_{s_0})$$

In particular, for particles moving through an equilibrium assembly:

$$f_{n|s}(0) = \frac{\Omega^s e^{-\beta V(q_1,\ldots,q_n)}}{Z_{q_n} g_s(q_1,\ldots,q_s)} \prod_{i=s+1}^{n} f_{eq}(p_i) \qquad \ldots\ldots \quad (3.24)$$

where

$$g_s(q_1,\ldots,q_s) \equiv \Omega^s \int dq_{s+1}\cdots dq_n \frac{e^{-\beta V(q_1,\ldots,q_n)}}{Z_{q_n}} \qquad \ldots\ldots \quad (3.25)$$

Also,

$$f_{s,s}(X_s;0|X_{s_o}) = \prod_{i=1}^{s} \delta(\vec{q}_i-\vec{q}_{i_o}) \, \delta(\vec{p}_i-\vec{p}_{i_o}) \qquad \ldots\ldots \quad (3.26)$$

As has already been indicated, $G_d(r,t)$ is related to $f_{2,2}(\underline{x}_1,\underline{x}_2;t|\underline{x}_{1_0},\underline{x}_{2_0})$. The latter quantity would be obtained from the eqn. 3.23 for which s = 2.

It has been already pointed out that whereas equations 3.23 and 3.18 are valid only in the absence of external forces, by starting with different projection operators and performing analysis similar to 3.6 - 3.9 one can obtain kinetic equations pertinent to the more general case. Suppose we had started with a projection operator:

$$Q \equiv \frac{1}{\Omega^{n-s}} \int d\vec{q}_{s+1} \cdots d\vec{q}_n \qquad \ldots\ldots\ldots \quad (3.27)$$

instead of that defined by 3.5. In a manner completely similar to that already used, one can show that the following equation is obtained for the s particle density:

$$\left\{ \partial/\partial t + \sum_{i}^{s} \frac{\vec{P}_i}{m} \cdot \vec{\nabla}_{q_i} - \sum_{i}^{s} \vec{\nabla}_{q_i} U_i^{ext} \cdot \vec{\nabla}_{P_i} + \frac{1}{2} \sum_{i \neq j}^{s,s} \vec{\nabla}_{q_i} \phi_{ij} \cdot \vec{D}_{ij} \right\} f_{s,s}(X;t|X_s)_o =$$

$$= \frac{\bar{Q}_s}{\Omega^{n-s}} L \int_0^t d\tau \, e^{\tau(1-Q)L} (1-Q)L f_{s,n}(t-\tau) +$$

$$+ \bar{Q}_s L \, e^{t(1-Q)L} (1-Q) \, f_{n,n}(X_n;0|X_{s_o}) \qquad \qquad \dots \dots (3.28)$$

In the above equation L is the _complete_ Liouville operator given by 3.4a - 3.4c (i.e. external fields are allowed). The other symbols appearing in 3.28 have the same meanings as their prior definitions except that the initial value term must now also demonstrate the presence of external fields.**

The memory term of 3.28 can be simplified by noticing that because momentum correlations specified independently of distance between particles must be very small (for systems of many particles) it is not unreasonable to factor $f_{s,n}(\vec{x}_1, \dots, \vec{x}_s, \vec{P}_{s+1}, \dots, \vec{P}_n;)$ into $\prod_{s+1}^{n} f_1(\vec{P}_i) \, f_{s,s}(X_s;t-\tau|X_{s_o})$. In particular, for a set of particles moving through an equilibrium assembly,

$$f_{s,n} \rightarrow f_{s,s} \cdot \prod_{s+1}^{n} f_{eq}(P_i) \qquad \text{where} \qquad f_{eq}(P_i) = e^{-\beta P_i^2/2m} /(2\pi mkT)^{3/2}$$

**Assuming the unconditioned n-particle density to be given by

$$f_{n,n}^{eq}(X_n) = e^{-\beta[V(q_1 \cdots q_n) + \sum_i U_i^{ext}(q_i)]} \frac{e^{-\beta \sum_i \frac{P_i^2}{2m}}}{(2\pi mkT)^{3n/2}} / Z_{q_n}(U^{ext}) \quad \text{with} \quad Z_{q_n}(U^{ext}) = \int dq_1 \cdots e^{-\beta[V + \sum U]}$$

then

$$f_{n,n}^{eq}(X_n) = \frac{e^{-\beta[V + \sum U^{ext}]}}{Z_{q_n}(U^{ext})} \frac{e^{-\beta \sum_i \frac{P_i^2}{2m}}}{(2\pi mkT)^{3n/2}} \frac{\prod_{i=1}^{s} \delta(x_i - x_{i_o})}{f_{eq}^{[s]}(X_{s_o})} \quad ,$$

where

$$f_{eq}^{[s]}(X_{s_o}) \equiv \frac{1}{Z_{q_n}} \frac{e^{-\beta \sum_i^s \frac{P_i^2}{2m}}}{(2\pi mkT)^{3s/2}} \int dq_{s+1} \cdots dq_n \, e^{-\beta[V + \sum U^{ext}]} \quad .$$

This factorization closes equation 3.28 in that the latter no longer contains unknown temporal probability densities of higher order than $f_{s,s}$. Setting the external forces equal to zero would provide an equation equivalent to 3.23. On the other hand, *a posteriori*, 3.23 rather than 3.28 is more amenable to solution (...certainly true for the function most intimately studied, i.e., $f_{1,1}$; it should be true in general since 3.23 does not contain an inhomogeneous initial value term.)

However, it is to be noted in passing that 3.23, taken with 3.28, provides an integral equation for $f_{s,s}(\, x_s ;t|\, x_{s_o})$. With the external forces set equal to zero, the left hand side of 3.28 is identical with the l.h.s. of 3.23. Also, the initial conditions for the two equations are equal. Hence, the r.h. sides of the equations must also be equal.

For example, for $f_{1,1}$:

$$\bar{\mathbb{Q}} \int_0^t d\tau \, L \, e^{\tau(1-\hat{\mathbb{Q}})L} \, (1-\hat{\mathbb{Q}})L \, f_{n|1}(0) \, f_{1,1}(\underline{x}_1;t-\tau|\underline{x}_{1_o}) = \qquad \ldots\ldots (3.29)$$

$$= \bar{\mathbb{Q}}_{\overline{\mathbb{Q}\pi}-1} \int_0^t d\tau \, Le^{\tau(1-Q)L} \, (1-Q)L \, f_{eq}(p_i)f_{1,1-1}(\underline{x}_1;t-\tau|\underline{x}_{1_o}) +$$

$$+ \, L \, e^{t(1-Q)L} \, (1-Q)f_{n,n}(X_n;0|x_{1_o})$$

The last relationship is stated merely for the sake of presenting a complete story. It is not important to the continuation of this analysis; rather, in the next chapters, 3.18 will be the object of major attention.

Before proceeding with the further reduction and solution of 3.18, a few words should be said in comparison of

the probability densities about which we are concerned
(cf., 3.1 and 3.2) with other non-equilibrium densities
and "distribution functions" which occur in similar studies
of non-equilibrium statistical mechanics.

The probability density functions defined by equation
3.2 are frequently referred to as "<u>specific</u>" densities be-
cause the arguments ($\vec{q}_1, \ldots, \vec{q}_a, \vec{p}_1, \ldots, \vec{p}_b$) pertain to desig-
nated members of the assembly.*

Closely related are Bogoliubov's "distribution func-
tions"**, which are defined by: $F(X_s) \equiv \int dx_{s+1} \ldots dx_n f_{n,n}(X_n;t)$;
it is clear that they are related to our density functions
by: $\qquad f_{s,s}(X_s;t|X_{r_0}) = \frac{1}{\Omega^s} F_s(X_s;t|X_{r_0})$

There also frequently appear in the literature the so-
called "generic distribution functions"*:

$$f_s^{gen.}(\vec{x}_1, \ldots, \vec{x}_s;t) = \frac{n!}{(n-s)!} \int d\vec{x}_{s+1} \ldots d\vec{x}_n f_{n,n}(X_n;t) .$$

In this case, it is to be noted that the integral provides
the probability density for finding a particular ordered
act of particles with a given momentum and configuration
distribution, whereas the factor $n!/(n-s)!$ is the number
of ways ordered sets of s particles can be chosen without
replacement from an assembly of n particles.

The generic distribution functions are useful in studies
of systems possessing a symmetry or equivalence between par-
ticles. However, in our study, where attention is focused

*See, e.g.; Hill[33], p.182; Vineyard[27]

**Bogoliubov[3], pp. 2, 51.

on particular groups of particles, they are of little pertinence.

Using the conditioned n-particle density defined by 3.1, one may obtain the conditional number density, $n(\underline{r};t|\underline{q}_{1_o})$, defined as the expected number of particles in the neighborhood of $\underline{r}$ at time t, given that particle designated #1 was at $\underline{q}_{1_o}$ at t = 0. In order to do so, one takes the expectation of the density operator defined by $N(X_n) \equiv \sum_{i=1}^{n} \delta(\vec{r}-\vec{q}_i)$ i.e.,

$$n(\vec{r};t|\vec{q}_{1_o}) \equiv \langle\sum_{i=1}^{n}\delta(\vec{r}-\vec{q}_i)\rangle = \int d\vec{x}_1..d\vec{x}_n [\sum_{i}^{w}\delta(\vec{r}-\vec{q}_i)] f_{n,n}(X_n;t|\vec{q}_{1_o})$$

$$= \int d\vec{q}_1 f_{1,0}(\vec{q}_1;t|\vec{q}_{1_o})\delta^3(\vec{r}-\vec{q}_1) + \sum_{2}^{n}\int d\vec{q}_i f_{1,0}(\vec{q}_i;t|\vec{q}_{1_o})\delta(\vec{r}-\vec{q}_i)$$

$$= f_{1,0}^{self}(\vec{r};t|\vec{q}_{1_o}) + (n-1) f_{1,0}^{distinct}(\vec{r};t|\vec{q}_{1_o})$$

where $f_{1,0}(\vec{r};t|\vec{q}_{1_o})$ is the probability density for finding a particle at r (configuration space) at time t, given that it was located at $\underline{q}_{1_o}$ at t = 0 ; $f_{1,0}^{dist.}(\vec{r};t|\vec{q}_{1_o})$ is the probability density for finding a specified particle at r at time t, averaged over the initial position of the particle, given only that a different specified particle was at $\underline{q}_{1_o}$ at t = 0. It has been implicitly assumed that the n-particle density is invariant upon permutation of the indices 2,......,n.

From the discussion of the preceding chapter, it is seen that

$$n(\vec{r};t|0) = \frac{1}{n} \langle\sum_{j}^{n}\sum_{k}^{n} \int d\vec{r}' \; \delta(\vec{r}+\vec{q}_k(0)-\vec{r}')\delta(\vec{r}'-\vec{q}_j(t))\rangle = G(\vec{r},t)$$

for a system composed of indentical particles. $G_s = f_{1,0}^{self}(\vec{r};t|0)$

and $\qquad G_d(r,t) = (n-1)\, f_{1,0}^{dist\cdot}(r;t|0)$.**

To relate to a more familiar case, had we taken the expectation of $N(X_n)$ with respect to an n-particle probability density which is symmetric in the configuration coordinates of all particles (rather than only $2, \ldots, n$ as per the previous example), we would have obtained

$$n(r,t) = \int dX_n\, f_{n,n}(X_n;t)\, N(X_n) = n\, f_{1,0}(r,t) .$$ For example, for a system in equilibrium, $f_{1,0} = 1/\Omega$, so that

$n(r,t) = n/\Omega = c = $ the macroscopic density.

**Anticipating somewhat $f_{1,0}^{self}(\vec{q}_1;t|\vec{q}_{1_0})$ and
$f_{1,0}^{dist}(\vec{q}_2;t|\vec{q}_{1_0})$ may be explicitly calculated from
$f_{1,1}(\vec{x}_1;t|\vec{x}_{1_0})$ and $f_{2,2}(X_2;t|X_{2_0})$ by

$$f_{1,0}^{self}(\vec{q}_1;t|\vec{q}_{1_0}) = \int d\vec{p}_0 d\vec{p}_1\, \frac{e^{-\beta p_0^2/2m}}{(2\pi m kT)^{\frac{3}{2}}} f_{1,1}(\vec{p}_1,\vec{q}_1;t|\vec{p}_{1_0},\vec{q}_{1_0})$$

$$f_{1,0}^{dist\cdot}(\vec{q}_2;t|\vec{q}_{1_0}) = \int d\vec{x}_1 d\vec{p}_2 d\vec{x}_{2_0} d\vec{p}_{1_0}\, f_0(\vec{p}_{1_0},\vec{p}_{2_0};\vec{q}_{2_0}|\vec{q}_{1_0})\, f_{2,2}(X_2;t|X_{2_0})$$

$$= \frac{1}{\Omega} \int d\vec{x}_1 d\vec{p}_2 d\vec{x}_{2_0} d\vec{p}_{1_0}\, g_2(\vec{q}_{2_0}-\vec{q}_{1_0})\, \frac{e^{-\frac{\beta(p_{1_0}^2+p_{2_0}^2)}{2m}}}{(2\pi m kT)^3} f_{2,2}(X_2;t|X_{2_0})$$.

CHAPTER IV

REDUCTION OF THE KINETIC EQUATION FOR
THE SINGLET DENSITY

It is shown in the preceding chapter how the Liouville equation may be reduced in order to provide kinetic equations for various conditional (i.e., two-time) probability densities. At first glance, the integro-differential equations so obtained seem to express the interaction between the particles of interest and their surroundings in a very concise form. Unfortunately, as closer examination of the pertinent operators shows, the perturbations of the surrounding medium (which are manifested in the collision integral) enter in a very complex way. To better understand these effects, additional investigation of the integral terms appearing in the equations is required.

In the following work, further consideration is given to the equation describing the temporal evolution of the one particle density, $f_{1,1}(\underline{x}_1; t/\underline{x}_{1_o})$. Specifically, manipulations are performed upon the collision integral in order to obtain expressions convenient for solution by an iteration procedure later employed.

We consider a system without external forces. In this case, the probability of finding a particle in the neighborhood of $(\underline{q}_1, \underline{p}_1)$ at time t, given that it was located at $(\underline{q}_{1_o}, \underline{p}_{1_o})$ at time $t = 0$, is provided by the solution of equation 3.18 :

$$\frac{\partial f}{\partial t}_{1,1}(\underline{q}_1,\underline{p}_1;t\,|\,\underline{q}_{1_o},\underline{p}_{1_o}) + \frac{\underline{p}_1}{m}\cdot\vec{\nabla}_{q_1}f_{1,1}(\underline{q}_1,\underline{p}_1;t\,|\,\underline{q}_{1_o},\underline{p}_{1_o}) = \qquad (4.1)$$

$$= \overline{\Theta}\int_o^t d\tau\, e^{-\tau L(1-\Theta)}\, L(1-\Theta)L\, f_{n|1}(X_n)\, f_{1,1}(\underline{q}_1,\underline{p}_1;t-\tau\,|\,\underline{q}_{1_o},\underline{p}_{1_o})$$

with initial condition:

$$f_{1,1}(\underline{q}_1,\underline{p}_1;0\,|\,\underline{q}_{1_o},\underline{p}_{1_o}) = \delta(\underline{q}_1-\underline{q}_{1_o})\,\delta(\underline{p}_1-\underline{p}_{1_o})$$

To reiterate, the terms appearing in eqn. 4.1 have the following definitions:

$$\overline{\Theta} \equiv \int d\vec{q}_2 \cdots d\vec{q}_n d\vec{p}_2 \cdots d\vec{p}_n \qquad \cdots\cdots (4.2a)$$

$$f_{n|1}(X_n) = \frac{e^{-\beta V(\vec{q}_1,\cdots,\vec{q}_n)}}{Z_{q_n}/\Omega} \prod_{i=2}^{n} f_{eq}(\vec{p}_i) \qquad \cdots\cdots (4.2b)$$

$$\Theta \equiv f_{n|1}(X_n)\,\overline{\Theta} \qquad \cdots\cdots (4.2c)$$

L is the Liouville operator defined previously by eqn. 3.4 (except, of course, $L_2 = 0$.) It is to be remembered that in this definition it has been assumed that the inter-action between particles can be described as the sum of central pair potentials.

Frequently, the six dimensional variable $\underline{x}$ shall appear in the following analysis to denote $(\underline{q},\underline{p})$. Further,

if ambiguity will not ensue, arguments of various functions

may not appear explicitly.

Note, also, that the 6-n dimensional vector has been

denoted by:

$$X_n \equiv (\underline{x}_1, \ldots\ldots, \underline{x}_n)$$

Let us focus our attention on the collision integral

of the kinetic equation. Making repeated use of the follow-

ing well-known* identity

$$e^{\tau L(1-\vartheta)} = e^{\tau L_0(1-\vartheta)} [\, 1 + \int_0^\tau d\tau' \, e^{-\tau' L_0(1-\vartheta)} L_1(1-\vartheta) e^{\tau' L(1-\vartheta)} \,] \qquad .. \ (4.3)$$

the integral term of eqn. 4.1 becomes. .

$$I = \bar{\vartheta} \int_0^t d\tau_1 \, e^{\tau_1 L_0(1-\vartheta)} L(1-\vartheta) L \, f_{n|1}(X_n) \, f_{1,1}(x_1; t-\tau_1 | x_{1_0}) +$$

$$+ \bar{\vartheta} \int_0^t d\tau_1 \, e^{\tau_1 L_0(1-\vartheta)} \int_0^{\tau_1} d\tau_2 \, e^{-\tau_2 L_0(1-\vartheta)} L_1(1-\vartheta) e^{+\tau_2 L_0(1-\vartheta)} L(1-\vartheta) L f_{n|1} f_1(t-\tau_1)$$

$$+ \bar{\vartheta} \int_0^t d\tau_1 \, e^{\tau_1 L_0(1-\vartheta)} \int_0^{\tau_1} d\tau_2 \, e^{-\tau_2 L_0(1-\vartheta)} L_1(1-\vartheta) e^{+\tau_2 L_0(1-\vartheta)} \times$$

$$\times \int_0^{\tau_2} d\tau_3 \, e^{-\tau_3 L_0(1-\vartheta)} L_1(1-\vartheta) e^{+\tau_3 L_0(1-\vartheta)} L(1-\vartheta) L f_{n|1} f_1(t-\tau_1)$$

$$+ \quad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ$$

$$\circ\circ\circ\circ\circ\circ\circ \ (4.4)$$

*See, e.g., Van Hove [34] ,Bernard and Callen [35] . 4.3 can be
verified by noticing that it holds for $\tau = 0$ and also, the
differentials re. τ of both sides of the equation are equal.

But, the integrals of (4.4) can be quickly simplified. To do so, use is made of the following relationships.

Identity:
$$\bar{\Theta}\, e^{\tau_1 L_0 (1-\Theta)} = \bar{\Theta} \qquad \ldots\ldots \quad (4.5)$$

(Proof:
$$\bar{\Theta}\, e^{\tau_1 L_0 (1-\Theta)} = \bar{\Theta}[\,1 + \tau_1 L_0(1-\Theta) + \frac{\tau_1^2}{2!} L_0(1-\Theta)L_0(1-\Theta) + ..]$$

But, because $\bar{\Theta}\,\vec{\triangledown}_{q_i}$, $i \neq 1$ yields boundary terms

which $\to 0$ as the volume of the system $\Omega_i \to \infty$,

$$\bar{\Theta}\, L_0(1-\Theta) = \bar{\Theta}(-\frac{\vec{P}_1}{m}\!\cdot\vec{\triangledown}_{q_1})(1-\Theta) = -\frac{\vec{P}_1}{m}\!\cdot\vec{\triangledown}_{q_1}\,\bar{\Theta}(1-\Theta)$$

Also, since $\bar{\Theta}\Theta = \bar{\Theta}$ in turn implying $\bar{\Theta}(1-\Theta) = 0$, it is clear that the identity holds.)

In a similar way, it is quickly seen that

$$\Theta L_0^{\,n}(1-\Theta) = 0 \text{ for } n \geq 0 \; ; \; \bar{\Theta}e^{tL_0}(1-\Theta) = 0. \qquad \ldots\ldots\ldots \quad (4.6)$$

As a consequence of (4.6) we have the following

Identity:
$$e^{\tau_2 L_0 (1-\Theta)} = [\, e^{\tau_2 L_0}(1-\Theta) + \Theta\,] \qquad \ldots\ldots \quad (4.7)$$

(Proof:
$$e^{\tau_2 L_0 (1-\Theta)} = 1 + \tau_2 L_0(1-\Theta) + \frac{\tau_2^2}{2} L_0(1-\Theta)L_0(1-\Theta) + \ldots$$

$$= 1 + \tau_2 L_0(1-\Theta) + \frac{\tau_2^2}{2}L_0^2(1-\Theta) + \ldots$$

$$= [\, e^{\tau_2 L_0}(1-\Theta) + \Theta\,]$$

$$\text{q.e.d.} \qquad)$$

Also, since Θ is a projection operator,
$$\ldots \quad (4.8)$$

$$(1-\Theta)\Theta = 0 \; ; \; L_1(1-\Theta)[e^{tL_0}(1-\Theta)+\Theta] = L_1(1-\Theta)e^{tL_0}(1-\Theta) \qquad .$$

Hence, in virtue of 4.5 - 4.8, the integral term (4.4) can be written as an infinite series of terms $I^{[r]}$, the latter being given by:

$$I^{[r]} = \bar{\Theta} \int_0^t d\tau_1 \ldots \int_0^{\tau_{r-1}} d\tau_r \, L_1 [e^{(\tau_2 - \tau_3)L_0}(1-\Theta)] L_1 [e^{(\tau_3 - \tau_4)L_0}(1-\Theta)] \ldots$$

$$\ldots L_1 [e^{(\tau_{r-1} - \tau_r)L_0}(1-\Theta)] L_1 [e^{\tau_r L_0}(1-\Theta)] L(1-\Theta) L f_{n|1}(X_n) f_{1,1}(t-\tau_1)$$

$$\ldots \ldots \text{(4.9)}$$

Let us continue with the simplification of (4.9). Notice, in these expressions, the appearance of terms:

$$(1-\Theta) L f_{n|1}(X_n) f_{1,1} = (1-\Theta) L e^{\frac{-\beta V(q_1, \ldots, q_n)}{Z_{q_n}/\Omega}} \prod_{i=2}^n f_{eq}(p_i) f_{1,1} \, .$$

But, $\Theta L_1 e^{-\beta V(q_1, \ldots, q_n)} \ne 0$ because $V(q_1, \ldots, q_n)$ is an even function of the spatial separations between particles, whereas L_1 is an odd function of these variables (see the discussion following 3.15). Also,

$$[\Theta L_0 f_{n|1}(X_n) = f_{n|1}(X_n)(-\frac{\vec{p}}{m} \cdot \vec{\nabla}_{q1}) \bar{\Theta} f_{n|1}(X_n) = f_{n|1}(X_n)(-\frac{\vec{p}}{m} \cdot \vec{\nabla}_{q1})] f_{1,1}(t-\tau_1)$$

Hence,

$$(1-\Theta) L \, f_{n|1}(X_n) \, f_{1,1}(t-\tau_1) =$$

$$\ldots \ldots \text{(4.10)}$$

$$= [L f_{n|1}(X_n) + f_{n|1}(+\frac{\vec{p}}{m} \cdot \vec{\nabla}_{q1})] f_{1,1}(t-\tau_1) \, .$$

Finally, it is convenient to perform the following coordinate transformation in (4.9). Let:

$$\vec{q}_1 \Longleftrightarrow \vec{q}_1 \; ; \; \vec{\xi}_i \Longleftrightarrow (\vec{q}_i - \vec{q}_1), \, i \ne 1 \qquad \ldots \text{(4.11a)}$$

which implies

$$\ldots \text{(4.11b)}$$

$$\vec{\nabla}_{q1} \to (\vec{\nabla}_{q1} - \sum_{i=2}^n \vec{\nabla}_{\xi_i}) \; ; \; \vec{\nabla}_{qi} \to \vec{\nabla}_{\xi_i} \quad , i \ne 1 \, .$$

The Jacobian of the transformation is unity.

Under this transformation, the operators appearing in 4.9 become

$$L(X_n) \rightarrow L(\Xi) = L_0(\Xi) + L_1(\Xi)$$

$$\cdots\cdots \quad (4.12)$$

where $L_0(\Xi)$ and $L_1(\Xi)$ are defined by:

$$\cdots\cdots \quad (4.13)$$

$$L_0(\Xi) \equiv -\sum_{i=2}^{n} (\frac{\vec{p}_i - \vec{p}_1}{m}) \cdot \vec{\nabla}_{\xi_i} - \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1}$$

$$L_1(\Xi) \equiv \sum_{j \neq 1} -\vec{F}_{1j}(\xi_j) \cdot (\vec{\nabla}_{p_1} - \vec{\nabla}_{p_j}) + \frac{1}{2}\sum_{\substack{j \neq k \\ \neq 1}}\sum \vec{F}_{jk}(\xi_j - \xi_k) \cdot (\vec{\nabla}_{p_j} - \vec{\nabla}_{p_k})$$

It is noted that $f_{n|1}(\Xi)$ is __not__ a function of $\underline{q}_1$. It will be seen later that this is of some importance. In fact, it is mainly for this reason that the transformation 4.11 is performed.

For example, under this transformation, the expression given by 4.10 becomes

$$[L(\Xi) f_{n|1}(\Xi) + f_{n|1}(\Xi) (\frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1})] f_{1,1}(\underline{x}_1;t-\tau_1|\underline{x}_{1o}) =$$

$$= L^{\dagger}(\Xi) f_{n|1}(\Xi) f_{1,1}(\underline{x}_1;t-\tau_1|\underline{x}_{1o}) \quad \cdots\cdots \quad (4.10)$$

where

$$L^{\dagger}(\Xi) \equiv L_0^{\dagger}(\Xi) + L_1(\Xi) \quad \cdots\cdots \quad (4.13)$$

and

$$L_0^{\dagger}(\Xi) \equiv -\sum_{i=2}^{n} \frac{(\vec{p}_i - \vec{p}_1)}{m} \cdot \vec{\nabla}_{\xi_i}$$

In summary, finally, the kinetic equation for $f_{1,1}$ $(\underline{x}_1; t/\underline{x}_{1_o})$ may be written as:

$$\frac{\partial f}{\partial t}_{1,1} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} f_{1,1}(\underline{x}_1;t|\underline{x}_{1_o}) = \sum_1^{\infty} I^{[r]}(\underline{x}_1;t|\underline{x}_{1_o}) \qquad (4.14)$$

with, $I^{[r]} = \bar{\Theta}(\Xi)\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \cdots \int_0^{\tau_{r-1}} d\tau_r L_1(\Xi) \times \qquad (4.15)^*$

$$\times [e^{(\tau_2-\tau_3)L_o^\dagger(\Xi)} \mathcal{S}_{-(\tau_2-\tau_3)}(1-\Theta(\Xi))] L_1 \times$$

$$\times [e^{(\tau_3-\tau_4)L_o^\dagger} \mathcal{S}_{-(\tau_3-\tau_4)}(1-\Theta)] \times \cdots \times L_1 [e^{(\tau_{r-1}-\tau_r)L_o^\dagger} \mathcal{S}_{-(\tau_{r-1}-\tau_r)}(1-\Theta)] \times$$

$$\times L_1 [e^{\tau_r L_o^\dagger} \mathcal{S}_{-\tau_r}(1-\Theta)] L(\Xi) L^\dagger(\Xi) f_{n|1}(\Xi) f_{1,1}(\underline{x}_1;t-\tau_1|\underline{x}_{1_o})$$

$\mathcal{S}_{-\tau}$ is the streaming operator (Taylor's series operator):

$$\mathcal{S}_{-\tau} \equiv e^{-\frac{\tau\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1}} \qquad (4.16)$$

having the property that, when acting upon a function of $\underline{q}_1$, $\underline{p}_1$, and t:

$$\mathcal{S}_{-\tau} \text{ fcn}(\underline{q}_1;\underline{p}_1;t) = \text{fcn} (\underline{q}_1-\underline{p}_1\tau/m;\underline{p}_1;t) \qquad (4.16a)$$

$\bar{\Theta}(\Xi)$ is defined by:

$$\bar{\Theta}(\Xi) \equiv \int d\vec{\xi}_2 \cdots d\vec{\xi}_n \int d\vec{p}_2 \cdots d\vec{p}_n \qquad (4.17)$$

there being obvious similar definitions for $\Theta(\underline{\Xi})$

and $f_{n|1}(\Xi)$.

Thus, it has been demonstrated how the collision integral may be expressed as an infinite series of integral

---

$$I^{[1]} = \bar{\Theta}(\Xi) \int_0^t d\tau_1 L(\Xi) L^\dagger(\Xi) f_{n|1}(\Xi) f_{1,1}(\underline{x}_1;t-\tau_1|\underline{x}_{1o})$$

operators. As shall be seen below, such arrangement (i.e.,

in series 4.15) expedites grouping the interaction terms

according to decreasing effect on the evolution of $f_{1,1}$

$(\underline{x}_1; \ t/\underline{x}_{1_0})$.

What, however, are the criteria for determining the

relative contribution of various terms in the collision

integral series? The identification of the necessary ex-

pansion parameters is, of course, one of the desired re-

sults of this study. In this regard, it can be asserted

a posteriori that further reduction of the interaction terms

will demonstrate the intrinsic importance of constants of

the following form:

$$\int d\xi_2 \circ \circ d\xi_k \ g_k(\xi_2, \circ\circ, \xi_k) \left(\frac{\partial^{m_{1,1}}\phi(\xi_2)}{\partial\xi_2^{m_{2,1}}} \ \frac{\partial^{m_{1,2}}\phi(\xi_2)}{\partial\xi_2^{m_{2,2}}} \ \circ\circ\circ\circ \ \frac{\partial^{m_{k,t}}\phi(\xi_k)}{\partial\xi_k^{m_{k,t}}} \right) \quad \circ\circ\circ \quad (4.18)$$

where $\phi(\xi)$ is the pair potential energy expressed as a

function of the distance between particles and,

$$g_k(\xi_2, \circ\circ, \xi_k) = \frac{\Omega^{k-1} \int d\vec{\xi}_{k+1} \circ\circ\circ d\vec{\xi}_n \ e^{-\beta V(\xi_2, \circ\circ, \xi_n)}}{\int d\xi_2 \circ\circ\circ\circ\circ d\xi_n \ e^{-\beta V(\xi_2, \circ\circ, \xi_n)}} \quad \circ\circ \quad (4.19)$$

The terms (4.18) are averages of derivatives of potentials,

weighted by the correlation functions $g_k(\xi_2, \ldots, \xi_k)$.

In general, the latter are dependent in a complicated

way upon the density and strength of the intermolecular in-

teractions. Dependence upon the variables $\xi_2, \ldots \xi_k$ has

been determined only for a few very special cases.** However,

in the limit that the density $\to 0$ and/or the temperature

$\to \infty$, the g_k are well approximated by

$$g_k \simeq \frac{\Omega^{k-1} e^{-\beta V(\xi_2,\dots,\xi_k)}}{\int d\xi_2 \dots d\xi_k \; e^{-\beta V(\xi_2,\dots,\xi_k)}} \qquad \dots\dots \quad (4.19')$$

It may now be asserted that the criterion for grouping

terms according to interaction strength is that M, defined

as the sum of the differentiation indexes appearing in 4.18,

be the same for all members of the group. In other words,

defining

$$M \equiv \sum_{j=1}^{k} \sum_{i=1}^{\ell} m_{j,i} \qquad \dots\dots\dots\dots \quad (4.20)$$

it is asserted that all terms of the form 4.18 for which M

is the same are of equal 'strength'.

Perhaps this determination seems rather arbitrary. How-

ever, it is noticed that when the approximation 4.19' is valid,

simple partial integrations show the equivalence of the order

of magnitude of seemingly different expressions. For example,

***

$$\int [e^{-\beta\phi(\xi)} \; \vec{\nabla}_\xi \phi(\xi) \cdot \vec{\nabla}_\xi \phi(\xi)] \, d^3\xi = \frac{1}{\beta} \int d^3\xi \; e^{-\beta\phi(\xi)} \; \nabla_\xi^2 \phi(\xi) \; .$$

(The factor of $1/\beta$ is always cancelled out when expectations

are taken, and is irrelevant to the present discussion.)

Also, for high temperatures, it is found that successively

**See, for example, Hill[33], p. 184 and ff.
*** This is not true for coulomb forces.

higher powers of M signify terms which are successively less important in their contribution to the collision integral. In effect, one is performing an expansion in a parameter characterizing the ratio of the average potential energy of the assembly to the average kinetic energy. Thus, the zero'th contribution is a collection of terms for which $M = 0$; the first order correction is that for which $M = 2$; the second order terms are those for which $M = 4$, etc.

All this will become clearer as we proceed.

At this point, some of the terms in the collision integral shall be explicitly evaluated. All those for which $M \leq 4$ shall be obtained. Unfortunately, the ensuing analysis is necessarily lengthy and complicated; we endeavor to present it as lucidly as possible.

First, consider the collision integral $I^{[1]}$. From 4.15:

$$I^{[1]} = \bar{\mathcal{O}}(\Xi) \int_0^t d\tau_1 \, L(\Xi) \, L^\dagger(\Xi) \, f_{n|1}(\Xi) \, f_{1,1}(\underline{x}_1; t-\tau_1 | \underline{x}_{1_0}) \quad \ldots \quad (4.20)$$

It is convenient to break the integral into two parts, $I_1^{[1]}$ and $I_2^{[1]}$, defined by:

$$I_1^{[1]} \equiv \bar{\mathcal{O}}(\Xi) \int_0^t d\tau \, L(\Xi) L_0{}^\dagger(\Xi) \, f_{n|1}(\Xi) \, f_{1,1}(t-\tau) \quad \ldots \quad (4.20')$$

$$I_1^{[2]} \equiv \bar{\mathcal{O}}(\Xi) \int_0^t d\tau \, L(\Xi) L_1(\Xi) \, f_{n|1}(\Xi) \, f_{1,1}(t-\tau) \quad \ldots \quad (4:20'')$$

$I_1^{[1]}$ can be quickly simplified. $\bar{\mathcal{O}}(\Xi) \, \vec{v}_{\xi_i}$ yields boundary terms in $\vec{\xi}_i$, which are zero in the limit that the volume of the assembly grows large, so that from

4.20'a it is seen that:

$$I^{[1]}_1 = \bar{\Theta}(\Xi) \int_0^t d\tau \, [\, L_1(\Xi) - \tfrac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} \,] \, L_0^\dagger(\Xi) f_{n|1}(\Xi) \, f_{1,1}(t-\tau)$$

But, for the same reason, $\bar{\Theta}(\Xi) L_0^\dagger(\Xi) \, f_{n|1}(\Xi) = 0$. Hence,

$$I^{[1]}_1 = \bar{\Theta}(\Xi) \int_0^t d\tau_1 \, L_1(\Xi) L_0^\dagger(\Xi) \, f_{n|1} f_{1,1}(t-\tau_1) \ .$$ Writing the explicit

form of the Liouville operators:

$$I^{[1]}_1 = \bar{\Theta}(\Xi) \int_0^t d\tau \, (\tfrac{1}{2} \sum_{i\neq j}\sum -\vec{F}_{ij}\cdot(\vec{\nabla}_{p_i}-\vec{\nabla}_{p_j}) + \sum_{j\neq 1}-\vec{F}_{1j}\cdot(\vec{\nabla}_{p_1}-\vec{\nabla}_{p_j}) - (\tfrac{\vec{p}_1-\vec{p}_j}{m})\cdot\vec{\nabla}_{\xi_j})f_{n|1}f(t-\tau)$$

But, because $\vec{F}_{kj}$ is an odd function in the variables $\vec{\xi}_k - \vec{\xi}_j$

whereas $f_{n|1}(\Xi)$ is an even function in these variables

and, whereas $\bar{\Theta}(\Xi) \vec{\nabla}_{p_k} \not\gtrless 0$ for $k \neq 1$:

$$I^{[1]}_1 = \bar{\Theta}(\Xi) \int_0^t d\tau \{\sum_{j\neq 1}-\vec{F}_{1j}(\xi_j)\cdot\vec{\nabla}_{p_1}\} \, (-(\tfrac{\vec{p}_j-\vec{p}_1}{m})\cdot\vec{\nabla}_{\xi j}) \, f_{n|1}(\Xi) \, f_{1,1}(t-\tau) \ .$$

Since all particles are alike, and because $\Theta(\Xi) \vec{p}_j \, f_{n|1}(\Xi) = 0$

(because integration is over an odd function of $\vec{p}_j$), we

finally have:

$$I^{[1]}_1 = c \, \chi^{(2)} \int_0^t d\tau_1 \, [\, \tfrac{3}{m} + \tfrac{\vec{p}_1}{m}\cdot\vec{\nabla}_{p_1} \,] \, f_{1,1}(\underline{x}_1; t-\tau_1 | \underline{x}_{1o}) \qquad (4.21)$$

where

$$\chi^{(2)} \equiv \lim_{\Omega\to\infty} \int_\Omega d^3\xi \, g_2(\xi) \, \frac{\partial^2}{\partial\xi_x^2} \, \phi(|\vec{\xi}|) \qquad \qquad (4.22)$$

In a similar way, $I^{[1]}_2 = \bar{\Theta}(\Xi) \int_0^t d\tau [L_1(\Xi) - \tfrac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1}] L_1(\Xi) f_{n|1} f_{1,1}(t-\tau)$

But, $\bar{\Theta}(\Xi)[\tfrac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1}] L_1(\Xi) f_{n|1}(\Xi) f_{1,1}(t-\tau) = 0$ because the $\bar{\Theta}$ inte-

gration is over an odd function of the variables ($\vec{\xi}_i - \vec{\xi}_j$)

The latter observation is a special case of the following

Lemma: If $Q \equiv \bar{\Theta}(\Xi)[L_1(\Xi)L_0^\dagger(\Xi)L_0^\dagger \ldots L_1 L_1 L_0^\dagger \ldots L_0 L_1 \ldots] f_{n|1}(\Xi)$ is to

be non-zero, then the integer representing the number of times

that L_1 terms appear when added to the integer signifying the number of times L_0 appears, must yield an even integer.

This restriction follows from the requirement that integration act upon an even function of spatial variables.

Thus, $I_2^{[1]} = \bar{\Theta}(\Xi) \int_0^t d\tau L_1(\Xi) \; L_1(\Xi) \; f_{n|1}(\Xi) \; f_{1,1}(t-\tau)$ or, finally,

$$I_2^{[1]} = c \; \eta^{(2)} \int_0^t d\tau \; \nabla_{p_1}^2 \; f_{1,1}(t-\tau) \qquad \ldots (4.23)$$

with

$$\eta^{(2)} \equiv \int d^3\vec{\xi} \; g_2(\xi) \; \overline{F_x(\xi)}^2 \qquad \ldots (4.24)$$

In summary, the **first** collision integral has been reduced to a form involving simple and well known operators, viz:

$$I^{[1]} = c \int_0^t d\tau \left(\chi_m^{(2)}[3 + \vec{p}_1 \cdot \vec{\nabla}_{p_1}] + \eta^{(2)} \nabla_{p_1}^2 \right) f_{1,1}(t-\tau) \quad \ldots (4.25)$$

$\chi^{(2)}$ and $\eta^{(2)}$ are defined by 4.22 and 4.24, respectively.
($c = n/\Omega =$ the average density.)

Now, consider the **second** collision integral. From 4.15, it is seen that $I^{[2]}$ can be written as the sum of two terms, defined by:

$$I^{[2a]} = \bar{\Theta}(\Xi) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 \; e^{\tau_2 L_0^\dagger(\Xi)} \mathcal{S}_{-\tau_2} \; L(\Xi) L^\dagger(\Xi) f_{n|1} f_{1,1}(t-\tau_1)$$

$$\ldots (4.26)$$

$$I^{[2b]} = -\bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 e^{\tau_2 L_0^\dagger} \mathcal{S}_{-\tau_2} \; \Theta(\Xi) \; L \; L^\dagger \; f_{n|1} f_{1,1}(t-\tau_1)$$

$$\ldots (4.27)$$

Considering the first of these contributions, it is convenient to further designate

$$I^{[2a]} = \sum_{i=1}^4 I_i^{[2a]} \qquad \text{with}$$

$$I_1^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 e^{-\tau_2 L_o^\dagger} \mathcal{S}_{-\tau_2} L_o L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.28a)$$

$$I_2^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 e^{-\tau_2 L_o^\dagger} \mathcal{S}_{-\tau_2} L_o L_1 f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.28b)$$

$$I_3^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 e^{-\tau_2 L_o^\dagger} \mathcal{S}_{-\tau_2} L_1 L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \ldots \quad (4.28c)$$

$$I_4^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 e^{-\tau_2 L_o^\dagger} \mathcal{S}_{-\tau_2} L_1 L_1 f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.28d)$$

It is immediately obvious that $I^{[2]}$ is rather involved; to continue with the reduction of the collision integrals, we procede as follows.

Consider $I_1^{[2a]}$ (4.28a). The exponential operator $e^{\tau_2 L_o^\dagger}$ may be expanded

$$e^{\tau_2 L_o^\dagger} = 1 + \tau_2 L_o^\dagger (\Xi) + \frac{\tau_2^2}{2} L_o^\dagger(\Xi) L_o^\dagger(\Xi) + \ldots \ldots \ldots \quad (4.29)$$

so that $\quad I_1^{[2a]} = {}^0I_1^{[2a]} + {}^1I_1^{[2a]} + {}^2I_1^{[2a]} + {}^3I_1^{[2a]} + \ldots$, where

$${}^0I_1^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 \; \mathcal{S}_{-\tau_2} L_o L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.30a)$$

$${}^1I_1^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1(\tau_2) L_o^\dagger \; \mathcal{S}_{-\tau_2} L_o L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.30b)$$

$${}^2I_1^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1(\frac{\tau_2^2}{2}) L_o^\dagger L_o^\dagger \; \mathcal{S}_{-\tau_2} L_o L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \ldots \quad (4.30c)$$

$${}^3I_1^{[2a]} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1(\frac{\tau_2^3}{6}) L_o^\dagger L_o^\dagger L_o^\dagger \; \mathcal{S}_{-\tau_2} L_o L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad \ldots \quad (4.30d)$$

and so forth.

Writing the Liouville operators explicitly, ${}^{0}I_{1}^{[2a]}$ is seen to be:

$$^{0}I_{1}^{[2a]} = \bar{\mathbb{Q}}(\Xi) \int_{0}^{t} d\tau_{1} \int_{0}^{\tau_{1}} d\tau_{2} (\tfrac{1}{2}\textstyle\sum\sum -\vec{F}_{ij} \circ \vec{D}_{ij} + \sum -\vec{F}_{1k} \circ \vec{D}_{1k}) \, \mathcal{S}_{-\tau_{2}} \times$$

$$\times \, (-\textstyle\sum(\vec{p}_{i}-\vec{p}_{1}) \circ \vec{\nabla}_{\xi_{i}} - \vec{p}_{1} \circ \vec{\nabla}_{q_{1}})(-\textstyle\sum(\vec{p}_{i}-\vec{p}_{1}) \circ \vec{\nabla}_{\xi_{i}}) f_{n|1} f_{1,1}(t-\tau_{1})$$

However, since $F_{ij}(|\vec{\xi}_{i}-\vec{\xi}_{j}|)$ is an odd function of the variable $(\vec{\xi}_{i}-\vec{\xi}_{j})$, whereas $f_{n|1}(\Xi)$ is an even function of this variable, and whereas the $\bar{\mathbb{Q}}$ operator integrates over these variables, upon a little reflection it is seen that the only non-zero terms in ${}^{0}I_{1}^{[2a]}$ are

$$^{0}I_{1}^{[2a]} = \bar{\mathbb{Q}}(\Xi) \int_{0}^{t} d\tau_{1} \int_{0}^{\tau_{1}} d\tau_{2} (\textstyle\sum -\vec{F}_{1k} \circ \vec{\nabla}_{p_{1}}) \, \mathcal{S}_{-\tau_{2}} (-\tfrac{\vec{p}_{1}}{m} \circ \vec{\nabla}_{q_{1}})(-\textstyle\sum \tfrac{\vec{p}_{i}-\vec{p}_{1}}{m} \circ \vec{\nabla}_{\xi_{i}}) f_{n|1} f_{1,1}(t-\tau_{1})$$

$$= \bar{\mathbb{Q}}(\Xi) \int_{0}^{t} d\tau_{1} \int_{0}^{\tau_{1}} d\tau_{2} \; L_{1} \, \mathcal{S}_{-\tau_{2}} (-\tfrac{\vec{p}_{1}}{m} \circ \vec{\nabla}_{q_{1}}) \, L_{o}^{\dagger} \, f_{n|1} f_{1,1}(t-\tau_{1})$$

But, $\mathcal{S}_{-\tau_{2}} (-\tfrac{\vec{p}_{1}}{m} \circ \vec{\nabla}_{q_{1}}) = \tfrac{\partial}{\partial \tau_{2}} \mathcal{S}_{-\tau_{2}}$. Hence, integrating over in the above equation yields

$$^{0}I_{1}^{[2a]} = \bar{\mathbb{Q}}(\Xi) \int_{0}^{t} d\tau_{1} \; L_{1} \mathcal{S}_{-\tau_{1}} \, L_{o}^{\dagger} \, f_{n|1} \, f_{1,1}(t-\tau_{1}) \; -$$

$$- \bar{\mathbb{Q}} \int_{0}^{t} d\tau_{1} \; L_{1} \, L_{o}^{\dagger} f_{n|1} \, f_{1,1}(t-\tau_{1}) \qquad \ldots\ldots \quad (4.31)$$

Notice that the second term in 4.31 is just the negative of $I_{1}^{[1]}$ as indicated at the top of pg. 47 . It is thus logical to define a term $\mathcal{Q}_{1}$:

$$\mathcal{Q}_{1} \equiv I_{1}^{[1]} + {}^{0}I_{1}^{[2a]} = c \, \chi^{(2)} \int_{0}^{t} d\tau_{1}[\tfrac{3}{m} + \tfrac{\vec{p}_{1}}{m} \circ \vec{\nabla}_{p_{1}}] \, \mathcal{S}_{-\tau_{1}} f_{1,1}(t-\tau_{1})$$

$$\ldots\ldots \quad (4.32)$$

$(L_{o}^{\dagger}(\Xi)$ and $\mathcal{S}_{-\tau_{1}}$ commute.)

As we shall see, $\mathcal{Q}_{1}$ is one of nine basic integrals into

which the collision integral, to the fourth power of the forces, shall be reduced.

The next step in the program is the reduction of the contribution given by 4.30b: $^1I_1{}^{[2a]}$. Since it provides an example of the increasing complexity of the arguments required in this endeavor, this too is to be presented in some detail. (However, rather than burden the reader with details, only the results shall be supplied for the other terms. If one is further interested, he may refer to appendix B for some additional comments.)

Thus, upon writing the Liouville operators in explicit form and after dropping some zero contributions:

$$^1I_1{}^{[2a]} = \overline{\mathbb{S}}(\Xi) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (-\tau_2) \left[-\vec{F}_{1_j}(\xi_j) \cdot \vec{\nabla}_{p_1} \left((\frac{\vec{p}_j - \vec{p}_1}{m}) \cdot \vec{\nabla}_{\xi_j} \right)^3 \times \right.$$

$$\times f_{n|1}(\Xi) \mathcal{S}_{-\tau_2} f_{1,1}(t-\tau_1) \qquad \ldots\ldots (4.33)$$

Consider $\overline{\mathbb{S}}(\Xi)\left(-F_x(\xi_j)\frac{\partial}{\partial p_{1_x}} (\frac{\vec{p}_j - \vec{p}_1}{m} \cdot \vec{\nabla}_{\xi_j})^3 f_{n|1}(\Xi)\right)$. The requirement that $\mathbb{S}$ act upon an even function of Ξ leaves only the following non-zero terms:

$$\overline{\mathbb{S}}(\Xi) \left(-F_x(\xi_j) \cdot \frac{\partial}{\partial p_{1_x}} ([\frac{p_{j_x} - p_{1_x}}{m^3}]^3 \frac{\partial^3}{\partial \xi_{j_x}^3} + 3\frac{(p_{j_y} - p_{1_y})^2(p_{j_x} - p_{1_x})}{m^3}\frac{\partial^3}{\partial \xi_x \partial \xi_y^2} + \right.$$

$$\left. + 3\frac{(p_{j_z} - p_{1_z})^2(p_{j_x} - p_{1_x})}{m^3}\frac{\partial^3}{\partial \xi_x \partial \xi_z^2} \right) f_{n|1}(\Xi)$$

However, $\overline{\Theta}(\Xi)$ must act upon an even function of $\vec{p}_j$. Thus, the above expression is:

$$\bar{\Theta}(\Xi)[\frac{-F_x(\xi)}{m^3}] \left((-3[p_{j_x}^2+p_{1_x}^2]p_{1_x}\partial/\partial p_{1_x} - 3[p_{j_x}^2+p_{1_x}^2])\frac{\partial^3}{\partial\xi_x^3} \right.$$

$$+3(p_j^2+p_{1_y}^2)(-1-p_{1_x}\frac{\partial}{\partial p_{1_x}})\frac{\partial^3}{\partial\xi^2\partial\xi_x} + 3(p_j^2-p_{1_z}^2)(-1-p_{1_x}\frac{\partial}{\partial p_{1_x}}\frac{\partial^3}{\partial\xi})f_{n|1}$$

$$= \bar{\Theta}(\Xi)\frac{F_x(\xi)}{m^3} \left(([\frac{3m}{\beta}p_{1_x}+p_{1_x}^3]\frac{\partial}{\partial p_{1_x}} +3[\frac{m}{\beta}+p_{1_x}^2])\frac{\partial^3}{\partial\xi_x^3} \right.$$

$$+3(\frac{m+p_{1_y}^2}{\beta})(1+p_1\frac{\partial}{\partial p_{1_x}})\frac{\partial^3}{\partial\xi\partial\xi_y^2}+3(\frac{m+p_{1_z}^2}{\beta})(1+p_{1_z}\frac{\partial}{\partial p_{1_z}})\frac{\partial^3}{\partial\xi_z^2\partial\xi_x})f_{n|1}$$

Next, adding the similar contributions from F_y and F_z and noting that:

$$\bar{\Theta}(\Xi)F_x\frac{\partial^3}{\partial\xi_x\partial^2\xi_y}f_{n|1}(\Xi) = \bar{\Theta}(\Xi) F_x\frac{\partial^2}{\partial\xi_x\partial\xi_z^2}f_{n|1}(\Xi) \qquad \text{etc.,}$$

we obtain for $^1I_1^{[2a]}$:

$$\dots\dots(4.34)$$

$$^1I_1^{[2a]} = -c/_m3\chi^{(4)}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2(-\tau_2)\{3(\frac{3m+p_1^2}{\beta})+\sum(\frac{3mp}{\beta}_{1_i}+p_{1_i}^3)\frac{\partial}{\partial p_{1_i}}\}\delta_{-\tau_2}f_{1,1}(t-\tau_1)$$

$$\frac{-3c}{m^3}\chi^{(2,2)}\int_0^t d\tau_1\int_0^{\tau_1}d\tau_2(-\tau_2)\{\frac{2m}{\beta}(3+\vec{p}_1\cdot\vec{\nabla}_{p_1})+2p_1^2+\sum(p_1^2-p_{1_i}^2)p_{1_i}\frac{\partial}{\partial p_{1_i}}\}\delta_{-\tau_2}f_{1,1}^{(t-\tau)}$$

where the system constants are defined by

$$\chi^{(4)} \equiv \int d^3\xi\ g_2(\xi)\frac{\partial^4}{\partial\vec{\xi}_x}\phi(\xi) \qquad\dots\dots \quad(4.35a)$$

and

$$\chi^{(2,2)} \equiv \int d^3\xi\ g_2(\xi)\frac{\partial^4}{\partial\xi_x^2\partial\xi_y^2}\phi(\xi) \qquad\dots\dots \quad(4.35b)$$

It is easily deconstrated that $^1I_1^{[2a]}$ is closely related to $^2I_1^{[2a]}$.

Note that, in light of the Lemma 4.23, 4.30c can be written:

$$2_{I_1^{[2a]}} = \bar{\delta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \; L_1 \frac{\tau^2}{2^2} L_o^\dagger L_o^\dagger \delta_{-\tau_2} (-\frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1}) L_o^\dagger \; f_{n|1} f_{1,1}(t-\tau_1) \quad ..(4.36)$$

But, integrate the above expression by parts to obtain:

$$2_{I_1^{[2a]}} = (\bar{\delta}(\Xi)) \int_0^t d\tau_1 \; L_1 \frac{\tau^2}{2} L_o^\dagger L_o^\dagger L_o^\dagger \delta_{-\tau_1} \; f_{n|1} f_{1,1}(t-\tau_1)) \; - \; 1_{I_1^{[2a]}}$$

Thus, logically, one defines a term consting of the sum of $1_{I_1}^{[2a]}$ and $2_{I_1}^{[2a]}$:

$$\mathcal{Q}_3 \equiv 1_{I_1}^{[2a]} + 2_{I_1}^{[2a]}$$

$$= \frac{c}{m^3} \chi^{(4)} \int_0^t d\tau_1 \frac{\tau^2}{2} \left(3(\frac{3m}{\beta} + p_1^2) + \sum_{i=1}^{3} (\frac{3mp_{1_i}}{\beta} + p_1^3) \frac{\partial}{\partial p_{1_i}} \right) \delta_{-\tau_1} f_{1,1}(t-\tau_1)$$

$$+ 3\frac{c}{m^3} \chi^{(2,2)} \int d\tau_1 \frac{\tau^2}{2} \left(\frac{2m(3+\vec{p}_1 \cdot \vec{\nabla}_{p_1})}{\beta} + 2p_1^2 + p_1^2(\vec{p}_1 \cdot \vec{\nabla}_{p_1}) - \sum_{i=1}^{3} p_{1_i}^3 \frac{\partial}{\partial p_{1_i}} \right) \delta_{-\tau_1} f_{1,1}(t-\tau_1)$$

However, further simplification is possible upon noting that $\chi^{(4)} = 3\chi^{(2,2)}$.** Thus, one obtains, finally

$$.....(4.37)$$

$$\mathcal{Q}_3 f_{1,1} = \frac{c}{m^3} \chi^{(4)} \int_0^t d\tau_1 \frac{\tau^2}{2} \left(\frac{15m}{\beta} + 5p_1^2 + \frac{5m\vec{p}_1 \cdot \vec{\nabla}_{p_1}}{\beta} + p_1^2 \vec{p}_1 \cdot \vec{\nabla}_{p_1} \right) \delta_{-\tau_1} f_{1,1}(t-\tau_1)$$

In this way, another of the 'basic' reductions of the interaction integral has been accomplished.

Next, one considers $3_{I_1}[2a]_o$. It is seen that this term is proportional to system constants of the order of the "sixth power of the forces"; i.e., constants for which M, as

**For a proof, see appendix C.

defined by 4.20, is equal to 6. Since we are here concerned with calculating contributions through the "fourth power of the forces", only, it need not be evaluated.

In this spirit, all termscontributing to the second order (M = 4) contribution of the collision integral are evaluated. In all cases, the resultant integral operators are found to be of the general form:

$$\sim \int_0^t d\tau_1 \ Op(\ \tau_1; p_1, \frac{\partial}{\partial p_1}, \frac{\partial^2}{\partial p_1^2}, \ldots; \frac{\partial}{\partial q_1}, \frac{\partial^2}{\partial q_1^2}, \ldots \ ) \Big\}_{-\tau_1} f_{1,1}(t-\tau_1) \qquad \ldots (4.38)$$

It is found that all non-zero terms to order M = 4 are contained in the collision integrals (of 4.15) for which $r \le 4$. These terms are best expressed as the sum of nine basic integral operators:

$$I = \sum_{k=1}^{q} \mathcal{Q}_k + o(\ M^6 \ ) \qquad \ldots \ldots \ldots (4.39)$$

where:**

$$\mathcal{Q}_1 = c\chi^{(2)} \int_0^t d\tau_1 \ (\ \frac{3}{m} + \vec{p}_1 \circ \vec{\nabla}_{p_1}) \Big\}_{-\tau_1} f_{1,1}(\vec{x}_1; t-\tau_1 | \vec{x}_{1_0}) \qquad \ldots \ldots (4.32)$$

$$\mathcal{Q}_2 = c\eta^{(2)} \int_0^t d\tau_1 \ (\nabla^2_{p_1} + \frac{\tau_1}{m} \nabla^2_{p_1,q_1}) \Big\}_{-\tau_1} f_{1,1}(t-\tau_1) \qquad \ldots \ldots (4.40)$$

$$\mathcal{Q}_3 = \frac{c}{m^3}\chi^{(4)} \int_0^t d\tau_1 \ \frac{\tau_1^2}{2} \ (15m + 5p_1^2 + 5m\vec{p}_1 \circ \vec{\nabla}_{p_1} + p_1^2\vec{p}_1 \circ \vec{\nabla}_{p_1}) \Big\}_{-\tau_1} f_{1,1}(t-\tau_1) \qquad \ldots \ldots (4.37)$$

$$\mathcal{Q}_4 = \frac{c}{m^3}\eta^{(4,xx)} \int_0^t d\tau_1 \ \frac{\tau_1^2}{2} (-20 + \frac{10}{3} \frac{m}{\beta} (\ \nabla^2_{p_1} + \frac{\tau_1}{m}\nabla^2_{p_1,q_1}) + \frac{16}{3} \frac{\tau_1}{m}\vec{p}_1 \vec{\nabla}_{q_1} + $$
$$+ \frac{2p^2}{3}_1(\nabla^2_{p_1} + \frac{\tau_1}{m}\nabla^2_{p_1,q_1}) - \frac{4}{3}\vec{p}_1 \vec{\nabla}_{p_1}(1-\vec{p}_1 \vec{\nabla}_{p_1} - \frac{\tau_1}{m}\vec{p}_1 \vec{\nabla}_{q_1})) \Big\}_{-\tau_1} f_{1,1}(t-\tau_1) \qquad \ldots \ldots (4.38)$$

** Additional details & typical calculations are to be found in Appendix B.

The system constant $\chi^{(4,xx)}$ is defined in table 4-1, below.

$$\ldots\ldots (4.42)$$

$$\begin{aligned}
\alpha_5 f_{1,1} = \frac{c_3}{m}\eta^{(4,xx)}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(&(5m + \frac{p_1^2}{3\beta})(3\nabla_{p_1}^2 +\frac{4}{3}\frac{\tau\nabla^2}{m}_{p_1 q_1}) + 20 + \\
&+\frac{44}{3}\vec{p}_1\vec{\nabla}_{p_1} + \frac{4\tau}{m}\vec{p}_1\vec{\nabla}_{q_1} +2(\vec{p}_1\vec{\nabla}_{p_1})^2+\frac{4}{9}(\vec{p}_1\vec{\nabla}_p\frac{\tau\vec{\nabla}}{m}_{q_1}+\vec{p}\frac{\tau\vec{\nabla}}{m}_q\vec{\nabla}_{p_1})\Big)\Big) f(t-\tau)_{-\tau} f_{1,1}
\end{aligned}$$

$$+\frac{c}{m_3}\chi^{\{2,xx\}}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(m(3\nabla_{p_1}^2 +\frac{4\tau\nabla^2}{3m}_{pq_1}) + 12 + 10\vec{p}_1\vec{\nabla}_{p_1} +\frac{8\tau}{3m}\vec{p}_1\vec{\nabla}_{q_1}\Big)\ \Big\}_{-\tau} f(t-\tau)_{1,1}$$

$$\begin{aligned}
+\frac{c}{m_3}\chi^{\{2,xy\}}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(&(2m+p_1^2)(3\nabla_{p_1}^2+\frac{4\tau\nabla^2}{3m}_{p_1 q_1})+6+5\vec{p}_1\vec{\nabla}_{p_1}+ \frac{2}{m}\vec{p}_1\vec{\nabla}_{q_1} + \\
&+3(\vec{p}_1\vec{\nabla}_{p_1})^2+\frac{2\tau}{3m}(\vec{p}_1\vec{\nabla}_{p_1}\vec{p}_1\vec{\nabla}_{q_1}+\vec{p}_1\vec{\nabla}_{q_1}\vec{p}_1\vec{\nabla}_{p_1})\Big)\Big\}_{-\tau} f_{1,1}(t-\tau)
\end{aligned}$$

$$+\frac{c}{m_3}\chi^{\{2,xx\}}_{yy}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(18+9\vec{p}_1\vec{\nabla}_{p_1}+3(\vec{p}_1\vec{\nabla}_{p_1})^2+\frac{2\tau}{m}\vec{p}_1\vec{\nabla}_{q_1}+\frac{2}{3m}(\vec{p}\vec{\nabla}_p\vec{p}\vec{\nabla}_q+\vec{p}\vec{\nabla}_q\vec{p}\vec{\nabla}_p)\Big)\Big\}_{-\tau} \times f_{1,1}(t-\tau)$$

$$+\frac{c}{m_3}\chi_3^4\int_0^t d\tau\ \frac{\tau^2}{2}\Big(33+20\vec{p}\vec{\nabla}_p+\frac{14\tau\vec{p}\vec{\nabla}}{3m}_q+ 3(\vec{p}\vec{\nabla}_p)^2+\frac{2\tau}{3m}(\vec{p}\vec{\nabla}_p\vec{p}\vec{\nabla}_q+\vec{p}\vec{\nabla}_q\vec{p}\vec{\nabla}_p)\Big)\Big\}_{-\tau} f_{1,1}(t-\tau)$$

$$\circ\circ\circ\circ\circ\circ\circ (4.43)$$

$$\alpha_6 f_{1,1} = \frac{c}{m}\Psi_4^{(x,x)}\int_0^t d\tau\tau\frac{\tau}{2}\Big(\nabla_{p_1}^2 +\frac{4\tau^2\nabla^2}{3m^2}_{q_1} +\frac{4\tau\nabla^2}{m}_{p_1,q_1}\Big)\ \Big\}_{-\tau} f_{1,1}(t-\tau)$$

$$\begin{aligned}
+\frac{c}{m}\Psi_4^{(x,y)}\int_0^t d\tau\tau\frac{\tau^2}{2}\Big(&6\nabla_{p_1}^2 +\frac{2\tau}{m}\nabla^2_{q_1} +\frac{8\tau\nabla^2}{m}_{p_1,q_1}+\frac{\tau}{3m}\vec{p}_1\vec{\nabla}_{q_1}(\nabla_{p_1}^2 +\frac{\tau\nabla^2}{m}_{p_1,q_1})+ \\
&+\vec{p}_1\vec{\nabla}_{p_1}(3\nabla_{p_1}^2 +\frac{4\tau\nabla^2}{m}_{pq_1} +\frac{\tau^2\nabla^2}{m^2}_{q_1})\Big)\Big\}_{-\tau} f_{1,1}(t-\tau)
\end{aligned}$$

$$\begin{aligned}
+\frac{c}{m}\Psi_4^{(xy,xy)}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(&-4\nabla_{p_1}^2 +\vec{p}_1\vec{\nabla}_{p_1}(6\nabla_{p_1}^2 +\frac{14\tau\nabla^2}{3m}_{p_1q_1} +\frac{1\tau^2\nabla^2}{3m^2}_{q_1}) + \\
&+\frac{2}{3}\frac{\tau^2\nabla^2}{m^2}_{q_1} + \tau\vec{p}_1\vec{\nabla}_{q_1}(4\nabla_{p_1}^2 +\frac{7}{3}\frac{\tau\nabla^2}{m}_{p_1q_1})\Big)\Big\}_{-\tau} f_{1,}(t-\tau)
\end{aligned}$$

$$\begin{aligned}
+\frac{c}{m}\Psi_{(3)}^{(4)}\int_0^t d\tau\ \frac{\tau^2}{2}\Big(&5\nabla_{p_1}^2 +\frac{4\tau\nabla^2}{m}_{p_1q_1} -\frac{\tau^2\nabla^2}{m^2}_{q_1}+\vec{p}\vec{\nabla}_p(\nabla_p^2+\frac{2\tau\nabla^2}{3m}_{pq} -\frac{1\tau^2\nabla^2}{3m^2}_{q_1})+ \\
&+ \frac{\tau}{3m}\vec{p}_1\vec{\nabla}_{q_1}(\nabla_{p_1}^2 + \frac{\tau\nabla^2}{m}_{p_1q_1})\Big)\ \Big\}_{-\tau} f_{1,1}(t-\tau)
\end{aligned}$$

$$\mathcal{A}_7 f_{1,1} = -c^2 \chi^{(2)} \int_0^t d\tau \; \frac{\tau^2}{2} \left[3 + \frac{\vec{p}_1}{m} \cdot \frac{\vec{\nabla}}{m} \right]_{p_1} \left(\chi^{(2)} \left[3 + \frac{\vec{p}_1}{m} \cdot \frac{\vec{\nabla}}{m} \right]_{p_1} + \frac{2\tau}{3m^2} \vec{p}_1 \cdot \vec{\nabla}_{q_1} \right] + \right.$$

$$\left. + \eta^{(2)} \left[\nabla_{p_1}^2 + \frac{5\tau}{3m} \nabla_{p_1,q_1}^2 + \frac{2\tau^2}{3m^2} \nabla_{q_1}^2 \right] \right) \mathcal{A}_{-\tau} f_{1,1}(t-\tau)$$

$$\cdots \cdot (4.44)$$

$$\mathcal{A}_8 f_{1,1} = c \left[\mu_3^{(4,xx)} + c_{(3)} \mu^{(4)} \right] \int_0^t d\tau \; \frac{\tau^2}{2} \left[\frac{3}{R} \nabla_{p_1}^2 + \frac{3\tau}{m} \nabla_{p_1,q_1}^2 + \frac{5\tau^2}{4m^2} \nabla_{q_1}^2 \right) + $$

$$+ \frac{\tau \nabla^2}{m} {}_{p_1,q_1} \left(3 \nabla_{p_1}^2 + \frac{5\tau}{2m} \nabla_{p_1,q_1}^2 + \frac{3\tau^2}{4m^2} \nabla_{q_1}^2 \right) \right) \mathcal{A}_{-\tau} f_{1,}(t-\tau)$$

$$+ c \left[\Psi_4^{(x,x)} + c \Psi_{(3)}^{(4)} \right] \int_0^t d\tau \; \frac{\tau^2}{2} \left(\nabla_{p_1}^2 \left(9 + 3\vec{p}_1 \cdot \frac{\vec{\nabla}}{p_1} + \frac{\tau}{m} \vec{p}_1 \cdot \vec{\nabla}_{q_1} \right) + \right.$$

$$\left. + \frac{\tau \nabla^2}{m} {}_{p_1,q_1} \left(6 + 2\vec{p}_1 \cdot \frac{\vec{\nabla}}{p_1} + \frac{1}{2m} \vec{p}_1 \cdot \vec{\nabla}_{q_1} \right) + \frac{\tau^2}{4m^2} \nabla_{q_1}^2 \left(3 + \vec{p}_1 \cdot \frac{\vec{\nabla}}{p_1} \right) \right) \mathcal{A}_{-\tau} f(t-\tau)_{1,1}$$

$$\cdots \cdot (4.45)$$

Finally: $\qquad\qquad\qquad\qquad\qquad\qquad\qquad \cdots\cdots (4.46)$

$$\mathcal{A}_9 f_{1,1} = -c^2 \int_0^t d\tau \; \frac{\tau^2}{2} \left(\eta^{(2)} \nabla_{p_1}^2 \left[\frac{\chi^{(2)}}{m} \left(3 + \vec{p}_1 \cdot \frac{\vec{\nabla}}{p_1} + \frac{2\tau p}{3m} \vec{\nabla}_1 \cdot \vec{q}_1 \right) + \right.\right.$$

$$\left. + \eta^{(2)} \left(\nabla_{p_1}^2 + \frac{5\tau}{3m} \nabla_{p_1 q_1}^2 + \frac{2\tau^2}{3m^2} \nabla_{q_1}^2 \right) \right]$$

$$+ \eta^{(2)} \frac{\tau \nabla^2}{3m} {}_{p_1 q_1} \left[\frac{\chi^{(2)}}{m} \left(3 + \vec{p}_1 \cdot \frac{\vec{\nabla}}{p_1} + \frac{3\tau p}{4m} \vec{\nabla}_1 \cdot \vec{q}_1 \right) + \eta^{(2)} \left(\nabla_p^2 + \frac{7\tau \nabla^2}{4m} {}_{pq} + \frac{3\tau^2 \nabla^2}{4m^2 q_1} \right) \right] \right\} \times$$

$$\times \mathcal{A}_{-\tau} f_{1,1}(t-\tau)$$

The system constants appearing in $\mathcal{A}_1$ through $\mathcal{A}_9$ are

defined in table 4-1, which appears on page 60.

It is unfortunate that things get so complicated so

quickly. In effect, we have expanded the collision integral

operator in a power series related to the relative strength

of internal interactions (i.e., a series similar to an inverse

temperature expansion): $\mathcal{A}_1$ and $\mathcal{A}_2$ are the first order

terms in the expansion; $\mathcal{A}_3$ through $\mathcal{A}_9$ constitute the second order term. It is apparent that it would be an extremely tedious task to obtain the third order terms of this expansion.

However, one can make remarks concerning the general form of the higher order terms, even if analytic complexity precludes specific evaluation. The expansion of the integral term (4.15) may be written figuratively as:

$$
\begin{aligned}
I = \mathcal{M}_{[2]} & \int_0^t d\tau \; Op^{[1]}(\vec{p}_1; \vec{\nabla}_{p_1}; \frac{\tau \vec{\nabla}}{m} q_1) \; \Big\}_{-\tau} f_{1,1}(t-\tau) \qquad (4.47) \\
+ \mathcal{M}_{[4]} & \int_0^t d\tau \; \frac{\tau^2}{2!} \; Op^{[2]}(\vec{p}_1; \vec{\nabla}_{p_1}; \frac{\tau \vec{\nabla}}{m} q_1) \; \Big\}_{-\tau} f_{1,1}(t-\tau) \\
+ \mathcal{M}_{[6]} & \int_0^t d\tau \; \frac{\tau^4}{4!} \; Op^{[3]}(\vec{p}_1; \vec{\nabla}_{p_1}; \frac{\tau \vec{\nabla}}{m} q_1) \; \Big\}_{-\tau} f_{1,1}(t-\tau) \\
+ & \quad o o o o o o o o o o o o o \\
= \sum_{k=1}^{\infty} \mathcal{M}_{[2k]} & \int_0^t d\tau \; \frac{\tau^{(2k-2)}}{(2k-2)!} \; Op^{[k]}(\vec{p}_1; \vec{\nabla}_{p_1}; \frac{\tau \vec{\nabla}}{m} q_1) \; \Big\}_{-\tau} f_{1,1}(t-\tau)
\end{aligned}
$$

where $\mathcal{M}_{[2k]}$ are system constants for which $M = 2k$ (cf. discussion following 4.20.)

Notice the manner in which the powers of τ in the integrals increase directly with increasing powers of M. Terms in the $Op^{[k]}$ which do not contain derivatives re.spatial coordinates do not contain the time τ explicitly. Spatial terms in the operators appear only as powers of derivatives re q_1; furthermore, every derivative term in q_1 is always coupled with a factor (τ/m).

It is to be noticed that the expansions for probability
densities and correlation functions to be obtained in the
following chapters will not be power series in the usual
sense. There is no <u>simple</u> parameter available for an expansion;
rather, expressions will contain the complicated parameters
of the type defined by eqn. 4.20.

Systems to which the analysis will be applied must be
chosen judiciously. Actually, we wish to apply these calcu-
lations to assemblies for which interparticle forces are
characterized by a hard repelling core plus short range at-
tracting well (cf. fig. 5.2, p. 77, below.) In this case
the system constants are roughly proportional to powers of
$\mathcal{E}_0$, where $\mathcal{E}_0$ is the depth of the potential well.

On the other hand, application of these expansions for
studying plasmas will, in many cases, be quite unsatisfactory
This is because, for the special case of a purely repulsive
potential, the system constants are proportional to successively
higher powers of the <u>reciprocal</u> of the appropriate coupling
constant.

For example, consider the system constants $\eta^{(2)}$ and $\eta^{(4,x,x)}$
(cf. table 4.1), evaluated for a repulsive coulomb potential,
$\varphi(\rho) \sim +e^2/\rho$. If one approximates $g_2(\rho)$ by $g_2(\rho) \approx \dfrac{\Omega e^{-\beta\varphi(\rho)}}{\int d\rho\, e^{-\beta\varphi(\rho)}}$
it is quite easily shown that $\eta^{(4,x,x)} \propto \dfrac{1}{(e^2\beta)^2}\eta^{(2)}$.
Thus, rather than becoming progressively smaller, the system
constants grow larger for high temperatures.

Even so, this does not necessarily preclude the employment

of these expansions to study particular aspects of ionized

media. For example, if one calculates the dielectric constant

of a partially ionized gas, it is found that successive terms

are actually related (to a close approximation) by $\propto \frac{1}{\omega^2} \frac{c}{m(e^2 c)\beta^3}$

where ω is the frequency of the incident radiation, and c

is the density of electrons. Hence, a useful expression is

obtained at high frequencies, for which the expansion is

strongly convergent. This point is examined in greater detail

at the end of the next chapter.

For systems with more complex force laws, it is quite

difficult to determine the exact relationships between system

constants of sucessively higher order. Suppose we make the

following approximation for $g_2(\rho)$ (corresponding to an

infinitely strong repulsive core).

$$g_2(r) = \begin{cases} 0 & \text{for } r < v_0 \\ e^{\beta\varphi_\alpha} & \text{for } r > v_0 \end{cases} \qquad\qquad (4.48)$$

Then, for example, $\mu^{(y,xx)}/\eta^{(z)} = \int d^3\xi\, g_2(\xi)\, \overline{F_x(\xi)}^4 \Big/ \int d^3\xi\, g_2(\xi)\, \overline{F_x(\xi)}^2 \propto O(\mathcal{E}_0^2)$

where $\mathcal{E}_o$ is the depth of the attractive potential well. Thus

in expansions for the slow neutron scattering cross-sections

(cf. chapter 6, below), where it is necessary to compare,

e.g., terms proportional to $\eta^{(z)}$ with those proportional to

$\beta^2 \mu^{(y,xx)}/\mathcal{K}^2$, one finds that the pertinent expansion

parameter is effectively $\beta \mathcal{E}_o$.

Table 4-1: Definitions of system constants appearing in the collision integral expansion.

$$\chi^{(2)} \equiv \int d^3\xi \; g_2(|\xi|) \; \frac{\partial^2}{\partial \xi_x^2} \phi(|\xi|)$$

$$\chi^{(4)} \equiv \int d^3\xi \; g_2(|\xi|) \; \frac{\partial^4}{\partial \xi_x^4} \phi(\xi)$$

$$\chi^{(2,2)} \equiv \int d^3\xi \; g_2(\xi) \; \frac{\partial^4 \phi(\xi)}{\partial \xi_x^2 \partial \xi_y^2}$$

$$\chi^{\{2xx\}}_{\{2yy\}} \equiv \int d^3\xi \; g_2(\xi) \; \frac{\partial^2 \phi}{\partial \xi_x^2} \frac{\partial^2 \phi}{\partial \xi_y^2}$$

$$\chi^{\{2xx\}}_{\{2xx\}} \equiv \int d^3\xi \; g_2(\xi) \left(\frac{\partial^2 \phi}{\partial \xi_x^2} \right)^2$$

$$\chi^{\{2xy\}}_{\{2xy\}} \equiv \int d^3\xi \; g_2(\xi) \left(\frac{\partial^2 \phi}{\partial \xi_x^2 \partial \xi_y^2} \right)^2$$

$$\chi^{(4)}_{(3)} \equiv \int d^3\xi_2 d^3\xi_3 g_3(\xi_2,\xi_3) \; \frac{\partial^2 \phi(\xi_2)}{\partial \xi_{2x}^2} \frac{\partial^2 \phi(\xi_3)}{\partial \xi_{3x}^2}$$

$$\eta^{(2)} \equiv \int d^3\xi \; g_2(\xi) \; \overline{F_x(\xi)}^2$$

$$\eta^{(4xx)} \equiv \int d^3\xi \; g_2(\xi) \; F_x(\xi) \; \frac{\partial^2}{\partial \xi_x^2} F_x(\xi)$$

$$\eta^{(4xy)} \equiv \int d^3\xi \; g_2(\xi) \; F_x(\xi) \; \frac{\partial^2}{\partial \xi_y^2} F_x(\xi)$$

$$\Psi^{(4xx)} \equiv \int d^3\xi \; g_2(\xi) \; \frac{\partial^2 \phi}{\partial \xi_x^2} \; \overline{F_x(\xi)}^2$$

$$\Psi^{(4xy)} \equiv \int d^3\xi \; g_2(\xi) \; \frac{\partial^2 \phi}{\partial \xi_x^2} \; \overline{F_y(\xi)}^2$$

$$\Psi^{(xy,xy)} \equiv \int d^3\xi \; g_2(\xi) \; \frac{\partial^2 \phi}{\partial \xi_x \partial \xi_y} \; F_x \; F_y$$

$$\Psi^{(4)}_{(3)} \equiv \int d\xi_2 d\xi_3 \; g_3(\xi_2,\xi_3) \; \frac{\partial^2 \phi(\xi)}{\partial \xi_{2x}^2} \overline{F_x(\xi_3)}^2$$

$$\mu^{(4xx)} \equiv \int d^3\xi \; g_2(\xi) \; \overline{F_x(\xi)}^4$$

$$\mu^{(4xy)} \equiv \int d^3\xi \; g_2(\xi) \; \overline{F_x(\xi)}^2 \overline{F_y(\xi)}^2$$

$$\mu^{(4)}_{(3)} \equiv \int d\xi_2 d\xi_3 \; g_3(\xi_2,\xi_3) \; \overline{F_x(\xi_2)}^2 \overline{F_x(\xi_3)}^2$$

Relationships between system constants:

a) $\chi^{(4)} = 3\chi^{(2,2)}$

b) $\Psi^{(4xx)} = 2 \Psi_4^{(xy,xy)} + \Psi^{(4xy)}$

c) $\eta^{(4xx)} = 3\eta^{(4xy)}$

d) $\chi^{\{2xx\}}_{\{2xx\}} = \chi^{\{2xx\}}_{\{2yy\}} + 2\chi^{\{2xy\}}_{\{2xy\}}$

e) $\mu^{(4xx)} = 3\mu^{(4xy)}$

(see appendix C for proof).

CHAPTER V

SOLUTION OF THE KINETIC EQUATION FOR $f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0})$;
MOMENTUM DENSITIES AND CORRELATION FUNCTIONS

In the previous chapter, considerable effort was expended in obtaining an expansion for the collision integral which appears in the evolutionary equation for $f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0})$. These expressions are a necessary preliminary for obtaining a solution of the kinetic equation. An iteration procedure for that purpose, consistent with the expansion of the collision integral, is developed in the following analysis.

It is frequently fruitful to study the properties of dense gases or liquids at high temperatures by extension of theories appropriate to a study of dilute gases. It is somewhat in this spirit that we here attempt to obtain expansions for $f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0})$ and related densities and correlation functions. Thus, let us search for an iteration solution to equation (4.1) (the kinetic equation for $f_{1,1}$) having the form

$$f_{1,1}(x_1;t|x_{1_0}) = f_{1,1}^{[0]} + f_{1,1}^{[1]} + f_{1,1}^{[2]} + \cdots\cdots$$
$$= \sum_{i=1}^{\infty} f_{1,1}^{[i]} \qquad \cdots(5.1)$$

where $f_{1,1}^{[0]}$ is the expression to be obtained were the assembly an ideal gas, and $f_{1,1}^{[1]}$, $f_{1,1}^{[2]}$, etc., represent successively higher order corrections due to the fact that there are

interactions between the members of the assembly. This scheme requires that the $f^{[i]}_{1,1}$ contain successively higher powers of a small parameter characterizing the importance of the interactions; the parameters appropriate to this task are those already introduced in the previous chapter (cf. eqn. 4.18 ff.)

It might be said that this procedure resembles the Enskog solution to the Boltzmann equation** except, of course, the latter is an expansion about the equilibrium density, $f = \dfrac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}}$, whereas the zero'th order term in our case is a time dependent six dimensional delta function in μ-space.

It is evident that the zero'th term of the solution for $f_{1,1}$ is given by:

$$\frac{\partial f^{[0]}_{1,1}}{\partial t} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} f^{[0]}_{1,1} = 0 \qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ \qquad (5.2)$$

with the initial condition: $f^{[0]}_{1,1}(\underline{x}_1;0) = \delta^6(\underline{x}_1 - \underline{x}_{1_0})$. The effects of collisions are absent from this equation.

The first correction is obtained by solving the following kinetic equation:

$$\frac{\partial f^{[1]}_{1,1}}{\partial t} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} f^{[1]}_{1,1} = \vartheta_1(f^{[0]}_{1,1}) + \vartheta_2(f^{[0]}_{1,1}) = \qquad \circ\circ\circ\circ\circ \quad (5.3)$$

$$= c \int_0^t d\tau \ [\ \frac{\chi^{(1)}}{m}(3 + \vec{p}_1 \cdot \vec{\nabla}_{p_1}) + \eta^{(2)}(\nabla^2_{p_1} + \tau \nabla^2 \frac{}{p_1 \, m \, p_1 q_1}) \ ] \ \oint_{-\tau} f^{[0]}_{1,1}(t-\tau)$$

with initial condition $f^{[1]}_{1,1}(\underline{x}_1;0) = 0$ for all $\underline{p}_1$, $\underline{q}_1$. Similarly

** Enskog [36]

the second order correction is provided by:

$$\frac{\partial f^{[2]}_{1,1}}{\partial t} + \frac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1} f^{[2]}_{1,1} = \qquad\qquad \circ\circ\circ\circ\circ\circ \qquad (5.4)$$

$$= \mathcal{A}_1(f^{[1]}_{1,1}) + \mathcal{A}_2(f^{[1]}_{1,1}) + \sum_{j=3}^{q}\mathcal{A}_j(f^{[0]}_{1,1})$$

with initial condition $\quad f^{[2]}_{1,1}(x_1,0) \equiv 0 \quad$, and so forth.

These kinetic equations may be solved by taking Fourier-Laplace transforms and then inverting the resulting expressions.

The Laplace transform, taken with respect to t, has the following definition:

$$\mathcal{L}_s[\ G(t)\ ] \equiv \int_0^{\infty} dt\ G(t)\ e^{-st} \qquad\qquad \circ\circ\circ\circ\circ \qquad (5.5)$$

For our purposes, the Fourier transform is defined by

$$\mathcal{F}_{\vec{k}}[\ g(\vec{q}_1)\ ] \equiv \frac{1}{(2\pi)^{3/2}} \lim_{\Omega\to\infty} \int_{\Omega} d^3\vec{q}_1\ g(\vec{q}_1)\ e^{+i\vec{k}\circ\vec{q}_1} \qquad \circ\circ\circ \qquad (5.6)$$

which, by the (Plancherel) Fourier Integral theorem converges in the mean to

$$\frac{1}{(2\pi)^{3/2}}\int_{-\infty}^{+\infty}\circ\circ \int_{-\infty}^{+\infty} d^3\vec{q}_1\ g(\vec{q}_1)\ e^{+i\vec{k}\circ\vec{q}_1} \qquad\qquad \circ$$

It is quickly seen that, in accord with these definitions,

$$\mathcal{F}\mathcal{L}f^{[0]}_{1,1} = \frac{e^{-i\vec{k}\circ\vec{q}_{1_0}}}{(2\pi)^{3/2}}\ \frac{1}{(s - i\frac{\vec{k}}{m}\circ\vec{p}_1)}\ \delta(\vec{p}_1 - \vec{p}_{1_0}) \qquad \circ\circ\circ\circ\circ\circ \qquad (5.7)$$

Inversion of the transform provides

$$f^{[0]}_{1,1}(\vec{x}_1;t\,|\,\vec{x}_{1_0}) = \delta(\vec{q}_1 - \vec{q}_{1_0} - \frac{\vec{p}_1}{m}t)\ \delta(\vec{p}_1 - \vec{p}_{1_0}) \qquad \circ\circ\circ\circ\circ\circ \qquad (5.8)$$

which, of course, would be the only term in the expansion were the system an ideal gas.

Similarly, for the first order correction, we obtain from 5.3:

$$f^{[1]}_{1,1} = \mathcal{T}^{-1}\mathcal{L}^{-1}\frac{1}{(s-\frac{i\underline{k}\circ p_1}{m})}\mathcal{T}\mathcal{L}\;[\mathcal{A}_1(f^{[0]}_{1,1}) + \mathcal{A}_2(f^{[0]}_{1,1})\;)\;] \qquad \ldots\ldots (5.9)$$

The explicit evaluation of this term is made considerably easier by noticing that

$$\mathcal{S}_{-\tau}f^{[0]}_{1,1}(\;t-\tau\;) = f^{[0]}_{1,1}(\;t\;) \qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ (5.10)$$

so that (referring to 4.32, 4.40) $\qquad\qquad \circ\circ\circ\circ\circ (5.11)$

$$\mathcal{A}_1(f^{[0]}_{1,1}) + \mathcal{A}_2(f^{[0]}_{1,1}) = ct[\;\overset{(l)}{n}(\nabla^2_{p_1} + \frac{t}{2m}\nabla^2_{p_1 q_1}) + \frac{\overset{(l)}{\chi}}{m}(3 + p_1\nabla_{p_1})]f^{[0]}_{1,1}(t)\;;$$

i.e., the integration in the collision integral becomes merely a simple integration of a polynomial in τ .

Consider a typical calculation with 5.11 and 5.9. One has

$$\mathcal{T}\mathcal{L}\;t\nabla^2_{p_1}f^{[0]}_{1,1}(t) = \nabla^2_{p_1}\mathcal{T}\mathcal{L}\;tf^{[0]}_{1,1}(t) = \nabla^2_{p_1}\frac{1}{(s-\frac{i\underline{k}\circ p_1}{m})^2}\delta(\vec{p}_1-\vec{p}_{1_o})$$

$$= \left(\frac{3!(-i\vec{k}/m)^2}{(s-\frac{i\underline{k}\circ p_1}{m})^4} - \frac{4(-i\vec{k}/m)\circ\vec{\nabla}}{(s-\frac{i\underline{k}\circ p_1}{m})^3 p_1} + \frac{\nabla^2_{p_1}}{(s-\frac{i\underline{k}\circ p_1}{m})^2}\right)\delta(\vec{p}_1-\vec{p}_{1_o})$$

Therefore*

$$\mathcal{T}^{-1}\mathcal{L}^{-1}\frac{1}{(s-\frac{i\underline{k}\circ p_1}{m})}\mathcal{T}\mathcal{L}\;t\nabla^2_{p_1}f^{[0]}_{1,1}(t) = t^2\left(\frac{t^2\delta^P\nabla^2_{q_1}}{4m^2}\delta^q(t) - \frac{2t\vec{\nabla}_{q_1}}{3m}\delta^q\circ\vec{\nabla}_{p_1}\delta^P + \right.$$

where

$$\left. + \frac{1}{2}\delta^q(t)\nabla^2_{p_1}\delta^P\;\right)$$

$$\delta^P \equiv \delta(\vec{p}_1-\vec{p}_{1_o})\quad ;\quad \delta^q(t) \equiv \delta(\vec{q}_1-\vec{q}_{1_o}-\frac{\vec{p}_1}{m}t) \qquad \circ\circ\circ\circ\circ\circ\circ\circ (5.12)$$

---

* $\mathcal{L}[t^n] = \Gamma(n+1)/s^{n+1} = n!/s^{n+1}\;;\;n = 0,1,2,\ldots$

In this way it is straight-forward determined that:

$$f^{[1]}_{1,1}(\underline{x}_1;t|\underline{x}_{1_0}) = \qquad\qquad\qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ \qquad (5.13)$$

$$= ct^2\Big(\eta^{(1)}[\ \delta^q(t)\nabla^2_{P_1}\delta^P - \frac{t}{m}\ \vec{\nabla}_{q_1}\delta^q\vec{\nabla}_{P_1}\delta^P + \frac{t^2}{4m^2}\delta^P\nabla^2_{q_1}\delta^q(t)\ ] +$$

$$+ \frac{\chi^{(2)}}{m}[\ 3\delta^q\delta^P - \frac{2t}{3m}\delta^P\vec{\nabla}_{q_1}\delta^q + \delta^q(t)\vec{P}_1\vec{\nabla}_{P_1}\delta^P\ ]\ \Big)$$

Proceding as before, one might calculate the explicit

expressions for $f^{[2]}_{1,1}$. Unfortunately, the expressions are

found to be very lengthy and complicated** On the other hand,

many dynamical quantities may be obtained without having full

---

** That this is so is quickly demonstrated when investigating
the contribution to $f^2_{1,1}$ due only to the first two terms of
the r.h.s. of 5.4.
From 4.40,4.32, and 5.13:

$$\mathscr{A}_1(f^{[1]}_{1,1}) + \mathscr{A}_2(f^{[1]}_{1,1}) = c^2\int_0^t d\tau\ \{\eta^{(1)}[\nabla^2_{P_1} + \frac{\tau}{m}\nabla^2_{P_1,q_1}] + \chi^{(1)}_m[3 + \vec{P}_1\cdot\vec{\nabla}_{P_1}]\}\ \delta_{q_1}\times$$

$$\times\frac{(t-\tau)^2}{2}\Big(\ \eta\ [\delta^q(t-\tau)\nabla^2_{P_1}\delta^P - \frac{(t-\tau)}{m}\ \vec{\nabla}_{q_1}\delta^q\vec{\nabla}_{P_1}\delta^P + \frac{(t-\tau)^2}{4m^2}\delta^P\nabla^2_{q_1}\delta^q\ ]+$$

$$+ \frac{\chi}{m}\ [3\delta^P\delta^q(t-\tau) - \frac{2}{3}\frac{(t-\tau)}{m}\delta^P\vec{P}_1\vec{\nabla}_{q_1}\delta^q + \delta^q\vec{P}_1\vec{\nabla}_{P_1}\delta^P\ ]\ \Big)$$

$$= c^2\int_0^t d\tau\ \Big(\eta^{(1)}[\nabla^2_{P_1} + \frac{\tau}{m}\nabla^2_{P_1 q_1}] + \frac{\chi^{(1)}}{m}[3 + \vec{P}_1\vec{\nabla}_{P_1}]\ \Big)\times$$

$$\times\frac{(t-\tau)^2}{2}\Big(\ \eta^{(1)}[\delta^q(t)\nabla^2_{P_1}\delta^P - \frac{(t-\tau)}{m}\vec{\nabla}_{q_1}\delta^q\vec{\nabla}_{P_1}\delta^P + (t-\tau)^2\delta^P\nabla^2_{q_1}\delta^q(t)]+$$

$$+ \frac{\chi^{(1)}}{m}[3\delta^P\delta^q(t) - \frac{2}{3}\frac{(t-\tau)}{m}\delta^P\vec{P}_1\vec{\nabla}_{q_1}\delta^q + \delta^q\vec{P}_1\vec{\nabla}_{P_1}\delta^P]\ \Big)$$

(footnote continued on bottom of next page. . .)

knowledge of $f_{1,1}(\underline{x}_1; t \,|\underline{x}_{1_0})$. Thus, rather than oppress the

reader with a detailed accounting of the second term, $f_{1,1}^{[2]}$,

we procede to calculate the dynamical quantities of primary

interest by methods which circumvent the complete calculation

of the μ-space density. The remainder of this chapter con-

cerns the calculation of momentum space densities and asso-

ciated expectation values and correlation functions. Speci-

fically, we shall obtain: $\Phi(\underline{p}_1; t\,|\underline{p}_{1_0})$, the momentum time-

relaxed density; $\langle\underline{p}_1(t)\,|\underline{p}_1(0)\rangle$, which is the expected

value of the momentum at time t, given the value of the momen-

tum at $t = 0$; $\langle\vec{p}_1(t)\circ\vec{p}_1(0)\rangle$ the momentum autocorrelation

function; and, $\langle p_{1_x}(0)p_{1_x}(t_1)p_{1_x}(t_2)p_{1_x}(t_3)\rangle$, which is a four-

time momentum correlation function to be related to the neu-

tron scattering cross-sections in a later chapter.

_____

(footnote continued from previous page)

$$= \frac{c^2 t^3}{6}\left(\eta^{(2)}\nabla^2_{p_1} +\chi^{(2)}[3+\vec{p}_1\frac{\vec{\nabla}}{m}_{p_1}]\right)\left(\eta^{(2)}[\delta^q\nabla^2_{p_1}\,\delta P-3t\vec{\nabla}_{q_1}\,\delta^q\vec{\nabla}_{p_1}\,\delta P\right.$$

$$+3\frac{t^2}{20m^2}\delta^P\nabla^2_{q_1}\,\delta^q] + \frac{\chi^{(2)}}{m}[3\delta^q\delta^P+\delta^q\vec{p}_1\vec{\nabla}_{p_1}\delta P-t\delta\hat{p}\vec{\nabla}\hat{\rangle}]\right) +$$

$$+\frac{c^2 t^4}{12}\eta^{(2)}\nabla^2_{p_1 q_1}\left(\eta^{(2)}[\delta^q\nabla^2_{p_1}\,\delta P-4t\vec{\nabla}_{q_1}\,\delta^q\vec{\nabla}_{p_1}\,\delta P+\frac{t^2}{6m^2}\delta^P\nabla^2\,\delta^q]\right.$$

$$+\frac{\chi^{(2)}}{m}[3\delta^q\delta^P+\delta^q\vec{p}_1\vec{\nabla}_{p_1}\,\delta P-\frac{8}{15m}t\delta^P\vec{p}_1\vec{\nabla}_{q_1}\,\delta^q]\right) \quad .$$

It is apparent that these contributions to the inhomogeneous
term of 5.4 are discouragingly lacking in simplicity. The
corresponding contributions to $f_{1,1}^{[2]}$ due to these terms are
found to be yet more involved. It is clear, however, that
with a little work they may be obtained in the same manner
as used to determine 5.13.

In chapter VI, consideration will be given to similar calculations of spatial densities and correlation functions.

Proceding with this program, it is clear from the discussions of chapter III that the momentum time-relaxed density may be obtained from $f_{1,1}(\underline{x}_1;\ t\ |\ \underline{x}_{1_o})$ by integrating over configurational coordinates. The probability density for finding particle #1 with momentum in the neighborhood of $\underline{p}_1$, at time t, given that at $t = 0$ the particle had momentum $\underline{p}_{1_o}$, is defined by:

$$\Phi(\underline{p}_1;t|\underline{p}_{1_o}) \equiv \int d^3q_{1_o}d^3q_1\ f_{1,1}(\underline{x}_1;t|\underline{x}_{1_o})f_{eq}(\underline{q}_{1_o}|\ \underline{p}_{1_o}) \qquad \ldots\ldots (5.14)$$

where $f_{eq}(\underline{q}_{1_o}|\underline{p}_{1_o})$ is the equilibrium probability density for finding the particle located at q_{1_o}, given that it has momentum $\underline{p}_{1_o}$. Of course, in an isolated homogeneous system, $f_{eq}(\underline{q}_{1_o}\ |\ \underline{p}_{1_o})$ is independent of $\underline{p}_{1_o}$; in fact, it is given by

$$f_{eq}(\underline{q}_{1_o}|\underline{p}_{1_o}) = 1/\Omega \qquad\text{, where}\quad \Omega = \text{ volume of the}$$

system.

Thus,

$$\Phi(\underline{p}_1;t|\underline{p}_{1_o}) = \frac{1}{\Omega}\int d^3q_{1_o}d^3q_1\ f_{1,1}(\underline{x}_1;t|\underline{x}_{1_o}) \qquad \ldots\ldots\ldots (5.14')$$

Let us expand Φ in a series in direct correspondence with the iteration series for $f_{1,1}$. Thus,

$$\Phi(\underline{p}_1;t|\underline{p}_{1_o}) = \sum_{i=0}^{\infty} \Phi^{[i]}(\underline{p}_1;t|\underline{p}_{1_o}) \qquad \ldots\ldots\ldots\ldots (5.15)$$

where

$$\Phi^{[i]}(\underline{p}_1;t\,|\,\underline{p}_{1_o}) \equiv \frac{1}{\Omega} \int d^3q_{1_o} d^3q_1 \; f^{[i]}_{1,1}(\underline{x}_1;t\,|\,\underline{x}_{1_o}) \quad \cdots\cdots (5.16)$$

In this way, using 5.16 and referring to 5.8, it is immediately found that the zero'th order (ideal gas) term for the momentum density is:

$$\Phi^{[0]}(\underline{p}_1;t\,|\,\underline{p}_{1_o}) = \delta(\underline{p}_1 - \underline{p}_{1_o}) \qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ \quad (5.17)$$

Similarly, referring next to 5.13, because spatial integrations of the spatial gradients of delta functions which appear in 5.13 provide zero boundary terms,** the first order correction is quickly seen to be:

$$\Phi^{[1]}(\underline{p}_1;t\,|\,\underline{p}_{1_o}) = \frac{ct^2}{2}[\eta^{(2)}\nabla^2_{p_1} + \frac{\chi^{(2)}}{m}(3 + \vec{p}_1 \cdot \vec{\nabla}_{p_1})]\Phi^{[0]}(\underline{p}_1;t\,|\,\underline{p}_{1_o})$$

$$\circ\circ\circ\circ\circ \quad (5.18)$$

In principle, one might calculate the higher order corrections in this manner. Observe, however, that $\Phi^{[1]}$ could have been calculated directly from equation 5.3. If, in that equation, the configuration space integration is performed on both sides of the equations, one obtains:

$$\frac{\partial \Phi^{[1]}}{\partial t} = \frac{1}{\Omega} \int dq_{1_o} dq_1 \; [\mathcal{J}_1(f^{[0]}_{1,1}) + \mathcal{J}_2(f^{[0]}_{1,1})] = \qquad \circ\circ\circ\circ\circ \quad (5.19)$$

$$= c \int d\tau \; (\frac{\chi^{(2)}}{m}[3 + \vec{p}_1 \cdot \vec{\nabla}_{p_1}] + \eta^{(2)}\nabla^2_{p_1})\delta(\vec{p}_1 - \vec{p}_{1_o}) \; \circ$$

which clearly has the solution given by 5.18.##

In the same way, the contributions to $\Phi^{[2]}(p_1;t\,|\,p_{1_o})$ are

---

** See, e.g., Arsac [37], Schwartz [38]

Since, as initial condition for 5.19, we know that $\Phi^{[0]}(0) \equiv 0$ for all $\underline{p}_1, \underline{q}_1$.

determined directly from 5.4. For example, the contribution

due to $\quad \mathcal{J}_1(f^{[1]}_{1,1}) + \mathcal{J}_2(f^{[1]}_{1,1}) \quad$ is found to be:

$$
\Phi^{[2]}_{\ell_1 + \ell_2} = c^2 \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 [\eta^{(2)} v^2_{p_1} + \frac{\chi^{(2)}}{m}(3 + \vec{p}_1 \vec{\nabla}_{p_1})]^2 \left(\frac{\tau_1 - \tau_2}{2}\right)^2 \delta(\vec{p}_1 - \vec{p}_{1_0})
$$

$$
= \frac{c^2 t^4}{24} [\eta^{(2)} v^2_{p_1} + \frac{\chi^{(2)}}{m}(3 + \vec{p}_1 \vec{\nabla}_{p_1})]^2 \delta(\vec{p}_1 - \vec{p}_{1_0})
$$

$$
(5.20)
$$

The other parts of the inhomogeneous term of 5.4 have been found by this procedure and the results are tabulated on the next page.

Table 5-1: Second order terms of momentum density

Collision term	Corresponding term of $\Phi^{[2]}(\vec{p}_1; t \mid \vec{p}_{1_o})$
$\vartheta_1(f_{1,1}^{[1]}) + \vartheta_2(f_{1,1}^{[1]})$	$\frac{c^2 t^4}{24} [\; \eta^{(2)} \nabla^2_{p_1} + \frac{\chi^{(2)}}{m}(3 + \vec{p}_1 \vec{\nabla}_{p_1})\;]^2\; \Phi^{[0]}$
$\vartheta_3(f_{1,1}^{[0]})$	$\frac{ct^4}{24 m^3}\, \chi^{(4)}[\; 15\frac{m}{\beta} + 5 p_1^2 + 5\frac{m}{\beta} \vec{p}_1 \vec{\nabla}_{p_1} + p_1^2\, \vec{p}_1 \vec{\nabla}_{p_1}\;]\; \Phi^{[0]}$
$\vartheta_4(f_{1,1}^{[0]})$	$\frac{ct^4}{24 m^2}\, \eta^{(4xx)}[\,-10 + 5\frac{m}{3\beta}\nabla^2_{p_1} + 1 p_1^2 \nabla^2_{p_1} \frac{2}{3} - 2\frac{2}{3}\vec{p}_1 \vec{\nabla}_{p_1}(1 - \vec{p}_1 \vec{\nabla}_{p_1})\,]\; \Phi^{[0]}$
$\vartheta_5(f_{1,1}^{[0]})$	$\frac{ct^4}{24 m^2} \left\{ \begin{aligned} &\eta^{(4xx)}[5\frac{m}{\beta}\nabla^2_{p_1} + p_1^2 \nabla^2_{p_1} + 20 + 44\frac{4}{3}\vec{p}_1 \vec{\nabla}_{p_1} + 2(\vec{p}_1 \vec{\nabla}_{p_1})^2]\; \Phi^{[0]} + \\ &+ \chi^{\{2xx\}}[3\frac{m}{\beta}\nabla^2_{p_1} + 12 + 10\vec{p}_1 \vec{\nabla}_{p_1}]\; \Phi^{[0]} + \\ &+ \chi^{\{2xy\}}[3(2m + p^2)\nabla^2_{p_1}\frac{1}{\beta} + 6 + 5\vec{p}_1 \vec{\nabla}_{p_1} + 3(\vec{p}_1 \vec{\nabla}_{p_1})^2]\; \Phi^{[0]} + \\ &+ \chi^{\{2yy\}}[18 + 9\vec{p}_1 \vec{\nabla}_{p_1} + 3(\vec{p}_1 \vec{\nabla}_{p_1})^2]\; \Phi^{[0]} + \end{aligned} \right.$ $+ \frac{c^2 t^4}{24 m^2} \chi^{(4)}_{(3)}[\; 33 + 20\vec{p}_1 \vec{\nabla}_{p_1} + 3(\vec{p}_1 \vec{\nabla}_{p_1})^2]\; \Phi^{[0]}$
$\vartheta_6(f_{1,1}^{[0]})$	$\frac{ct^4}{24 m}[\; \Psi^{(4xx)} \nabla^2_{p_1} + \Psi^{(4xy)}_{(xy, xy)1}(6\nabla^2_{p_1} + 3\vec{p}_1 \vec{\nabla}_{p_1} \nabla^2_{p_1}) + \Psi^{(4)}_4(-4\nabla^2_{p_1} + 6\vec{p}_1 \vec{\nabla}_{p_1} \nabla^2_{p_1})\;]\; \Phi^{[0]} +$ $+ \frac{c^2 t^4}{24 m} \Psi^{(4)}_{(3)}[\; 5\nabla^2_{p_1} + (\vec{p}_1 \vec{\nabla}_{p_1})\nabla^2_{p_1}\;]\; \Phi^{[0]}$
$\vartheta_7(f_{1,1}^{[0]})$	$-\frac{c^2 t^4}{24 m} \chi^{(2)}[3 + \vec{p}_1 \vec{\nabla}_{p_1}]\, [\frac{\chi^{(2)}}{m}(3 + \vec{p}_1 \vec{\nabla}_{p_1}) + \eta^{(2)}\nabla^2_{p_1}]\; \Phi^{[0]}$

Table 5.1 (cont'd)

Collision term	Corresponding term of $\phi^{[2]}(\vec{p}_1;t\|\vec{p}_{1_0})$
$\partial_8(f_{1,1}^{[0]})$	$\dfrac{ct^4}{24}[\ \mu^{(4xx)}\nabla^2_{p_1}\nabla^2_{p_1}+\dfrac{\psi}{m}^{(4xx)}\nabla^2_{p_1}(9+3\vec{p}_1\vec{\nabla}_{p_1})\ ]\ \phi^{[0]}+$ $+\dfrac{c^2t^4}{24}[\ 3\ \mu^{(4)}_{(3)}\nabla^2_{p_1}\nabla^2_{p_1}+\dfrac{\psi^{(4)}}{m_{(3)}}\nabla^2_{p_1}(9+3\vec{p}_1\vec{\nabla}_{p_1})\ ]\ \phi^{[0]}$
$\partial_9(f_{1,1}^{[0]})$	$-\dfrac{c^2t^4}{24}\ \eta^{(2)}\nabla^2_{p_1}[\ \dfrac{\chi}{m}^{(2)}(3+\vec{p}_1\vec{\nabla}_{p_1})+\eta^{(2)}\nabla^2_{p_1}\ ]\ \phi^{[0]}$

We are now in a position to notice that, referring to the kinetic equation for $f_{1,1}$, had we earlier replaced the complete collision integral by the first correction term, i.e., had the kinetic equation for the full $f_{1,1}$ been approximated by

$$\frac{\partial f_{1,1}}{\partial t}+\frac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1}f_{1,1}=c\int_0^t d\tau\ [\ \frac{\chi}{m}^{(2)}(3+\vec{p}_1\vec{\nabla}_{p_1})+\eta^{(2)}(\nabla^2_{p_1}+\tau\frac{\vec{p}_1}{m}\cdot\nabla^2_{p_1q_1})\ ]\Big|_{-\tau}f(t-\tau)_{1,1}$$

then only the first term in table 5.1 would have appeared as the contribution to $\phi^{[2]}(\underline{p}_1;t\|\underline{p}_{1_0})$. This would have been in error, for not only would we have overlooked the other terms comprising $\phi^{[2]}$ but, as is seen by this more rigorous calculation, the terms predicted by an approximate kinetic equation do not even appear; $\{\partial_1(f_{1,1}^{[1]})+\partial_2(f_{1,1}^{[2]})\}$contributions are exactly

cancelled by $\{\mathcal{L}_7(f^{[0]}_{1,1})+\mathcal{L}_9(f^{[0]}_{1,1})\}$ contributions!! It is

suspected that examination of the higher order terms of

$\Phi(\vec{p}_1;t|\vec{p}_{1_o})$ would lead to similar conclusions. Thus, it is

to be construed that one must be very cautious when deducing

information from an incomplete kinetic equation; truncation

of a kinetic equation for a probability density or distribu-

tion function. F, precludes determination of the functional

form of F to higher order than the order of the truncation.

It is now easy to calculate associated expressions for

$< \vec{p}_1(t)|\vec{p}_1(0) >$, the expected value of the momentum of a par-

ticle at t, given that the particle's initial momentum was

p_{1_o}. By definition,

$$< \vec{p}_1(t) \ |\vec{p}_1(0) > \equiv \int d^3p_1 \ \vec{p}_1 \ \Phi(\vec{p}_1;t|\vec{p}_{1_o}) \qquad \ldots\ldots \qquad (5.21)$$

It has already been demonstrated that the terms appearing

in $\Phi(\vec{p}_1;t|\vec{p}_{1_o})$ are of the form $p_{1_i}^m \ \frac{\partial^n}{\partial p_{1_i}^n} \ \delta(\vec{p}_1-\vec{p}_{1_o})$.

Appealing to the definition, 5.21, it is noticed that only

those terms of Φ for which m $\geq$ n-1 contribute to

$< \vec{p}_1(t) \ |\vec{p}_1(0) >$. This simplifies matters considerably

and, by a straightforward calculation, one obtains:

$$< \vec{p}_1(t)|\vec{p}_1(0) > = \vec{p}_{1_o} - \frac{t^2}{2m} [c\chi^{(2)}\vec{p}_{1_o}] + \qquad \ldots\ldots\ldots \qquad (5.22)$$

$$+\frac{t^4}{4!m^2}\left(c^2\chi^{(4)}_{(3)}\vec{p}_{1_o} + c[(2\chi^{(?xx)} +4\chi^{(?x?)}-5m\chi^{(4,xx)}+10n^{(4,x)})\vec{p}_{1_o} - \right.$$
$$\left. -\chi^{(4,xx)}p_{1_o}^2 \ \frac{\beta}{p}\vec{p}_{1_o}] + \right.$$

$$+o(\ t^6, \text{ and terms of "sixth power of the forces" })_o$$

Next, let us use 5.22 to calculate the auto-correlation

function, $< \vec{p}_1(t) \cdot \vec{p}_1(0) >$.

The momentum auto-correlation function is defined by

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > \equiv \int d^3p_{1_0} d^3p_1 (\vec{p}_1 \cdot \vec{p}_{1_0}) f_{p_1,p_{1_0}} (\vec{p}_1(t), \vec{p}_1(0)) \qquad (5.23)$$

or, alternatively, (recognizing that the system of interest

is an equilibrium assembly):

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > \equiv \int d^3p_{1_0} d^3p_1 (\vec{p}_1 \cdot \vec{p}_{1_0}) \frac{e^{-\frac{\beta p_{1_0}^2}{2m}}}{(2\pi mkT)^{\frac{3}{2}}} \Phi(\vec{p}_1;t|\vec{p}_{1_0}) \qquad (5.24)$$

However, it is clear that from the latter expression:

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = \int d^3p_o \frac{e^{-\frac{\beta p_o^2}{2m}}}{(2\pi mkT)^{3/2}} \vec{p}_o \cdot < \vec{p}_1(t) | \vec{p}_o > \qquad (5.24')$$

Thus, referring to 5.22, the following iteration is obtained

for $< \vec{p}_1(t) \cdot \vec{p}_1(0) >$:

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = <p_o^2>_{eq} \left\{ 1 - \frac{ct^2}{2m} \chi^{(2)} + \right. \qquad (5.25)$$

$$\left. + \frac{c^2 t^4}{4!m^2} \chi^{(4)}_{(3)} + \frac{ct^4}{12m^2} [5\eta^{(4,xx)} - 5\chi^{(4,x)} + \chi^{(2xx)} + 2\chi^{(4xy)}] + \cdots \right\}$$

In the above expression, $<p_o^2>_{eq} = 3m/\beta = \int d^3p_o \, p_o^2 \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}}$ is

the momentum auto-correlation function for an ideal gas.

It has already been noted by other investigators[**] that,

as an approximation, the momentum auto-correlation function

may be represented by an exponential function, viz.,

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > \doteq 3m/\beta \, e^{-At^2/2} \qquad (5.26)$$

[**]e.g., Rice[39], De Gennes[40]

with

$$A \equiv \frac{c}{m} \chi^{(2)} \qquad \ldots\ldots \quad (5.26')$$

This expression is exact to $o(t^2)$ and the "second power of the forces." Furthermore, it satisfies the requirement that correlations vanish for long times, i.e.,

$$\lim_{t \to \infty} < \vec{p}_1(t)\cdot\vec{p}_1(0) > \; = \; 0 \qquad \ldots\ldots \quad (5.27)$$

We should like to suggest here, however, that if one can seriously accept 5.26 as an approximation to 5.25, then the following observations are, at the least, of equal merit.

It is not unreasonable to approximate $\chi^{(4)}_{(3)}$ by $\overline{\chi^{(2)}}^2$. Certainly, in the high temperature limit where $g_2(\xi) \approx \dfrac{\Omega\, e^{-\beta\phi(\xi)}}{\int d^3\xi\, e^{-\beta\phi(\xi)}}$ and $g_3(\xi_2,\xi_3) \approx \dfrac{\Omega^2 e^{-\beta V(\xi_2,\xi_3)}}{\int d\xi_2 d\xi_3\, e^{-\beta V(\xi_2,\xi_3)}}$, $g_3(\xi_2,\xi_3) \approx g_2(\xi_2)\, g_2(\xi_3)$, except for a small region of hyperspace for which $|\xi_2 - \xi_3| < r^*$, r^* being of the order of a molecular radius. In addition, unless $|\xi_2| < r^*$ and $|\xi_3| < r^*$, $\dfrac{\partial^2\phi(\xi_2)}{\partial\xi_{2x}^2}\cdot\dfrac{\partial^2\phi(\xi_3)}{\partial\xi_{3x}^2} \approx 0$ so that integration over much of the excluded region of hyperspace provides zero contribution to $\chi^{(4)}_{(3)}$, anyhow. Thus:

$$\chi^{(4)}_{(3)} = \Omega^2 \frac{\int d^3\xi_2 d^3\xi_3\, e^{-\beta V(\xi_2,\xi_3)}[\frac{\partial^2\phi(\xi_2)}{\partial\xi_{2x}^2}\frac{\partial^2\phi(\xi_3)}{\partial\xi_{3x}^2}]}{\int d^3\xi_2 d^3\xi_3\, e^{-\beta V(\xi_2,\xi_3)}} \approx \qquad \ldots\ldots (5.28)$$

$$\approx \frac{\Omega^2 \int d^3\xi_2 d^3\xi_3\, e^{-\beta\phi(\xi_2)-\beta\phi(\xi_3)}[\frac{\partial^2\phi(\xi_2)}{\partial\xi_{2x}^2}\cdot\frac{\partial^2\phi(\xi_3)}{\partial\xi_{3x}^2}]}{\int d^3\xi_2 e^{-\beta\phi(\xi_2)}\cdot\int d^3\xi_3 e^{-\beta\phi(\xi_3)}} = \overline{\chi^{(2)}}^2$$

In light of 5.28, it is noticed that the term of order

$\left(\underline{c}t^2\,\chi^{(2)}\right)^2$ which actually occurs in $< \underline{p}_1(t)\cdot\underline{p}_1(0) >$ is the
  m
third term in a Taylor's series expansion of $\cos\left(\underline{c}\chi^{(1)}t^2\right)^{1/2}$,
                                                           m
rather than being the appropriate term of the series expansion
of 5.26. For very dense systems, for which as a first approx-
imation one may neglect terms of $o(ct^n)$ compared with

terms $o(c^2t^n)$, one obtains only the cosine term, viz.,

$$< \vec{p}_1(t)\cdot\vec{p}_1(0) > \;\simeq\; \cos A^{1/2}t \qquad \ldots\ldots (5.29)$$

This result is satisfying in that it demonstrates the exis-
tence of negative correlations, necessarily present in all
dense systems. It is certainly unsatisfactory, however, in
that the condition expressed by 5.27 is not fulfilled.

Most likely, for moderately dense systems, the momentum
auto-correlation function has a functional form intermediate
between 5.26 and 5.29. For liquids, $< \vec{p}_1(t)\cdot\vec{p}_1(0) >$ prob-
ably has, in a rough way, the form of a damped oscillation
(cf. fig 5-1.) However, 5.25 does not contain enough infor-
mation to demonstrate this hypothesis explicitly.

For example, suppose one tries to fit 5.25 to a damped
cosine, e.g.,

$$< \vec{p}_1(t)\cdot\vec{p}_1(0) > \;\simeq\; \cos A^{1/2}t\, e^{+Bt^4} \qquad \ldots\ldots (5.30)$$

where

$$B \equiv \frac{c}{12m^2}\, [5\eta^{(4,\chi\chi)} - 5\chi^{(4,\chi\chi)} + \chi^{\binom{2\chi\chi}{2\chi\chi}} + 2\chi^{\binom{2\chi\eta}{2\chi\eta}}] \qquad \ldots(5.30')$$

The expression given by 5.30 is exact through the fourth power
of the forces. But, unfortunately, B is a positive quantity.

Thus, while (5.30) is an acceptable approximation to 5.25 for short times, it cannot be correct in general. The determination of the functional form of $< \vec{p}_1(t) \cdot \vec{p}_1(0) >$ for longer times requires an expansion to higher powers of the interaction parameters.
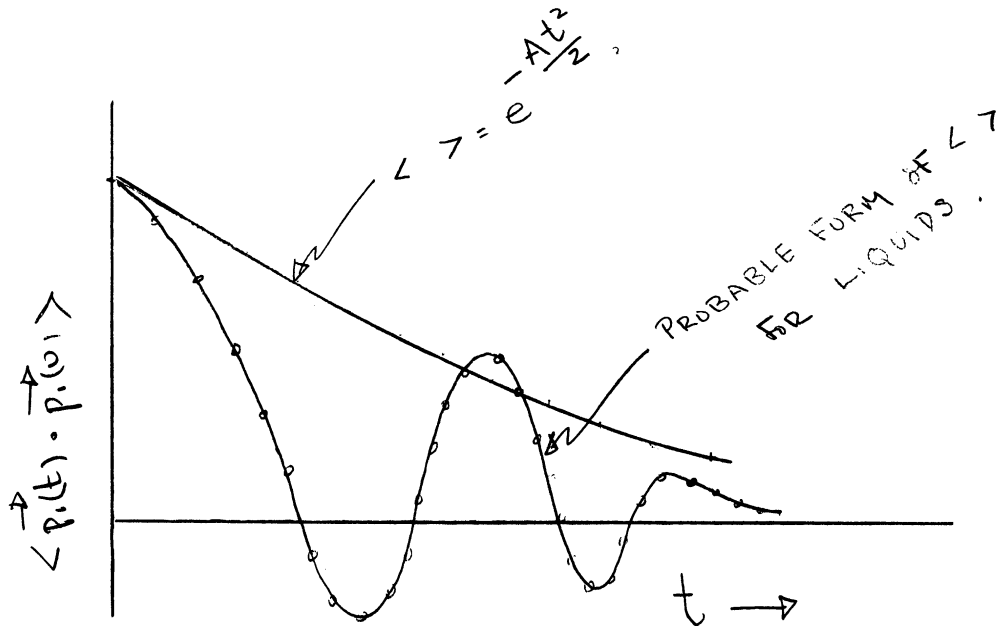

Fig. 5-1: Momentum auto-correlation functions

Are A and B actually positive constants, as has been asserted?

The model two-particle potentials for which this exposition is valid are typically of the form sketched in fig. 5.2; they are characterized by a steep repelling core plus attracting well, the latter falling to zero in a distance of the order of the molecular radius. In figure 5.2, the potentialanditsfirst two derivatives are plotted as a function of ρ, the intermolecular separation distance.
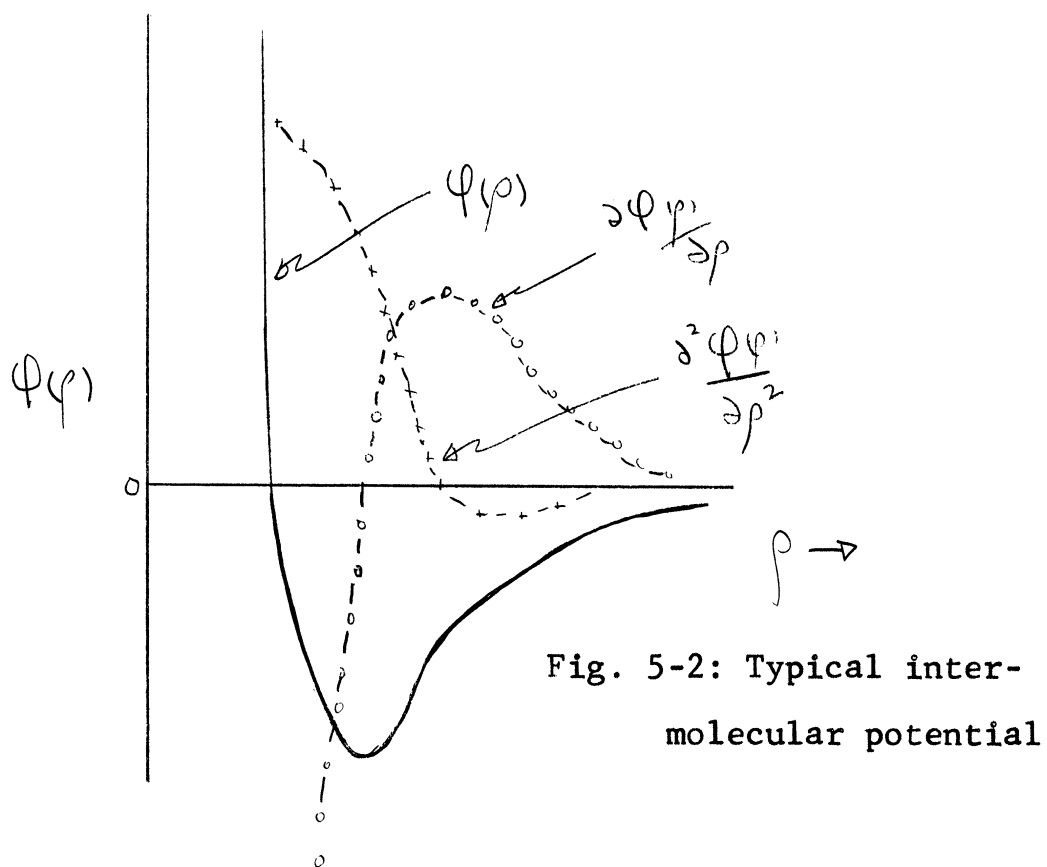
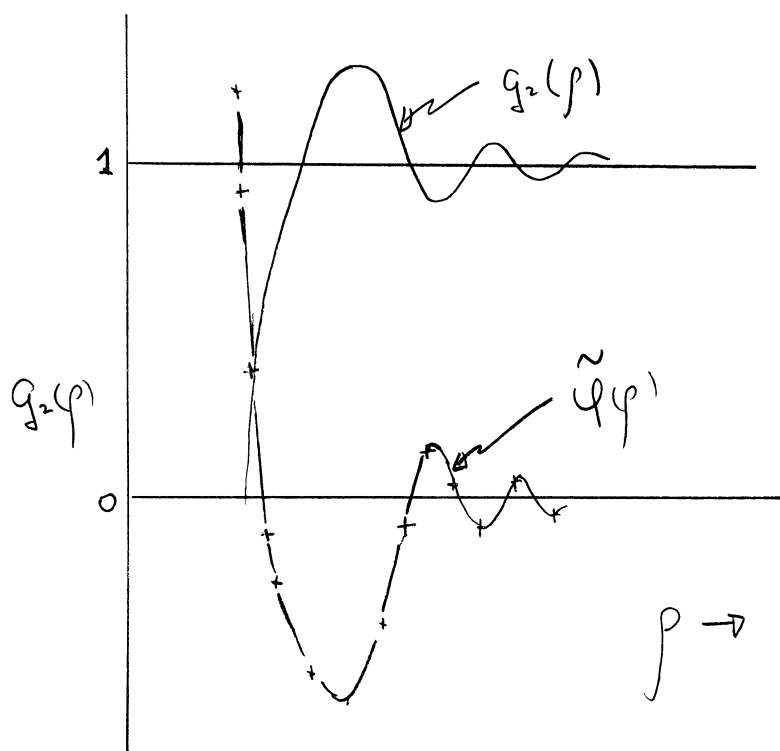Fig. 5-2: Typical inter-
molecular potential

Fig. 5-3: Typical static pair correlation function

Consider the first of the constants, A, defined by 5.26'. Using spherical coordinate, we can express $\chi^{(2)}$ as:

$$\chi^{(2)} \equiv \int d^3\xi \ g_2(\xi)\frac{\partial^2\phi(\xi)}{\partial\phi^2}\Big|_x = \frac{4\pi}{3} \int_0^\infty d\rho \ \rho^2 \ g_2(\rho) \ [\ \frac{\partial^2\phi}{\partial\rho^2} + \frac{2}{\rho}\frac{\partial\phi}{\partial\rho}\ ]$$

From figures 5.2 & 5.3 it is apparent that $\chi^{(2)}$ is positive. The positive portion of $\frac{\partial^2\phi}{\partial\rho^2}$ is greater than the negative; furthermore, $g_2(\rho)$ is greatest over the same range as is $\frac{\partial^2\phi}{\partial\rho^2}$ positive. Similarly, the positive part of $\frac{\partial\phi}{\partial\rho}$ seems to exceed its negative contribution to the integral.

This argument is most secure in the high temperature limit, where $g_2(\xi) = \Omega e^{-\beta\phi(\xi)}/\int e^{-\beta\phi(\xi)}d\xi$. Then, simple integration provides the relationship $\chi^{(2)} = \beta\eta^{(2)}$ where $\eta^{(2)} \equiv \int d^3\xi \ g_2(\xi) \ \overline{F_x(\xi)}^2$ (see table 4-1, p. 60). The latter is obviously a positive quantity. In general,

$$\chi^{(2)} = \int d^3\xi \ g_2(\xi) \ \frac{\partial\phi}{\partial\xi_x}\frac{\partial\tilde\phi}{\partial\xi_x} \equiv \beta\tilde\eta^{(2)}$$, where $\tilde\phi$ is a ficti-

tious potential defined by $g_2(\xi) \propto e^{-\beta\tilde\phi(\xi)}$ (see fig. 5.3.)

We see that $\tilde\phi$ has essentially the same form as ϕ . $\eta^{(2)}$ most likely is a good approximation of $\tilde\eta^{(2)}$.

Since $\chi^{(2)}$ is positive, it follows that A is also a positive quantity.

The second constant, B, defined by 5.30', may be analyzed in the same way. Let us first consider it in the high temperature limit. In this case, replacing $g_2(\xi)$ by $\Omega e^{-\beta\phi(\xi)}/\int \Omega_4 e^{-\beta\phi(\xi)}$ the following useful relationships between system constants (cf. table 4-1) may be obtained.

Previously, it has been shown that, in limit $T \to \infty$,

$$\chi^{(2)} = \beta \eta^{(2)} \qquad \ldots \ldots \quad (5.31)$$

In addition, it is easy to show:

$$\chi^{(4)} = \beta \eta^{(4,xx)} \quad ; \quad \chi^{(2,2)} = \beta \eta^{(4,xy)} \qquad \ldots \ldots \quad (5.32a,b)$$

$$\psi^{(4,xx)} = \frac{\beta \mu}{3}^{(4,xx)} \quad ; \quad \psi^{(4,xy)} + 2\psi_4^{(xy,xy)} = \beta \mu^{(4,xy)} \quad \ldots (5.33a,b)$$

$$\chi^{\{2xx\atop 2xx\}} = \frac{\beta^2 \mu}{3}^{(4xx)} - \eta^{(4xx)} \quad ; \quad \chi^{\{2xx\atop 2yy\}} = \beta\Psi^{(4xy)} - \eta^{(4xy)} \quad ; \quad \ldots (5.34a,b,c,)$$
$$\chi^{\{2xy\atop 2xy\}} = \beta\Psi_4^{(xy,xy)} - \eta^{(4xy)}$$

$$\chi^{\{2xx\atop 2yy\}} + 2\chi^{\{2xy\atop 2xy\}} = \beta^2 \mu^{(4xy)} - 3\,\eta^{(4xy)} = \chi^{\{2xx\atop 2xx\}} \qquad \ldots \ldots \quad (5.34d)$$

Not all of these relationships are needed here but, as they are useful in the discussion appearing in the next chapter, they are included at this time. Here, let 5.32a be used to obtain

$$B = \frac{c}{12m^2} [\chi^{\{2xx\atop 2xx\}} + 2\chi^{\{2xy\atop 2xy\}}] \qquad \ldots \ldots \quad (5.35)$$

Certainly, then, in the high temperature limit, because $\chi^{\{2xx\atop 2xx\}}$ and $\chi^{\{2xy\atop 2xy\}}$ are both positive constants (cf. table 4-1), B must be a positive quantity. The same conclusion is probably valid at lower temperatures.

Before concluding this chapter, let brief consideration be given to the determination of multiple-time auto-correlation

functions(i.e., time-relaxed correlation functions for more than two times.) Aside from satisfaction of our curiosity, these quantities are of interest because they may be related in certain approximations to neutron scattering cross-section** (see chapter VI.)

Specifically, consider the four-time auto-correlation function:

.... (5.36)

$$< p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) > = \int d^3p_0...d^3p_3 [p_0...p_3] \, \Phi(\underline{p}_0,t_0;...;\underline{p}_3,t_3)$$

i.e. the joint expectation of the xth component of the momentum of a particle at t_0,t_1,t_2,t_3. $\Phi(\underline{p}_0,t_0;\underline{p}_1,t_1;\underline{p}_2,t_2;\underline{p}_3,t_3)$ is the joint probability density for finding a specified particle with momentum $\vec{p}_3$ at $t = t_3,....,\vec{p}_0$ at $t = t_0$.

In principle, a multiple time correlation function could be obtained by summing over the probability measure of all initial states consistent with the desired subsequent behavior of the system; i.e.,

$$f(X_{s_0},t_0; ... ; X_{s_r},t_r) = \int_{X_{n_0}: \, X_s(t_0)=X_{s_0},......,X_s(t_r)=X_{s_r}} d[F_0(X_n)] \quad .$$

Or, one might integrate over all disregarded coordinates of a total system multiple-time correlation function, determined from solution of eqns. of motion, viz.,

$$f(X_{s_0},t_0; .. ;X_{s_r},t_r) = \int dX_{n_0}^{/\cancel{X}_{s_0}} ....\, dX_{n_r}^{/\cancel{X}_{s_r}} f(X_{n_0},t_0;..;X_{n_r},t_r) =$$

$$= \int dX_{n_0}^{/\cancel{X}_{s_0}}...dX_{n_r}^{/\cancel{X}_{s_r}} f(X_{n_0}) \; \delta(X_{n_1} - e^{-(t_1-t_0)L}X_{n_0})..\delta(X_{n_r} - e^{-(t_r-t_0)L}X_{n_0})$$

**A. Rahman, et al.[41]

Unfortunately, these two schemes are useless for actual calculation of reduced multiple time correlation functions, except in very special (and trivial) cases. What is required is an equation akin to the Liouville equation but, as yet, such an equation remains unknown.

However, it is noticed that $\Phi(\vec{p}_0, t_0; \ldots; \vec{p}_3, t_3) =$

$$= \Phi(\vec{p}_3, t_3 \,|\, \vec{p}_2, t_2; \vec{p}_1, t_1; \vec{p}_0, t_0) \times \Phi(\vec{p}_2, t_2 \,|\, \vec{p}_1, t_1; \vec{p}_0, t_0) \times$$

$$\times \Phi(\vec{p}_1, t_1 \,|\, \vec{p}_0, t_0) \times \Phi(\vec{p}_0, t_0)$$

If one now makes a Markoffian assumption, viz., that the probability of finding a particle with specific momentum at a later time is a function only of the momentum of the particle at t = 0, and not of the momentum of the particle at preceding times, then

$$\ldots\ldots \quad (5.37)$$

$$< p_{1_x}(t_0) p_{1_x}(t_1) p_{1_x}(t_2) p_{1_x}(t_3) > \quad =$$

$$= \int d\vec{p}_0 \ldots d\vec{p}_3 \,[p_{0_x} p_{1_x} p_{2_x} p_{3_x}] \, \Phi(\vec{p}_3, t_3 - t_2 \,|\, \vec{p}_2) \times$$

$$\times \Phi(\vec{p}_2, t_2 - t_1 \,|\, \vec{p}_1) \times \Phi(\vec{p}_1, t_1 - t_0 \,|\, \vec{p}_0)$$

It can be seen from the memory term of 3.18 that $f_{1,1}$ ($\underline{x}_1; t \,|\, \underline{x}_{1_0}$) is not strictly Markoffian (the kinetic equation involves integration over the previous history of the system.) However, it can be shown** that the system is Markoffian in momentum space for all except very short times (of the order of a 'collision time'); furthermore, 5.37, being an expectation value, in some sense averages over the errors introduced

** Prigogine [24]

by assuming the Markoffian decomposition. In regard to the last point, it has been shown that for the calculation of many transport coefficients, rigorous expressions are obtained even after replacement of non-markoffian kinetic equations by approximate Markoffian equations.**

Referring to 5.17, 5.18, the approximate expression (5.37) is given by:

$$< p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) > = \quad \circ\circ\circ\circ\circ\circ\circ\circ \quad (5.38)$$

$$= \int d\vec{p}_0 \circ\circ\circ d\vec{p}_3 \; [p_{0_x} \circ\circ p_{3_x}] \; \Big(\; \delta(\vec{p}_3-\vec{p}_2) \; \delta(\vec{p}_2-\vec{p}_1) \; \delta(\vec{p}_1-\vec{p}_0) \; +$$

$$+ \; \delta(\vec{p}_3-\vec{p}_2)\delta(\vec{p}_2-\vec{p}_1)\frac{c(t_1-t_0)}{2m}^2[\eta^{(\ell)}\nabla^2_{p_1}+ \frac{\chi^{(\ell)}}{m}(3+\vec{p}_1\vec{\nabla}_{p_1})]\delta(\vec{p}_1-\vec{p}_0) \; +$$

$$+ \; \delta(\vec{p}_3-\vec{p}_2)\frac{c(t_2-t_1)}{2m}^2[\eta^{(\ell)}\nabla^2_{p_1}+ \frac{\chi^{(\ell)}}{m}(3+\vec{p}_1\vec{\nabla}_{p_1})]\delta(\vec{p}_2-\vec{p}_1)\delta(\vec{p}_1-\vec{p}_0) \; +$$

$$+ \; \frac{c(t_3-t_2)}{2m}^2[\eta^{(\ell)}\nabla^2_{p_1}+ \frac{\chi^{(\ell)}}{m}(3+\vec{p}_1\vec{\nabla}_{p_1})]\delta(\vec{p}_3-\vec{p}_2)\delta(\vec{p}_2-\vec{p}_1)\delta(\vec{p}_1-\vec{p}_0) +$$

$$+ \; o(\text{"fourth power in the forces"}) \; \Big) \quad ;$$

$$(t_0 < t_1 < t_2 < t_3)$$

Upon making the high temperature assumption, $\eta^{(2)} \simeq \chi^{(2)}/\beta$, a straight-forward calculation provides

$$< p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) > \simeq \quad (5.39)$$

$$\simeq \; \frac{3m^2}{\beta^2} \left(1+\frac{c\chi^{(2)}}{2m} \; [\; -t_3^2 + 2t_3t_2 - \frac{7t_2^2}{3} + \frac{8t_2t_1}{3} - \frac{7t_1^2}{3} +2t_1t_2-t_0^2 \;] \right.$$

$$\left. +\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ \right)$$

$$\simeq \; \frac{3m^2}{\beta^2} \; \exp\frac{-c\chi^{(2)}}{2m}[\; t_3^2-2t_3t_2+\frac{7t_2^2}{3}-\frac{8t_2t_1}{3}+\frac{7t_1^2}{3}-2t_1t_0+t_1^2 \;]$$

_____

** e.g. Balescu[42]

$3m^2/\beta^2$ is the value to be obtained were the assembly an ideal gas.

We shall return to 5.39 at the end of the next chapter, when considering approximations to the slow neutron scattering cross-section.

Finally, let us emphasize the appearance of secular terms in the expansions obtained for momentum densities and correlation functions. The presence of terms which increase with time is a basic deficiency of this exposition, resulting from the particular method chosen to solve the kinetic equation On the other hand, the expressions for densities and correlation functions thus obtained are useful in that they are exact for short times. As such, they serve as checks for any approximate solutions to the kinetic equation.

In addition, in spite of these difficulties, the expansions obtained for momentum densities and correlation functions are often useful for the calculation of various transport coefficients. For example, it is known that the dielectric constant for an ionized assembly can be related to the Laplace transform of the momentum auto-correlation function [31,32]. Upon assuming a linear relationship for the current produced by an external electric field of frequency ω , the dielectric constant is found to be given by [**]

$$\varepsilon(\omega) = 1 + \frac{4\pi}{3\beta\omega} \, \text{Im} \, \lim_{\lambda \to 0} \int_o^\infty dt \, e^{-(\lambda + i\omega)t} \, \sum_{i=1}^{n} \sum_{j=1}^{n} \frac{e_i e_j}{m_i m_j} \langle \vec{p}_i(o) \cdot \vec{p}_j(t) \rangle \quad (5.40)$$

[**] .. also here assuming a zero external magnetic field. Eqn. 5.40 can be modified for more general relationships between current and applied fields.

The summation is over all charge carriers of the assembly.

Let us apply 5.40 to calculate the dielectric constant for a weakly ionized gas. Assuming that, due to the heavier mass of the ions, one need only consider the contribution to the current due to the electrons, we obtain

$$\varepsilon(\omega) = 1 + \frac{4\pi}{3\omega\beta} \frac{e^2 c_e}{\beta m_e} < \vec{p}(\omega) \cdot \vec{p}(t) >_e \qquad \dots \quad (5.41)$$

In the above equation, c_e is the density of electrons, m_e is the electron mass, and $< \vec{p}(\omega) \cdot \vec{p}(t) >_e$ is the momentum auto-correlation function for electrons. To obtain 5.41 we have also neglected electron-ion interactions.

Neglecting, also, electron-electron interactions, from 5.25 and 5.41 one obtains:

$$\varepsilon(\omega) \doteq 1 + \frac{4\pi\alpha c}{m_e \omega^2} \left\{ 1 + \frac{\alpha \chi_{e-o}^{(2)}}{m_e \omega^2} + \mathcal{O}(\frac{1}{\omega^4}) + \dots \right\} \qquad (5.42)$$

α is the fraction of the atoms which are ionized. $\chi_{e-o}^{(2)}$ is defined similarly to previous definitions:

$$\chi_{e-o}^{(2)} \equiv \int d^3\vec{\xi} \; g_2(\xi) \frac{\partial^2 \varphi_{e-o}}{\partial \xi_x^2} \qquad \dots \quad (5.43)$$

where $\varphi_{e-o}(\xi)$ is the interaction between electrons and neutral atoms; $g_2(\xi)$ is probably well approximated by

$$g_2(\xi) \approx \frac{\Omega e^{-\beta \varphi_{e-o}}}{\int d\xi \, e^{-\beta \varphi_{e-o}}} \qquad (5.44)$$

In the next chapter corresponding expansions will be obtained for spatial time-relaxed densities. Secular terms also appear in those expansions. However, the expansions are not simple time expansions but are a sort of asymptotic expansion. In this form they are quite useful for calculating the scattering function; the secular terms in $G(r,t)$ are not an impediment to taking the double Fourier transforms necessary for obtaining $S(k,\omega)$.

CHAPTER VI

DETERMINATION OF $G_s(r,t)$

As has been discussed in some detail in chapter 2, there is a close connection between the space-time correlation function, $G(r,t)$, and the slow neutron scattering cross section. Primarily because of our interest in the latter, in this chapter attempts are made at calculation of $G_s(r,t)$, the 'self' part of the correlation function, which is related to the incoherent part of the cross section.

As a continuation of the work of the preceding two chapters, $G_s(r,t)$ (classical) is calculated through the 'fourth power of the forces'; i.e., an expression is obtained for G_s which contains all terms for which M (as defined by 4.20) is ≤ 4. Corresponding expressions for the incoherent scattering function are then derived from the expressions for $G_s(r,t)$. As is demonstrated, below, the cross section may be expressed as a sum of terms, each of which becomes successively more important as the temperature of the scattering system is lowered.

The question of the calculation of the 'distinct' part of the space-time correlation function, G_d, is deferred to chapter 8, below.

Just as for the case of the momentum density discussed in the previous chapter, an expansion for $G_s(r,t)$ may be found in direct correspondence with the expansion obtained for $f_{1,1}(\underline{x}_1; t \mid \underline{x}_{1_0})$. $G_s(r,t)$ is defined as the conditional

probability density for finding a specified particle in the neighborhood of configuration phase point $\vec{q}_{1_o} + \vec{r}$ at time t, given that at t = 0 the same particle was at $\vec{q}_{1_o}$. Since the systems to which this investigation pertain are isotropic, G_s does not depend on $\vec{q}_{1_o}$; furthermore, $G_s(r,t)$ is a function only of the absolute value of $\vec{r}$.

Hence,

$$G_s(r,t) \equiv \int d^3 p_1 \int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}} \; f_{1,1}(\vec{p}_1,\vec{q}_{1_o}+\vec{r};t \mid \vec{q}_{1_o},\vec{p}_{1_o}) \qquad \ldots \ldots (6.1)$$

$$= \sum_{i=0}^{\infty} G_s^{[i]}(r,t)$$

with

$$G_s^{[i]}(r,t) = \int d^3 p_1 \int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}} \; f_{1,1}^{[i]}(\vec{p}_1,r;t \mid \vec{p}_{1_o},0) \qquad \ldots \ldots (6.2)$$

Hence, from 5.8,

$$G_s^{[0]}(r,t) = \int d^3 p_1 \int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}} \; \delta(\vec{r}-\frac{\vec{p}_1}{m}t)\delta(\vec{p}_1-\vec{p}_o) \qquad \ldots \ldots (6.3)$$

$$= (m\beta/2\pi t^2)^{3/2} \; e^{-m\beta r^2/2t^2} \quad,$$

which is the result for an ideal gas.

The first order correction, i.e., that through the 'second power of the forces', may be obtained from 5.13:

$$G_s^{[1]} = \int d^3 p_1 \int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}} \; f_{1,1}(\underline{x}_1;t \mid \underline{x}_{1_o}) \qquad \ldots \ldots (6.4)$$

Integrating by parts re. p_1:

$$= \frac{ct^2}{2}\int d^3 p_1 \int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}}\left\{ \eta^{(2)}\delta^P[\nabla_{p_1}^2 \delta^q + t\nabla^2_{pq}\delta^q + \frac{t^2}{4m^2}\nabla^2_q \delta^q] + \frac{\chi^{(2)}}{m}\delta^P[-\frac{2t}{3m}\vec{p}_1\cdot\vec{\nabla}-\vec{p}_1\vec{\nabla}]\delta^q \right\}$$

$$= \frac{ct^2}{2}\int d^3 p_o \frac{e^{-\beta p_o^2/2m}}{(2\pi mkT)^{3/2}} \left\{ \frac{\eta}{4}\nabla^2_{p_o} - \frac{1}{3}\frac{\chi}{m}\vec{p}_o\cdot\vec{\nabla}_{po} \right\} \delta(\vec{q}_1-\vec{q}_o-\vec{p}_o t/m)$$

Again, integrating by parts:

$$= \frac{ct^2}{2} \left(\frac{\beta}{4m} n^{(2)} [\frac{m\beta r^2}{t^2} - 3] - \frac{1}{3}\chi^{(2)} [\frac{m\beta r^2}{t^2} - 3] \right) G_s^{[0]}(r,t)$$

Finally:

$$G_s^{[1]}(r,t) = \frac{ct^4}{2m^2} \left(\frac{n^{(2)}}{4} - \frac{\chi^{(2)}}{3\beta} \right) \nabla_r^2 G_s^{[0]}(r,t) \qquad \ldots\ldots \quad (6.5)$$

At high temperatures, $n^{(2)} \simeq \chi^{(2)}/\beta$, so that

$$\lim_{T \to \infty} G_s^{[1]}(r,t) = -\frac{1}{24} \frac{ct^4}{m^2} \chi^{(2)}/\beta \; \nabla_r^2 G_s^{[0]}(r,t) \qquad \ldots\ldots\ldots \quad (6.5')$$

However, one could have obtained 6.5 directly from the kinetic equation for $f_{1,1}^{[1]}$ (5.3). In general, the $f_{1,1}^{[i]}$ are to be found from a kinetic equation of the form

$$\frac{\partial f^{[i]}}{\partial t} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_i} f^{[i]} = S(q_1,p_1,t) \quad \text{with} \quad f^{[i]}(t=0) = 0 \qquad \text{having}$$

the solution

$$f^{[i]} = \mathcal{F}\mathcal{J}^{-1} \frac{1}{[s-\frac{ik\cdot p_1}{m}]} \mathcal{F}\mathcal{L} \qquad S = \mathcal{F}\mathcal{L}^{-1} \frac{1}{[s-\frac{ik\cdot p_1}{m}]} \sum Op_j^{[i]}(p_1,s,k) \frac{1}{[s-\frac{ik\cdot p_1}{m}]^{kj}} \delta p$$

The $Op_j^{[i]}$ are derivative operators on $\underset{\sim}{p_1}$. Thence:

$$G_s^{[i]} \sim \int d^3 p_0 \int d^3 p_1 \frac{e^{-\beta p_0^2/2m}}{(2\pi mkT)^{3/2}} \mathcal{F}\mathcal{J}^{-1} \frac{1}{[s-\frac{ik\cdot p_1}{m}]} \sum Op_j^{[i]} \frac{1}{[s-\frac{ik\cdot p_1}{m}]^{kj}} \delta(\vec{p}_1 - \vec{p}_0)$$

If one next integrates by parts re. $\underset{\sim}{p_1}$, he can immediately and easily perform the integration over $\underset{\sim}{p_0}$, yielding:

$$G_s^{[i]} \sim \int d^3 p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}} \mathcal{F}\mathcal{J}^{-1} \frac{1}{[s-\frac{ik\cdot p_1}{m}]^{kj}} \sum \hat{Op}_j^{[i]} \frac{1}{[s-\frac{ik\cdot p_1}{m}]} \qquad \circ$$

As an illustration, let us apply this procedure to a calculation leading to 6.5. It has previously been shown that

$$\frac{\partial f^{[1]}_{1,1}}{\partial t} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} f^{[1]}_{1,1} =$$
$$\quad\quad\quad\quad\quad \cdots\cdots (5.3)$$

$$= ct\left(\eta^{(2)}[\nabla^2_{p_1} + \frac{t}{2m}\nabla^2_{p_1 q_1}] + \chi^{(2)}[3 + \vec{p}_1 \vec{\nabla}_{p_1}]\right) f^{[0]}_{1,1}(t)$$

$$f^{[1]}_{1,1}(p_1, q_p; 0) \equiv 0$$

Thus,

$$G^{[1]}_s = c\int d^3p_1\, e^{-\beta p^2_1/2m} \frac{1}{(2\pi mkT)^{3/2}} \vec{\nabla}\Big(\eta^{(2)}[\frac{1}{[s-\frac{ikp}{m}]^2}\nabla^2_{p_1} - \frac{(-\frac{i\vec{k}}{m}\vec{\nabla}p_1)}{[s-\frac{ikp}{m}]^3}] +$$

$$+ \frac{\chi^{(2)}}{m}[\frac{-\vec{p}_1\vec{\nabla}_{p_1}}{[s-\frac{ikp}{m}]^2}]\Big) \frac{1}{[s-\frac{i\vec{k}\cdot\vec{p}_1}{m}]}$$

$$= c\int d^3p_1\, e^{-\beta p^2_1/2m} \frac{1}{(2\pi mkT)^{3/2}}\left(\frac{\eta^{(2)}}{8}\frac{t^4}{m^2}\nabla^2_{q_1} + \frac{\chi^{(2)}}{m^2}\frac{t^3}{6}\vec{p}_1\vec{\nabla}_{q_1}]\right)\delta(\vec{q}_1 - \vec{q}_o - \frac{\vec{p}_1}{m}t)$$

$$= \frac{ct^4}{2m^2}\left(\frac{1}{4}\eta^{(2)} - \frac{1}{3}\chi^{(2)}/\beta\right)\nabla^2_r G^{[0]}_s(r,t)\,, \quad\quad \text{as before.}$$

In this way the complete calculation of $f^{[2]}_{1,1}$ may be circumvented but the second correction to G_s may still be obtained. We start with the kinetic equation for $f^{[2]}_{1,1}$:

$$\frac{\partial f^{[2]}_{1,1}}{\partial t} + \frac{\vec{p}_1}{m}\cdot\vec{\nabla}_{q_1} f^{[2]}_{1,1} = [\mathcal{A}_1 + \mathcal{A}_2]f^{[1]}_{11} + \sum_{k=3}^{9}\mathcal{A}_k f^{[0]}_{11} \quad ; \quad f^{[2]}_{11}(x_1;0)\equiv 0 \,,..(5.4)$$

where $\mathcal{A}_1 \rightarrow \mathcal{A}_9$ are defined by 4.32, 4.37, 4.40-46. Corresponding to each of the $\mathcal{A}_i$ will be a contribution to $G^{[2]}_s$,

Consider, for example, the contribution due to $(\mathcal{A}_1 + \mathcal{A}_2)f^{[1]}_{11}$. From 4.32 and 4.40:

$$(\mathcal{A}_1 + \mathcal{A}_2)f^{[1]}_{1,1} = c^2\int_0^t d\tau\left(\eta^{(2)}[\nabla^2_{p_1} + \frac{\tau}{m}\nabla^2_{p_1 q_1}] + \chi^{(2)}[3 + \vec{p}_1\vec{\nabla}_{p_1}]\right)\mathcal{A}_{-\tau}f_{1,1}(t-\tau) \quad\cdots(6.6)$$

Thus, since q_1 is present in the integral only as derivatives, except in $f_{1,1}^{1}$:

$$\mathcal{J}(\ell_1+\ell_2)f_{1,1}^{[1]} = c^2\int_0^t d\tau(\hat{n}^{(2)}[\nabla_{p_1}^2+\tau(-\frac{ik\nabla}{m}_p)]+\underline{\chi}^{(2)}[3+p_1\vec{\nabla}_p]e^{\frac{ik\cdot p_1}{m}\tau}\mathcal{J}f_{1,1}^{[1]}(t-\tau)$$

Next, taking the Laplace transform and using the convolution theorem:

$$\mathcal{J}\mathcal{J}(\ell_1+\ell_2)f_{1,1}^{[1]} = c^2(\eta^{(2)}[\nabla_{p_1}^2\frac{1}{[s-\frac{ikp}{m}]} - ik\vec{\nabla}_{p_1}\frac{1}{[s-\frac{ikp}{m}]^2}]$$
$$+ \frac{\chi^{(2)}}{m}[3+p_1\cdot\vec{\nabla}]\frac{1}{p_1[s-\frac{ikp}{m}]})\mathcal{J}\mathcal{J}f_{1,1}^{[1]}$$

Finally, referring to 5.13:

$$\mathcal{J}\mathcal{J}(\ell_1+\ell_2)f_{1,1}^{[1]} = \quad\quad\quad\quad\quad\quad\quad\dots\dots\dots\dots (6.7)$$

$$=c^2\overline{[\eta^{(2)}]}^2 ((\nabla_{p_1}^2\frac{1}{[s-\frac{ikp}{m}]} -ik\vec{\nabla}_{p_1}\frac{1}{[\ ]^2})(3\frac{(ik/m)^2}{[\ ]^5}-3\frac{(-ik\cdot\vec{\nabla})}{[\ ]^4}p_1+\frac{\nabla_{p_1}^2}{[\ ]^3}) +$$

$$+ \frac{\eta^{(2)}\chi^{(2)}}{m} (([3+p\nabla]\frac{1}{p_1[s-\frac{ikp}{m}]})(3\frac{(-\frac{ik}{m})^2}{[s-\frac{ikp}{m}]^5}-3\frac{(-\frac{ik}{m}\nabla_{p_1})}{[\ ]^4} + \frac{\nabla_{p_1}^2}{[\ ]^3}) +$$

$$+(\nabla_{p_1}^2\frac{1}{p_1[\ ]} -\frac{ik\nabla}{m}\frac{1}{p[\ ]^2})(3+p_1\vec{\nabla}-2(\frac{-ik\cdot p_1}{m})p_1\frac{1}{[\ ]^4})) +$$

$$+ \frac{\overline{\chi^{(2)}}^2}{m^2} (([3+p_1\nabla_{p_1}]\frac{1}{[\ ]})(3+p_1\vec{\nabla}_p\frac{1}{[s-\frac{ik\cdot p_1}{m}]^3} - 2(\frac{-ik\cdot p_1}{m})\frac{1}{[\ ]^4}))]\delta(\vec{p}_1-\vec{p}_{1o})$$

Now, utilize the procedure described on the bottom of page 6-4. For example, the contribution due to the $\overline{\chi^{(2)}}^2$ term is (after integrating by parts twice)

$$\propto \int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}} \mathcal{J}^{-1}\mathcal{J}^{-1}[(\frac{(-ik\cdot p_1)}{m})\frac{1}{[s-\frac{ik\cdot p_1}{m}]^4}-\vec{p}_1\cdot\vec{\nabla}\frac{1}{[s-\frac{ik}{m}p_1]^3})(\frac{-ik\cdot p_1/m}{[s-\frac{ik\cdot p_1}{m}]^3})]$$

$$\propto \int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}}(\frac{4t^6}{6!m^2}(\vec{p}_1\cdot\vec{\nabla}_{q_1})^2-\frac{t^5}{5!m}(\vec{p}_1\cdot\vec{\nabla}_{q_1}))\delta(\vec{q}_1-\vec{q}_o-\frac{\vec{p}_1}{m}t)$$

$$\propto t^2 \left(\frac{t^4}{180m^2\beta^2} \nabla_r^2 \nabla_r^2 + \frac{7}{360m\beta} \nabla_r^2 \right) G_s^{[0]}(r,t)$$

where, in the last step, use has been made of table 6-1 of Appendix E . In this way, it is determined that the total contribution to $G_s^2(r,t)$ due to $(\mathcal{J}_1 + \mathcal{J}_2)f_{1,1}^{[1]}$ is

$$G_s^{[2]} \text{ due to } \mathcal{J}_1 + \mathcal{J}_2 = \frac{c^2 t^4}{2} \left(\overline{n^{(2)}}^2 \beta^2 \left[\frac{9}{8} \frac{t^4}{280m^2\beta^2} \nabla_r^2 \nabla_r^2 \right] - \right. \qquad \ldots\ldots \quad (6.8)$$

$$- \frac{\overline{\chi^{(2)} n^{(2)}}}{m^2} \beta \left[\frac{3}{280m^2\beta^2} \frac{t^4}{\nabla_r^2} \nabla_r^2 + \frac{1}{40} \frac{t^2}{m\beta} \nabla_r^2 \right] +$$

$$\left. + \frac{\overline{\chi^{(2)}}^2}{m^2} \left[\frac{1}{90} \frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 + \frac{7}{180} \frac{t^2}{m\beta} \nabla_r^2 \right] \right) G_s^{[0]}(r,t)$$

As another example, consider the contribution due to $\mathcal{J}_3 f_{1,1}^{[0]}$. Again remembering that $\mathcal{J}_{-\tau} f_{1,1}^{[0]}(t-\tau) = f_{1,1}^{[0]}(t)$, and referring to 4.37, it it quickly seen that

$$\mathcal{J}_3 f_{1,1}^{[0]} = \frac{ct^3}{6m^3} \chi^{(4)} \left(\frac{15m}{\beta} + 5p_1^2 + \frac{5m}{\beta} p_1 \circ \vec{\nabla}_{p_1} + p_1^2 \vec{p}_1 \circ \vec{\nabla}_{p_1} \right) f_{1,1}^{[0]}(t)$$

Thus, the contribution to G_s^2 is

$$= \frac{c\chi^{(4)}}{m^3} \int d^3 p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}} \mathcal{F}^{-1} \mathcal{L}^{-1} \left(-(\frac{5m}{\beta} + p_1^2) \vec{p}_1 \circ \vec{\nabla} \right) \frac{1}{\frac{\beta[s-i\underline{k}\circ p_1]}{m} \vec{p}_1} \frac{1}{[s - i\underline{k}\circ p_1]}{m}$$

$$= \frac{c\chi^{(4)}}{m^3} \int d^3 p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mkT)^{3/2}} \left(\frac{t^5}{5!m} (\frac{5m}{\beta} + p_1^2) \vec{p}_1 \circ \vec{\nabla}_{p_1} \right) \delta(\vec{q}_1 - \vec{q}_0 - \frac{\vec{p}_1}{m} t)$$

so that we finally have

$$G_s^{[2]}(r,t)\Big|_{\text{due to } \mathcal{J}_3} = \qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.9)$$

$$= -c\frac{^{(4)}}{m^2}\frac{t^4}{2}\Big(\frac{1}{60}\frac{t^4}{m^2\beta^2}\ \nabla_r^2\ \nabla_r^2 + \frac{1}{6}\frac{t^2}{m\beta}\ \nabla_r^2\ \Big)G_s^{[0]}(r,t)$$

One procedes to calculate the contributions due to

$\mathcal{J}_4 \longrightarrow \nabla \mathcal{J}_q$ in the same way. However, rather than perform

each calculation separately, since many of the terms in

the collision integrals occur more than once, it is conven-

ient to make a table (see appendix E, table II) in which are

listed these terms and their corresponding contributions to

$G_s^{[2]}$. Then, after performing the τ integration in the

collision integrals, one can read off the contributions to

$G_s^{[2]}$. One finds:

$$\qquad\qquad\qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.10)$$

$$G_s^{[2]}(r,t)\Big|_{\text{due to } \mathcal{J}_4} =$$

$$= c\frac{n}{m}\ \frac{^{(4xx)}}{}\frac{t^4}{2}\ \Big(\ \frac{t^4}{36m^2\beta^2}\ \nabla_r^2\ \nabla_r^2 + \frac{1}{3}\frac{t^2}{m\beta}\ \nabla_r^2\ \Big)G_s^{[0]}(r,t)$$

$$\qquad\qquad\qquad\qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (6.11)$$

$$G_s^{[2]}(r,t)\Big|_{\text{due to } \mathcal{J}_5} =$$

$$= c\frac{n}{m^2}\ \frac{^{(4xx)}}{}\frac{t^4}{2}\ \Big(\ \frac{t^4}{36m^2\beta^2}\ \nabla_r^2\ \nabla_r^2 + \frac{1}{6}\frac{t^2}{m\beta}\ \nabla_r^2\ \Big)G_s^{[0]}(r,t)+$$

$$+ c\frac{\chi}{m^2}\ \frac{^{\{2xx\}}}{}\frac{t^4}{2}\ \Big(\ \frac{t^4}{36m^2\beta^2}\ \nabla_r^2\ \nabla_r^2 + \frac{7}{60}\frac{t^2}{m\beta}\ \nabla_r^2\ \Big)G_s^{[0]}(r,t)+$$

$$+ c\frac{\chi}{m^2}\ \frac{^{\{2xy\}}}{}\frac{t^4}{2}\ \Big(\ \frac{3}{20}\frac{t^2}{m\beta}\ \nabla_r^2\ \Big)G_s^{[0]}(r,t) +$$

$$+ c^2\frac{}{m^2}\ \chi_{(3)}^{(4)}\ \frac{t^4}{2}\Big(\frac{t^4}{36m^2\beta^2}\ \nabla_r^2\ \nabla_r^2 + \frac{13}{180}\frac{t^2}{m\beta}\ \nabla_r^2\Big)G_s^{[0]}(r,t)$$

$$G_s^{[2]}(r,t) \bigg|_{\text{due to } Q_6} = \quad \ldots\ldots\ldots \quad (6.12)$$

$$= -\frac{c\Psi}{2m^2}^{(4xx)} \beta t^4 \left(\frac{1}{42}\frac{t^4}{2m^2\beta^2}\nabla_r^2\nabla_r^2 + \frac{1}{6}\frac{t^2\nabla_r^2}{m\beta}\right) G_s^{[0]}(r,t) +$$

$$+ \frac{c\Psi}{2m^2}^{(4xy)} \beta t^4 \left(\frac{1}{60}\frac{t^2\nabla_r^2}{m\beta}\right) G_s^{[0]}(r,t) \; -$$

$$- \frac{c^2}{2m}2(3)\Psi^{(4)}\beta t^4 \left(\frac{t^4}{210m^2\beta^2}\nabla_r^2\nabla_r^2 + \frac{t^2}{180m\beta}\nabla_r^2\right)G_s^{[0]}(r,t)$$

$$G_s^{[2]}(r,t) \bigg|_{\text{due to } Q_7} = \quad \ldots\ldots\ldots\ldots \quad (6.13)$$

$$= -\frac{c^2}{2m}\chi^{(2)}t^4 \left(\frac{\chi^{(2)}}{m}[\frac{7}{180}\frac{t^2\nabla_r^2}{m\beta}+\frac{1}{90}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2] +\right.$$

$$\left.+\frac{n^{(2)}}{m}\beta[-\frac{t^2}{40m\beta}\nabla_r^2 - \frac{t^4}{105m^2\beta^2}\nabla_r^2\nabla_r^2]\right) G_s^{[0]}(r,t)$$

$$G_s^{[2]}(r,t) \bigg|_{\text{due to } Q_8} = \quad \ldots\ldots\ldots \quad (6.14)$$

$$= \frac{ct^4}{2m}\beta\left((\frac{\beta\mu}{192m}^{(4xx)} - \frac{\Psi}{56}^{(4xx)})\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right) G_s^{[0]}(r,t) +$$

$$+ \frac{c^2}{2m}t^4\beta\left((\frac{\beta\mu^{(4)}}{64m}(3) - \frac{\Psi^{(4)}}{56}(3))\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right) G_s^{[0]}(r,t)$$

$$G_s^{[2]}(r,t) \bigg|_{\text{due to } Q_9} = \quad \ldots\ldots\ldots\ldots \quad (6.15)$$

$$= -\frac{c^2}{2}t^4 \left(\frac{\chi^{(1)}n^{(1)}}{m^2}\beta[-\frac{1}{168}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2]+ \frac{\overline{n^{(1)}}^2}{m^2}\beta[\frac{t^4}{192m^2\beta^2}\nabla_r^2\nabla_r^2]\right) \times$$

$$\times G_s^{[0]}(r,t)$$

Upon adding these contributions (6.8 - 6.15) one obtains

for the total second order correction to $G_s(r,t)$:

$$G_s^{[2]}(r,t) = \quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (6.16)$$

$$= c^2 \frac{t^4}{2m^2} \frac{\overline{(\eta^{(2)})^2}}{m^2} \beta^2 \left[\frac{-t^4}{180m^2\beta^2} \nabla_r^2\nabla_r^2 \right] + \frac{\chi^{(2)}\eta^{(2)}}{m} \beta \left[\frac{t^4}{210m^2\beta^2} \nabla_r^2\nabla_r^2 \right] \right) G_s^{[0]}(r,t)$$

$$+ c^2 \frac{t^4}{2m^2} \left(\left[\frac{\beta^2\mu^{(4)}}{64}_{(3)} - \frac{19\beta\Psi^{(4)}}{840}_{(3)} + \frac{\chi^{(4)}}{36}_{(3)} \right] \frac{t^4}{m^2\beta^2} \nabla_r^2\nabla_r^2 \right.$$

$$\left. + \left[\frac{-\beta\Psi^{(4)}}{180}_{(3)} + \frac{13\chi^{(4)}}{180}_{(3)} \right] \frac{t^2}{m\beta} \nabla_r^2 \right) G_s^{[0]}(r,t)$$

$$+ c \frac{t^4}{2m^2} \left(\left[\frac{\eta^{(4xx)}}{18} - \frac{\chi^{(4xx)}}{60\beta} + \frac{\chi^{\{2xx\}}}{36} - \frac{\beta\Psi^{(4xx)}}{24} + \frac{\beta^2\mu^{(4xx)}}{192} \right] \frac{t^4}{m^2\beta^2} \nabla_r^2\nabla_r^2 \right.$$

$$\left. + \left[\frac{\eta^{(4xx)}}{2} - \frac{\chi^{(4xx)}}{6\beta} + \frac{7\chi^{\{2xx\}}}{60} + \frac{3\chi^{\{2xy\}}}{20} + \frac{\beta\Psi^{(4xy)}}{60} - \frac{\beta\Psi^{(4xx)}}{6} \right] \times \right.$$

$$\left. \times \frac{t^2}{m\beta} \nabla_r^2 \right) G_s^{[0]}(r,t)$$

At high temperatures, where $g_{2} \sim e^{-\beta\phi}$, one may make use of

the relationships 5.30 - 5.33, also noting that $\beta^2\mu^{(4)}_{(3)} \simeq$

$\simeq \beta \Psi^{(4)}_{(3)} \simeq \chi^{(4)}_{(3)} \simeq \overline{\chi^{(2)2}}$, so that:

$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (6.17)$$

$$G_s^{[2]}(r,t) \simeq$$

$$\begin{array}{c} \text{Lim} \\ T\to\infty \end{array} = \frac{c^2 t^4}{2m^2} \overline{\chi^{(2)2}} \left(\left[\frac{23}{630} \frac{t^4}{m^2\beta^2} \nabla_r^2\nabla_r^2 + \frac{1}{15} \frac{t^2}{m\beta} \nabla_r^2 \right] \right) G_s^0(r,t) +$$

$$+ c \frac{t^4}{2m^2} \left(\left[\frac{\eta^{(4xx)}}{90} + \frac{\beta^2\mu^{(4xx)}}{1728} \right] \frac{t^4}{m^2\beta^2} \nabla_r^2\nabla_r^2 \right.$$

$$\left. + \left[\frac{13}{60} \eta^{(4xx)} - \beta^2\mu^{(4xx)} + \frac{3\chi^{\{2xy\}}}{20} + \frac{\beta\Psi^{(4xy)}}{60} \right] \times \right.$$

$$\left. \times \frac{t^2}{m\beta} \nabla_r^2 \right) G_s^{[0]}(r,t)$$

On the other hand, as a result of equations 6.3, 6.5, and

6.16, the general form of an expansion for $G_s(r,t)$ appears:

$$G_s(r,t) = \sum_{n=0}^{\infty} t^{2n} \, D_R^{[n]} \, G_s^{[0]}(R,t) \quad \text{\small ∘∘∘∘∘∘∘∘∘∘∘∘} \quad (6.18)$$

where

$$\vec{R} \equiv (m\beta)^{1/2} \frac{\vec{r}}{t} \quad ; \quad G_s^{[0]}(R,t) = (m\beta/2\pi t^2)^{3/2} \, e^{-R^2/2} \quad \text{\small ∘∘∘∘∘} \quad (6.19)$$

The $D_R^{[n]}$ are purely differential operators in R and are not explicit functions of t. The differential order of $D_R^{[n]}$ is $\leq 2n$.

From 6.18 one can determine that the "intermediate scattering function" (classical) is of the form

$$\quad (6.20)$$

$$\mathcal{J}(k,t) = e^{-t^2 k^2/2m\beta} \sum_{n=0}^{\infty} t^{2n} \, w^{[n]}\left(\frac{tk}{(m\beta)^{1/2}}\right) \quad \text{\small ∘∘∘∘∘∘∘∘}$$

where the $w^{[n]}\left(\frac{tk}{(m\beta)^{1/2}}\right)$ are polynomials in $tk/(m\beta)^{1/2}$ corresponding to the $D^{[n]}$ and contain terms of even power of $tk/(m\beta)^{1/2}$ less or equal to than $2n$. For example $w^{[n]} \sim -t^2 k^2/m\beta$ corresponds to the differential operator $D_R^{[n]} \sim \nabla_R^2$.

It is now easy to obtain an inverse temperature expansion for the classical approximation to the incoherent scattering function pertinent to slow-neutron scattering cross-section. We have:

$$\quad \text{\small ∘∘∘∘∘∘∘∘∘} \quad (6.21)$$

$$S_{inc.}^{cl.}(k,\omega) \equiv \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \int_{-\infty}^{\infty} d^3 r \, e^{-ik\cdot r} \, G_s^{cl.}(r,t)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \, e^{-i\omega t} \, \mathcal{J}_{inc.}^{cl.}(k,t) = \int_{-\infty}^{\infty} \frac{dt}{2\pi} \, e^{-[i\omega t + k^2 t^2/2m\beta]} \sum_{n=0}^{\infty} t^{2n} w^{[n]}\left(\frac{tk}{(m\beta)^{1/2}}\right)$$

so that, from 6.3, 6.5, and 6.19:

$$S_{inc}^{cl}(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-(i\omega t + k^2 t^2)\overline{2m}} [\, 1 - \frac{ct^2}{2m}(\beta\eta^{(2)} - \frac{\chi^{(z)}}{3}) + o(\epsilon^4) +\ldots] \qquad \ldots\ldots\ldots (6.22)$$

$$= \frac{1}{2\pi} e^{-\frac{m\beta\omega^2}{2k^2}} \int_{-\infty}^{\infty} d\tau\, e^{-\frac{k^2\tau^2}{2m\beta}} [\, 1 - \frac{ck^2}{2m^2\beta} (\tau + im\omega\,\frac{4}{k^2}(\beta\eta^{(2)} - \frac{\chi^{(z)}}{3}) +\ldots]$$

$$= \sqrt{\frac{m\beta}{2\pi k^2}}\, e^{-\frac{m\beta\omega^2}{2k^2}} [\, 1 - \frac{c\beta}{2k^2}(3-10m\beta\omega^2 + \frac{m^2\beta^2\omega^4}{k^2})(\beta\eta^{(2)} - \frac{\chi^{(z)}}{3}) +\ldots]$$

Thus, in the high temperature limit:

$$S_{inc}^{cl}(k,\omega) = \sqrt{\frac{m\beta}{2\pi k^2}}\, e^{-\frac{m\beta\omega^2}{2k^2}} [\, 1 + \frac{c\beta}{24k^2}(3-10m\beta\omega^2+m\beta^2\omega^4)\chi^{(2)} + \qquad \ldots\ldots\ldots\ldots (6.22')$$

$$+ \text{terms in the"fourth power of the forces"} +\ldots]$$

However, there yet remains the task of correcting 6.22 so as to take into account the basic quantum nature of neutron scattering processes. Rosenbaum* has investigated quantum corrections to the classical scattering function and has found%:

$$S_{inc}(k,\omega) = e^{\beta\hbar\omega/2}\, e^{-\beta\hbar^2 k^2/8m} [\, S_{inc}^{cl}(k,\omega) + \qquad\qquad \ldots\ldots (6.23)$$

$$+ \frac{c\hbar^2\beta^2}{48}\chi^{(2)} \sqrt{\frac{\beta}{2\pi mk^2}}\, e^{-\frac{m\beta\omega^2}{2k^2}} (1-\omega^2 m\beta + \frac{2k^2\beta}{k^2} + \frac{8m}{8m}) + o(\hbar^4)+\ldots]$$

---

*Rosenbaum, thesis[43] - especially eqn. 5.45;% Rewritten to our notation.

Thus, using 6.22', one can express the exact scattering function at high temperature as:

$$S_{inc}(k,\omega) = \sqrt{\frac{m\beta}{2\pi k^2}} \; e^{\beta\hbar\omega/2} \; e^{-\beta\hbar^2k^2/8m} \; e^{-m\beta\omega^2/2k^2} \times \quad \circ\circ\circ\circ\circ\circ \quad (6.24)$$

$$\times \left[\; 1 + \frac{c\beta\chi^{(2)}}{24k^2}\left(3-10m\beta\omega^2 + \frac{m^2\beta^2\omega^4}{k^4}\right)\Delta_2(k,\omega,\beta) + \right.$$

$$\left. + \text{ terms of } o(\hbar^4,\epsilon^4) \; \circ\circ\circ\circ\circ \;\right]$$

In the above equation, $\Delta_2(k,\omega,\beta)$ describes the quantum correction to the second term in the scattering function and would be unity if no correction were necessary. Explicitly,

$$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad (6.25)$$

$$\Delta_2(k,\omega,\beta) \equiv \left[\; 1 + \frac{\beta h^2 k^2}{2m}\left\{\frac{\frac{1-\omega^2 m\beta}{k^2} + \frac{h^2 k^2 \beta}{8m}}{3 - \frac{10m\beta\omega^2}{k^2} + \frac{m^2\beta^2\omega^4}{k^4}}\right\}\right] \quad \circ\circ\circ\circ\circ\circ\circ$$

Rosenbaum's analysis has not been explicitly developed beyond the statement given by 6.23, above. But, it can be surmised that the exact scattering function can probably be expressed as a sum of terms, each proportional to one of the system constants which we have already defined; i.e.,

$$S_{inc}(k,\omega) = e^{\beta\hbar\omega/2} \; e^{-\beta\hbar^2k^2/8m} \;\left[\; S_{inc}^{cl}(k,\omega) + a_1(k,\hbar,\omega)\chi^{(2)} + \right.$$

$$\left. + a_2(k,\hbar,\omega)\chi^{(4)} + \circ\circ\circ \text{ etc. }\right]$$

The same system constants which demonstrate the deviation of $S_{inc}^{cl\circ}(k,\omega)$ from that for an ideal gas are also intimately involved in expressing the intrinsic quantum nature of the

scattering process (cf., 6.24, 6.25). In general, one cannot separate the "quantum effects" in the cross-section from contributions due to interactions between particles.

On the other hand, referring to 6.25, it is seen that for small momentum and energy transfer, $\Delta_2(k,\omega,\beta) \simeq 1$. Thus, under these conditions, quantum corrections to the scattering function are much less significant than the normal corrections due to interactions between particles (at least, to an order of the "fourth power of the forces.") Of course, the fundamental quantum correction manifest in the multiplicative factors, $e^{\beta\hbar\omega/2}\; e^{-\beta\hbar^2 k^2/8m}$, remains; however, the quantum interference effects demonstrated by $\Delta_2(k,\omega,\beta)$ may be neglected if $\dfrac{\beta\hbar^2 k^2}{2m} \ll 1$. If this requirement is met, the $A=C=R=Z$ prescription[%%], viz.,

$$S_{inc}(k,\omega) \simeq e^{\beta\hbar\omega/2}\; e^{-\beta\hbar^2 k^2/8m}\; S_{inc}^{cl}(k,\omega) \qquad\qquad\qquad (6.26)$$

is probably valid. For high momentum and energy transfer quantum interference terms are comparable to interaction terms and 6.26 must be employed with care.

Equations 6.22-6.24 suggest that it may be feasible to measure the temperature dependence and magnitudes of the basic system constants $\left[\dfrac{\beta\eta^{(2)}}{4} - \dfrac{\chi^{(2)}}{3}\right]$. The measured values could eventually serve as a check on values yet to be determined by direct calculation from postulated interparticle forces. In addition, though, many physical phenomena are probably adequately described

%% Aamodt, Case, Rosenbaum, Zweifel [8]

by theories for which the basic parameters are the system constants, rather than the forces, so that there is sufficient reason to obtain information about these constants for their own sake.

In measuring the $M = 2$ system constants, as demonstrated by eqns. 6.22 & 6.22', it would be desirable to scatter neutrons from a high pressure gas at very high temperature, studying neutrons which have experienced a low net momentum and energy transfer with the bombarded system. Under these circumstances, the second order term in 6.24 is a small correction to the zero'th, and the fourth and higher terms may be neglected. Quantum effects would not be too important, but they could be calculated. One would measure $S_{inc}(k,\omega)$ at constant k and ω, as a function of $T \Leftrightarrow \beta$.

Of course, 6.24 is related to the incoherent part of the scattering cross-section, only. Hence, these last remarks are conditional upon the possibility of determining the temperature dependence of the coherent part of the cross-section also. This point shall be considered in chapter 8, where determination of $G_d(r,t)$ is discussed.

At this time, let us return to consideration of (classical) $G_s(r,t)$. From equations 6.3 & 6.5,

$$G_s(r,t) = [1 + \frac{ct^4}{2m^2} (\frac{n^{(2)}}{4} - \frac{\chi^{(2)}}{3\beta}) \nabla_r^2 + o(\epsilon^4)_{\circ\circ\circ\circ}] G_s^{[0]}(r,t) \qquad (6.27)$$

But,

$$G_s^{[0]}(r,t) \equiv (m\beta/2\pi t^2)^{3/2} e^{-m\beta r^2/2t^2} \qquad \circ \circ \circ \circ \circ \circ \circ \circ \circ \circ \quad (6.28)$$

$$= e^{(t^2/2m\beta) \nabla_r^2} \delta(\vec{r}) \qquad **$$

$$= [1 + \frac{t^2}{2m\beta} \nabla_r^2 + \frac{t^4}{4m^2\beta^2} \nabla_r^2 \nabla_r^2 + \circ\circ\circ\circ] \delta(\vec{r}) \qquad \circ$$

As a consequence, one might wish to represent $G_s(r,t)$ for short times as:

$$G_s(r,t) \simeq (m\beta/2\pi W^2(t))^{3/2} e^{-m\beta r^2/2W^2(t)} \qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ \quad (6.29)$$

with

$$W(t) = t^2[1 + \frac{ct^2}{m} (\frac{\beta \eta^{(2)}}{4} - \frac{\chi^{(2)}}{3})] \qquad \circ\circ\circ\circ\circ\circ\circ \quad (6.30)$$

$$\underset{\sim}{\simeq} t^2[1 - \frac{ct^2}{12m} \chi^{(2)}]$$

The higher the temperature, and/or the lower the density, the better is this representation.

For consistency, let $G_s(r,t)$ be calculated according to the "Gaussian approximation".@@ If an ansatz is made to impose a Gaussian form on $G_s(r,t)$, then it has been shown that

$$G_s(r,t) \overset{\circ}{=} [2\pi w^2(t)]^{-3/2} e^{-r^2/2w^2(t)} \qquad \circ\circ\circ\circ\circ\circ \quad (6.31)$$

_____

**One notices that the Fourier transforms of $\left(\frac{m\beta}{2\pi t}\right)^{\frac{3}{2}} e^{-m\beta r^2/2t^2}$ and $e^{(t^2/2m\beta)} \nabla_r^2 \delta(\vec{r})$ are identical, so that the functions themselves must be equal.

@@
See, e.g., Vineyard[10], Schofield[9]

where

$$w^2(t) \equiv \frac{2}{3} \int_0^t dt' \ (t-t') \ \langle \vec{v}(0) \cdot \vec{v}(t') \rangle \qquad \ldots\ldots\ldots \quad (6.32)$$

Reference to eqn. 5.25 demonstrates

$$w^2(t) = \frac{t^2}{m\beta} [\ 1 - \frac{ct^2}{12m} \chi^{(2)} + o(\epsilon^4) + \ldots\ldots\ ] \qquad \ldots\ldots\ldots \quad (6.33)$$

i.e., for short times, the Gaussian approximation provides the correct expression for $G_s(r,t)$.** This result is well known; it is also known that the Gaussian approximation does not hold for intermediate times. Here, however, it is explicitly demonstrated that the higher the temperature, the better is the approximation and the longer will be the interval for which it is valid.

Rahman et al.[41] have indicated how the Gaussian approximation may be improved upon, and have suggested

$$\mathcal{A} \frac{cl}{inc}(k,t) = \exp \sum_{n=1}^{\infty} (-k^2)^n \ \gamma_n(t) \qquad \ldots\ldots\ldots \quad (6.34)$$

where

$$\gamma_1(t) \equiv \int_0^t dt_1 \int_0^{t_1} dt_2 \ \langle v_k(t_2) \cdot v_k(t_1) \rangle \qquad \ldots\ldots\ldots \quad (6.35)$$

$$\gamma_2(t) \equiv \int_0^t dt_1 \int_0^{t_1} dt_2 \ \circ\circ \int_0^{t_3} dt_4 \ \langle v_k(t_4) \circ\circ\circ\circ v_k(t_1) \rangle -$$

$$- \frac{1}{2} [\gamma_1(t)]^2$$

and so forth. . .

Calculating γ_1 and γ_2 from 5.25 and 5.39, 6.34 provides

**Assuming, of course, that the correct expansion for $\langle \vec{p}_i(0) \cdot \vec{p}_i(t) \rangle$ is used, as per 5.25.

(at high temperature):

$$\mathcal{A}^{cl.}_{inc}(k,t) = e^{-k^2\left[\frac{t^2}{2m\beta}\left(1-\frac{ct^2}{12m}\chi^{(2)}\right)+..\right]}e^{+k^4\left[\frac{ct^6}{8m^3\beta^2}\frac{\chi^{(2)}}{18}+..\right]}e^{-k^6\gamma_6}....$$

$$= 1 - \frac{k^2t^2}{2m\beta} + \frac{ct^4\chi^{(2)}}{24m^2\beta}k^2 + \frac{k^4t^4}{8m^2\beta^2} - \frac{k^4ct^6\chi^{(2)}}{m^3\beta^2}\left[\frac{1}{48} + \frac{1}{288}\right] +$$

$$+ \text{terms } o(t^6\varepsilon^0),\ o(t^8\varepsilon^2),\ o(\varepsilon^4),\ \text{etc}........$$

$$.....\quad(6.36)$$

On the other hand, from the exact calculation, 6.20 and 6.5, it is found that

$$\mathcal{A}^{cl.}_{inc}(k,t) = e^{-k^2t^2/2m\beta}\left[1+\frac{ct^4\chi^{(2)}}{24m^2\beta} + o(\varepsilon^4)\ ..\right] \qquad ....\quad(6.37)$$

$$= 1 - \frac{k^2t^2}{2m\beta} + \frac{ct^4\chi^{(2)}}{24m^2\beta}k^2 + \frac{k^4t^4}{8m^2\beta^3} - \frac{k^4ct^6\chi^{(2)}}{m^3\beta^2}\left[\frac{1}{48}\right] +$$

$$+ \text{terms } o(t^6\varepsilon^0),\ o(t^8\varepsilon^2),\ o(\varepsilon^4),\ \text{etc}.......$$

Comparing 6.37 with 6.36, it is seen that the $k^4t^6\chi^{(2)}$ terms do not agree; the imposition of the Markoffian assumption in calculating the four-time momentum correlation function is probably the source of error.

CHAPTER VII

BOGOLIUBOV FORMULATION; EXPANSIONS IN DENSITY

In the previous chapters, an investigation has been performed to obtain expansions for conditional probability densities and associated time-relaxed correlation functions. As it turns out, however, the resulting expressions demonstrate, only, the successively higher order contributions of the interparticle forces; it is not clear from the preceding work how one might also arrange the terms of the expansions to observe effects due primarily to changes in the average density of particles.

In the work that follows, below, a kinetic equation is derived for $f_{1,1}$ $(\underline{x}_1; t | \underline{x}_{1_0})$ in which the terms of the collision integral are arranged not only according to increasing powers of the interaction between particles, but in powers of the average density, as well. As such, this work follows closely that of Bogoliubov,[3] who studied the more usual case of a system which is totally symmetric under interchange of particles.**

Bogoliubov considered models with repulsive interactions only, searching for an asymptotic kinetic equation for $f_{1,1}$ of the form:

$$\frac{\partial f}{\partial t}_{1,1}(\underline{x}_1; t | \underline{x}_{1_0}) = \sum_{n=0}^{\infty} c^n A_n(t) \qquad \ldots\ldots\ldots\ldots \quad (7.1)$$

**The system of interest here is not, because attention is focussed on specific members of the assembly.

A_0 was found to be the streaming operator;[**] A_1 is closely related to binary collisions; A_2, ternary collisions, etc. The denser the system, the more important are the effects of multiple collisions.

In the following derivation the more usual systems, in which attractive forces are also important, are considered. Hence, also needed is a parameter with which to characterize the effects of the attractive forces. The van der Waals theory for the equilibrium equation of state[44] suggests choosing ϵc for this purpose. ϵ is designated as a coupling parameter for the attractive forces which appear in the Hamiltonian, measuring the importance of the attractive potential energy relative to the average kinetic energy of the particles.[**] It is typically proportional to the depth of the potential well, divided by kT.

Hence, rather than in Eq. (7.1), our asymptotic collision integrals will appear as coefficients of a <u>double</u> expansion, in c and ϵc .

Bogoliubov makes yet another important assumption, which is the essence of his approach to the problem. He assumes that after a very short time, of the order of the time during which two particles are close enough to interact (i.e., the "collision time"), all correlations between particles are destroyed. From that time onward, the temporal dependence of the densities, $f_{s,s}(\underline{x}_1,.., \underline{x}_s;t)$, for $s > 1$, is assumed to be only implicit : the higher order

[**] Specifically, $-\vec{p}_1 \cdot \vec{\nabla}_{q_1} f_{1,1}(x_1;t)$

densities are time independent functionals of $f_{1,1}(x_1;t)$ and depend on the time only through the change of $f_{1,1}$ with time.

Bogoliubov   considers   dilute, non-crystalline systems characterized by purely repelling forces. Hence, his assumption is plausible because, by virtue of the latter characteristic, if two particles were to interact they would always move away from each other. After a short time it would be impossible to specify, with anything more than a very small probability, which molecules might have interacted to give rise to the dynamical state in which the particles are found. Hence, higher order correlations are being destroyed too quickly to be of importance in the gross evolution of the distribution functions.

As an extension of this argument, it is assumed that $\frac{\partial f_{1,1}}{\partial t}$ is also dependent on the time in this way.

In the case of systems with attractive forces it is harder to find a plausible argument to justify the assumption. The great difficulty here is that, due to the forces of attraction, particles can be trapped in each others' force fields and correlations would persist for longer periods of time. However, if the systems are not too dense, the frequency of occurrence of these arrangements will be very low,

In accord with these remarks, perform the following expansions:

$$\frac{\partial f}{\partial t}_{1,1}(\underline{x}_1;t|\underline{x}_{1_o}) = A(f_{1,1}) = \sum_m \sum_n c^m(\epsilon c)^n A_{m,n-1}(\underline{x}_1;f_{1,1}) \quad \text{....}(7.2)$$

and, for $s \geq 2$,

$$f_{s,s}(X_s;t|\underline{x}_{1_o}) = \sum_m \sum_n c^m(\epsilon c)^n f^{m,n}_{s,s}(X_s;f_{1,1}(\underline{x}_1;t|\underline{x}_{1_o})) \quad \text{.....}(7.3)$$

As has already been discussed in Chapter 2 (and, also, Appendix 7-2) the Liouville equation may be transformed into a set of coupled differential equations (the BBGKY hierarchy) which provide the temporal evolution of the reduced probability density functions for specified sets of particles in the assembly. The hierarchy may be written in the following form (having singled out for attention only **one** particle of the assembly)[**]:

$$\frac{\partial f}{\partial t}_{s,s}(X_s;t|\underline{x}_{1_o}) + [\, H_s - \Theta^r_s\,]\, f_{s,s} =$$

$$= -\epsilon\Theta^a_s\, f_{s,s} + c\int d\vec{x}_{s+1}[\, \Phi^r_s - \epsilon\Phi^a_s]\, \cap f_{s+1,s+1}(X_{s+1};t|\underline{x}_{1_o}) \quad \text{..}(7.4)$$

$$1 \leq s \ll n\;.$$

The operators appearing in the equation have the following definitions:[##]

[**]At the end of this chapter, in preparation for studying $G_d(r,t)$, which is related to a probability density conditional upon the initial positions of **two** particles, a different form of the hierarchy is employed (see, also, Appendix 7.2).

[##]Relating to the notation of the preceding chapters, it is seen that $L_o = -H_n$ and $L_1 = \Theta^r_n - \epsilon\Theta^a_n$ (see next page.)

$$H_s \equiv \sum_{i=1}^{s} \frac{\vec{p}_i}{m} \cdot \vec{\nabla}_{q_i} \quad ; \quad \Theta_s^r \equiv \sum_{i<j}^{s} \sum \frac{\partial \phi_r ij}{\partial q_i} \cdot (\vec{\nabla}_{p_i} - \vec{\nabla}_{p_j}) \quad ;$$

$$\Theta_s^a \equiv \sum_{i<j}^{s} \sum \frac{\partial \phi_a ij}{\partial q_i} \cdot (\vec{\nabla}_{p_i} - \vec{\nabla}_{p_j}) \quad ; \quad \Theta_1^r = \Theta_1^a = 0 \quad ;$$

$$\phi_{s,j}^r \equiv \sum_{i=1}^{s} \frac{\partial \phi_r ij}{\partial q_1} \cdot (\vec{\nabla}_{p_i} - \vec{\nabla}_{p_j}) \quad ; \quad \phi_{s,j}^a \equiv \sum_{i=1}^{s} \frac{\partial \phi_a ij}{\partial q_i} \cdot (\vec{\nabla}_{p_i} - \vec{\nabla}_{p_j})$$

$\phi(|q_i - q_j|)$ is the two particle interaction potential energy, and has been broken into two terms, ϕ_r and ϕ_a, which represents respectively, the repulsive and attractive terms. ϵ is a positive constant; ϕ_a is the absolute value of the attractive part of the potential.

As in the earlier parts of this study, it is being assumed that the interaction between particles is adequately represented by two-body, additive, potentials each consisting of a strong repulsive core and weak short-range attractive "tail". c is the average density of the assembly.

Placing 7.2 and 7.3 into the BBGKY hierarchy (7.4) with s = 1, and equating coefficients of powers of the expansion parameters, one finds: .... (7.5)

a) $A_{o,o} = -H_1 f_{1,1}(x_1;t)$; b) $A_{m,n} = \Omega \int dx_2 [\phi_1^r f_{2,2}^{m-1,n} - \phi_1^a f_{2,2}^{m,n-1}]$,

for m,n $\geq$ 1 ;

c) $A_{m,o} = \Omega \int dx_2 \, \phi_1^r(x_2) \, f_{2,2}^{m-1,o}$; d) $A_{o,n} = \Omega \int dx_2 \phi_1^a(x_2) \, f_{2,2}^{o,n-1}$.

Also, for s $\geq$ 2:

$$\frac{\partial f}{\partial t}_{s,s}(X_s;f_{1,1}|x_{l_0}) = \frac{\delta f}{\delta f_{1,1}}_{s,s} \circ \frac{\partial f}{\partial t}_{1,1} = \frac{\delta f}{\delta f_{1,1}}_{s,s} A(x_1;f_{1,1}|x_{l_0})$$

$$= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^m(c\epsilon)^n A_{m,n}(\cdot;f_{1,1}) \circ \frac{\delta f}{\delta f_{1,1}}_{s,s} \qquad \cdots\cdots (7.6)$$

Define $D_{m,n}$ as the operator which takes the partial derivative with respect to time according to the chain rule, and then replaces $\frac{\partial f}{\partial t}_{1,1}$ by $A_{m,n}$. In other words,

$$D_{m,n} \equiv \left(\frac{\delta}{\delta f_{1,1}} \circ \frac{\partial f}{\partial t}_{1,1} \right)_{\frac{\partial f}{\partial t}_{1,1} \to A_{m,n}} \qquad \cdots\cdots (7.7)$$

Hence,

$$\frac{\partial f}{\partial t}_{s,s} = \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^m(\epsilon c)^n D_{m,n} f_{s,s}(X_s;f_{1,1}) \qquad \cdots\cdots (7.8)$$

In this way, using Equations (7.8) and (7.3) in the BBGKY hierarchy for s $\geq$ 2, and then equating coefficients of powers of the expansion parameters, the following equation is derived.

$$D_{o,o} f_{s,s}^{m,n} + (H_s - \Theta_s^r) f_{s,s}^{m,n}(X_s;f_{1,1}|x_{l_0}) =$$

$$= - \sum_{p=1}^{m} D_{p,o} f_{s,s}^{m-p,n} - \sum_{q=1}^{n} D_{o,q} f_{s,s}^{m,n-q} - \sum_{p=1}^{m}\sum_{q=1}^{n} D_{p,q} f_{s,s}^{m-p,n-q} -$$

$$- \Theta_s^a f_{s,s}^{m+1,n-1} + \Omega \int d\vec{x}_{s+1}[\Phi_s^r f_{s+1,s+1}^{m-1,n} - \Phi_s^a f_{s+1,s+1}^{m,n-1}] \circ \qquad \cdots\cdots (7.9)$$

Equations (7.9) and (7.5) are the basis for obtaining the asymptotic evolutionary equations which we are seeking. However, before we can proceed it is necessary to impose some boundary conditions on the $f_{s,s}$. To this end, in the spirit of Bogoliubov, assume that:

$$\lim_{\tau \to \infty} \mathcal{S}^{r(s)}_{-\tau} [\ f_{s,s}(X_s; \mathcal{S}^{(1)}_{+\tau} f_{1,1}(x_1; t|x_{1_0})) -$$

$$\mathcal{S}^{(1)}_{+\tau} f_1(x_1) \prod_{i \neq 1}^{n} \mathcal{S}^{(1)}_{+\tau} f_1(x_i) \ ] = 0 \qquad \cdots \cdots (7.10)$$

$\mathcal{S}^{r(s)}_t$ is the reduced "kinetic operator" for an s-body reduced dynamical problem which involves only the repulsive part of the forces. The definition of this operator is that when acting on the coordinates of a particle at time zero, it transforms the phase space position of the particle to that which it would have at time t were it acted upon by only the repulsive part of the forces of the other particles.

Hence, $\mathcal{S}^{r(s)}_t \Lambda(X_{s_0}) = \Lambda(X_s)$ where $\Lambda(X_s)$ is the solution of

$$\frac{\partial \Lambda(X_s)}{\partial t} = [\ H_s - \Theta^r_s \ ] \ \Lambda(X_s) \qquad ,$$

$\Lambda(X_{s_0})$ being any arbitrary function of the coordinates of the s-dimensional phase space. i.e., $\mathcal{S}^{r(s)}_{-t} = e^{-(H_s - \Theta^r_s)t}$.

Condition 7.10 corresponds, in a physical sense, to the weakening of correlations when the interacting particles move far away, in space-time, from the region of interaction. The full meaning of the assertion is far from clear, but, as Uhlenbeck says, "it works."[**] Hollinger[22] has indicated

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[**] Uhlenbeck[18] p. 47.

that this assumption is equivalent to the Strosszahlansatz,
implying the lack of correlations before a collision takes
place.

In any event, (7.10) implies, after equating coefficients
of powers of the expansion parameters:

$$\lim_{\tau \to \infty} \delta^{r(s)}_{-\tau} f^{0,0}_{s,s}(X_s ; \delta^{(1)}_{+\tau} f_{1,1}) =$$

$$= \lim_{\tau \to \infty} \delta^{r(s)}_{-\tau} [\delta^{(1)}_{+\tau} f_{1,1}(x_1) \prod_{i=1}^{s} \delta^{(1)}_{+\tau} f_{1,1}(x_i)] \qquad \ldots\ldots (7.11a)$$

and

$$\lim_{\tau \to \infty} \delta^{r(s)}_{-\tau} f^{m,n}_{s,s}(X_s ; \delta^{(1)}_{+\tau} f_{1,1}(x_1 ; t)) = 0,$$

$$\text{for m or n} \neq 0 \qquad \ldots\ldots (7.11b)$$

It is now possible to obtain explicit representations
for the $A_{m,n}$ which make up the collision terms in the evolu-
tionary equation for $f_{1,1}$. In Equation (7.9), let $m = n = 0$.
In this case, the equation reads:

$$D_{0,0} f^{0,0}_{s,s}(; f_{1,1}) + [H_s - \theta^r_s] f^{0,0}_{s,s}(; f_{1,1}) = 0$$

$$\ldots\ldots (7.12)$$

However, this equation, which holds for $f_{1,1}$, is equally
valid for $\delta^{(1)}_{+\tau} f_{1,1}$. Noting that,

$$D_{0,0} f^{0,0}_{s,s}(; \delta^{(1)}_{+\tau} f_{1,1}) = (\frac{\delta f^{0,0}_{s,s}}{\delta^{(1)}_{+\tau} f_{1,1}} \cdot \delta^{(1)}_{+\tau} \frac{\partial f_{1,1}}{\partial t}) \frac{\partial f_{1,1}}{\partial t} \vec{A}_{op} \cdot (7.13a)$$

$$= \text{ref.7.5a} = - H_1 \delta^{(1)}_{+\tau} f_{1,1} \frac{\delta f^{0,0}_{s,s}}{\delta^{(1)}_{+\tau} f_{1,1}}$$

so that, because $\delta^{(1)}_{+\tau} = e^{H_1 \tau}$, we can write

$$D_{0,0} f^{0,0}_{s,s}(; \delta^{1}_{+\tau} f_{1,1}) = - \frac{d f^{0,0}_{s,s}}{d\tau}(; \delta^{1}_{+\tau} f_{1,1}) \qquad \ldots\ldots\ldots (7.13b)$$

Equation (7.12) becomes:

$$(d/d\tau - [H_s - \theta_s^r]) f_{s,s}^{o,o}(\;;\mathcal{J}_{+\tau}^1 f_{1,1}) = 0 \quad \ldots\ldots\ldots \quad (7.14)$$

This equation has the formal solution,

$$f_{s,s}^{o,o}(\;;\mathcal{J}_{+\tau}^1 f_{1,1}) = \mathcal{J}_{+\tau}^{r(s)} f_{s,s}^{o,o}(\;;f_{1,1}) \quad \ldots\ldots\ldots \quad (7.15)$$

Multiplying 7.15 by $\mathcal{J}_{-\tau}^{r(s)}$, the equation yields:

$$f_{s,s}^{o,o}(\;;f_{1,1}) = \mathcal{J}_{-\tau}^{r(s)} f_{s,s}^{o,o}(\;;\mathcal{J}_{+\tau}^1 f_{1,1}) \quad \ldots\ldots\ldots \quad (7.15a)$$

Since the left hand side of the above equation does not depend on τ, the right hand side may be evaluated at any value of τ which is convenient. For this purpose, let $\tau \to \infty$ so that in virtue of Equation (7.11a):

$$f_{s,s}^{o,o}(\;;f_{1,1}) = \mathcal{J}_{-\tau}^{r(s)}[\mathcal{J}_{+\tau}^1 f_{1,1}(x_1;t|x_{1_0} \prod_{i=2}^{n} \mathcal{J}_{+\tau}^1 f_{1,1}(x_i)] \quad \ldots(7.16)$$

How about expressions for $f_{s,s}^{0,n}$? From (7.9):

$$D_{o,o} f_{s,s}^{o,n} + [H_s - \theta_s^r] f_{s,s}^{o,n} =$$

$$= -\theta_s^a f_{s,s}^{1,n-1} - \Omega \int d\vec{x}_{s+1} \phi_s^a f_{s+1,s+1}^{o,n-1} - \sum_{q=1}^{\hat{n}} D_{o,q} f_{s,s}^{o,n-q} \quad (7.17)$$

In general, for equations of the form

$$D_{o,o} f_{s,s}^{o,n}(\;;f_{1,1}) + [H_s - \theta_s^r] f_{s,s}^{o,n} = - \psi_s(\;;f_{1,1}) \quad \ldots\ldots (7.18)$$

it is noticed that, upon letting $f_{1,1} \to \mathcal{J}_{+\tau}^1 f_{1,1}$ and by virtue of

$$(\frac{d}{d\tau} - [H_s - \theta_s^r]) f_{s,s}^{o,n}(\;;\mathcal{J}_{+\tau}^{(1)} f_{1,1}) \equiv (\frac{d}{d\tau} - [H_s - \theta_s^r]) \mathcal{J}_{+\tau}^{r(s)} \mathcal{J}_{-\tau}^{r(s)} f_{s,s}^{o,n}(\;;\mathcal{J}_{+\tau}^1 f_{1,1})$$

$$= \mathcal{J}_{+\tau}^{r(s)} \frac{d}{d\tau} [\mathcal{J}_{-\tau}^{r(s)} f_{s,s}^{o,n}(\;; \mathcal{J}_{+\tau}^1 f_{1,1})$$

that (7.18) becomes

$$\lambda_{+\tau}^{r(s)} \frac{d}{d\tau} [\lambda_{-\tau}^{r(s)} f_{s,s}^{o,n}(;\int_{+\tau}^{1} f_{1,1})] = -\psi_s(;\int_{+\tau}^{1} f_{1,1}) \ .$$

This has the solution:

$$\lambda_{-\tau}^{r(s)} f_{s,s}^{o,n}(;\int_{+\tau}^{1} f_{1,1}) = f_{s,s}^{o,n}(;f_{1,1}) - \int_{0}^{\tau} d\tau' \lambda_{-\tau'}^{r(s)} \psi_s(;\int_{+\tau'}^{1} f_{1,1}) \ .$$

Using (7.11b), we obtain finally:

$$f_{s,s}^{o,n}(;f_{1,1}) = + \int_{0}^{\infty} d\tau' \lambda_{-\tau'}^{r(s)} \psi_s(;\int_{+\tau'}^{(l)} f_{1,1}) \qquad \circ\circ\circ\circ\circ\circ \quad (7.19)$$

In this way, Equation (7.17) has the solution:

$$f_{s,s}^{o,n}(;f_{1,1}) =$$

$$= \int_{0}^{\infty} \lambda_{-\tau}^{r(s)} (\sum_{q=1}^{m} D_{0,q} f_{s,s}^{o,n-q}(;\int_{+\tau}^{} f_{1,1}) + \theta^a f_{s,s}^{1,n-1}(;) + \qquad \circ\circ\circ\circ\circ\circ\circ\circ \quad (7.20)$$

$$+ \Omega \int dx_{s+1} \phi_s^a f^{o,n-1}(;\int_{+\tau}^{} f_{1,1})) \ d\tau$$

In particular, for s = 2, n = 1:

$$f_{2,2}^{o,1}(;f_{1,1}) =$$

$$= \int_{0}^{\infty} \lambda_{-\tau}^{r(s)} (D_{01} f_{2,2}^{o,o}(;\int_{+\tau}^{} f_{1,1}) + \theta_s^a f_{2,2}^{1,o} + \Omega \int dx_3 \phi_2^a f_{3,3}^{o,o}(;\int_{+\tau}^{} f_{1,1})) d\tau \qquad \circ\circ\circ\circ\circ\circ\circ\circ \quad (7.20a)$$

Similarly,

$$f_{s,s}^{m,o}(;f_{1,1}) =$$

$$= \int_{0}^{\infty} \lambda_{-\tau}^{r(s)} (\sum_{p=1}^{m} D_{p,o} f_{s,s}^{m-p,o} - \Omega \int dx_{s+1} \phi_s^r f_{s+1,}^{o,o}(;\int_{+\tau}^{} f_{1,1})) \ d\tau \qquad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ\circ \quad (7.21)$$

and, in particular:

$$f_{2,2}^{1,o}(x_1,x_2;f_{1,1}) =$$

$$= \int_{0}^{\infty} \lambda_{-\tau}^{r(s)} (D_{1,0} f_{2,2}^{o,o}(;\int_{+\tau}^{} f_{1,1}) - \Omega \int d\vec{x}_3 \phi_2^r(x_2) f_{3,3}^{o,o}(;\int_{+\tau}^{} f_{1,1})) \ d\tau \qquad (7.21a)$$

Finally, using Equations (7.2), (7.5), (7.20), and (7.21), the kinetic equation can be written as:

$$\frac{\partial f}{\partial t}_{1,1} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_{q_1} f_{1,1} = c\, I_1(\underline{x}_1;t) + c^2 I_2(\underline{x}_1;t) +$$
$$+ o(c^3) + \ldots \ldots \qquad \ldots \ldots \ (7.22)$$

where,

$$I_1(x_1;t) = \Omega \int dx_2 [\phi_1^r(x_2) - \epsilon \phi_1^a(x_2)] \int_{-\infty}^{(2)} \int_{+\infty}^{1,1} f_{1,1}(x_1;t|x_{1_0}) f_{1,1}(x_2)$$

$$\ldots \ldots \ (7.23)$$

$$I_2(x_1;t) = \Omega \int dx_2 [\phi_1^r(x_2) - \epsilon \phi_1^a(x_2)] \times \qquad \ldots \ldots \ (7.24)$$

$$\times \int_0^\infty \int_{-t}^{\tau} \{([D_{1,0} + \epsilon D_{0,1}] f_{2,2} - \Omega \int dx_3 [\phi_2^r - \epsilon \phi_2^a] f_{3,3}^{0,0}(x_3; \int_{+\tau}^{} f_{1,1}) +$$
$$+ \epsilon \theta_2^a f_{2,2}^{1,0}(; \int_{-t}^{} f_{1,1})\} \, d\tau$$

It is clear how one would proceed were he interested in obtaining higher order terms.

Equation (7.22) might now be solved for $f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0})$. Of course, these may be illusory hopes, for it is noticed that successively higher order collision integrals contain within them solutions to many-body mechanical problems of correspondingly higher order. The latter, themselves, have unfortunately never been solved except in the most trivial cases. Truly, this is a serious limitation to the scheme, and it is one reason why the methods used earlier in this dissertation have been preferred.

However, let us extend this investigation in preparation for work which follows in the next chapter. Suppose, now, that instead of focussing attention, initially, on only one particle, we specify the initial positions in phase space of two of the particles. In this case, the proper form of the BBGKY hierarchy is not (7.4), but rather (see App. F):

$$\frac{\partial f}{\partial t}_{1,1}(x_1;t|x_{1_o},x_{2_o}) + H_1(x_1)\, f_{1,1}(x_1;t|\;) =$$

$$\cdots\cdots \quad (7.25a)$$

$$= \int dx_2 [\Phi_{1,2}^r - \epsilon\Phi_{1,2}^a] f_{2,2}(x_1,x_2;t|x_{1_o},x_{2_o}) +$$

$$+(n-2) \int dx_3 [\Phi_{1,3}^r - \epsilon\Phi_{1,3}^a] f_{2,2}(x_1,x_3;t|)$$

$$\frac{\partial f}{\partial t}_{1,1}(x_2;t|x_{1_o},x_{2_o}) + H_1(x_2)\, f_{1,1}(x_2;t|\;) = \quad\cdots\cdots \quad (7.25b)$$

$$= \int dx_1 [\Phi_{1,2}^r - \epsilon\Phi_{1,2}^a] f_{2,2}(x_1,x_2;t|x_{1_o},x_{2_o}) +$$

$$+(n-2) \int dx_3 [\Phi_{2,3}^r - \epsilon\Phi_{2,3}^a] f_{2,2}(x_2,x_3;t|)$$

$$\frac{\partial f}{\partial t}_{s,s} + [\,H_s - \theta_s^r\,] f_{s,s} = \quad\quad\quad (7.25c)$$

$$\cdots\cdots\cdots\cdots$$

$$= -\epsilon\theta_s^a f_{s,s} + (n-s) \int dx_{s+1} [\Phi_s^r - \epsilon\Phi_s^a]\, f_{s+1,s+1}$$

$$(s \geq 2;\; (1,2)\epsilon\{s\}\,) \quad\quad .$$

Now, let us make the assumption, analogous to (7.3),

that $f_{s,s}(X_s;\; t|\underline{x}_{1_o},\underline{x}_{2_o})$ is not an explicit function of the

time; rather, is functionally dependent on <u>both</u>

$f_{1,1}(\underline{x}_1;\; t|\underline{x}_{1_o},\underline{x}_{2_o})$ and $f_{1,1}(x_2;\; t|x_{1_o},x_{2_o})$ and changes

with time as the latter change.[**] Thus, one performs an

expansion:

$$f_{s,s}(X_s;t|x_1,x_2) = \quad\quad\quad \circ\circ\circ\circ\circ\circ\circ\circ\circ\circ \quad (7.26)$$

$$= \sum_{m=0}^{\infty}\sum_{n=0}^{\infty} c^m(\epsilon c)^n\, f_{s,s}^{m,n}(X_s;\; f_{1,1}(x_1),\, f_{1,1}(x_2)\,)$$

[**] ...but, we do not assume explicit dependence upon a two
particle density. As such, this assumption might be re-
garded as a "superposition approximation."

Also assume:

$$\frac{\partial f}{\partial t}_{1,1}(\underline{x}_1; t|\underline{x}_{1_o}, \underline{x}_{2_o}) = \sum_0^\infty \sum_0^\infty c^m(\epsilon c)^n A_{m,n}(\underline{x}_1; f_1(\underline{x}_1)) \ldots \quad (7.27a)$$

$$\frac{\partial f}{\partial t}_{1,1}(\underline{x}_2; t|\underline{x}_{1_o}, \underline{x}_{2_o}) = \sum_0^\infty \sum_0^\infty c^m(\epsilon c)^n A_{m,n}(\underline{x}_2; f_1(\underline{x}_2)) \ldots \quad (7.27b)$$

Inserting (7.27a) into (7.25a) and equating coefficients of expansion parameters, one obtains exactly the same set of functions for the $A_{m,n}(\underline{x}_1; f_{1,1}(\underline{x}_1)$ as obtained previously (Eq. (7.5), above).[**] Also, from (7.27b) and (7.25b), a similar set is obtained for $A(\underline{x}_2; f_{1,1}(\underline{x}_2))$.

Continuing as before, one obtains the same equations as (7.8) and (7.9), _except that_, now, $D_{m,n}$ must be interpreted as follows:

$$D_{m,n} = [\frac{\delta}{\delta f_{1,1}(x_1)} \circ \frac{\partial f}{\partial t}_{1,1}(x_1) + \frac{\delta}{\delta f_{1,1}(x_2)} \circ \frac{\partial f}{\partial t}_{1,1}(x_2)] \quad \ldots \ldots (7.28)$$

with: $\frac{\partial f}{\partial t}_{1,1}(x_1) \rightarrow A_{m,n}(x_1); \frac{\partial f}{\partial t}_{1,1}(x_2) \rightarrow A_{m,n}(x_2)$

The boundary conditions (7.10) and (7.11) are unchanged. Similarly, with minor modification, Eq. (7.15a, 7.20, 7.21) follow, except that one must keep in mind the new definition of $D_{m,n}$. For illustration, let us now write down some explicit terms of the expansion for $f_{2,2}$. Immediately, one obtains:

$$f_{2,2}^{0,0}(\underline{x}_1, \underline{x}_2; t|\underline{x}_{1_o}, \underline{x}_{2_o}) =$$

$$= \int_{-\infty}^{(2)}(\underline{x}_1, \underline{x}_2) \int_{+\infty}^{(1)}(\underline{x}_1) \int_{+\infty}^{(1)}(\underline{x}_2) f_{1,1}(\underline{x}_1; t|x_{2_o}) f_{1,1}(\underline{x}_2; t|x_{2_o}) \ldots (7.29)$$

_____

[**] However, to do so, one neglects the first integrals occurring on the right hand sides of Equations (7.25a,b) as compared with the second.

To obtain the terms providing the first order density correction we must calculate $f_{2,2}^{1,0} + f_{2,2}^{0,1}$, as provided by (7.20a) and (7.21a). To this end, consider

$$[D_{1,0} + \varepsilon D_{0,1}] \, f_{2,2}^{0,0}(x_2; \int_{+\tau}^1 f_{1,1}(x_1), \int_{+\tau}^1 f_{1,1}(x_2)) =$$

$$= \left[\frac{\delta f_{2,2}^{0,0}}{\delta \int_{+\tau} f_{1,1}(x_1)}(; \int_{+\tau}^1 f_{1,1}(x_1), \int_{+\tau}^1 f_{1,1}(x_2)) \circ \frac{\partial \int_{+\tau} f_{1,1}(x_1)}{\partial t} \right.$$

$$\left. + \frac{\delta f_{2,2}^{0,0}}{\delta \int_{+\tau} f_{1,1}(x_1)}(;\dots) \circ \frac{\partial \int_{+\tau} f_{1,1}(x_2)}{\partial t} \right] \qquad \dots\dots (7.30)$$

$$\frac{\partial \int_{+\tau} f_{1,1}(x_1)}{\partial t} \to A_{1,0}(x_1; \int_{+\tau} f_{1,1}(x_1)) +$$

But,
$$\qquad\qquad + \varepsilon A_{0,1}$$

$$\frac{\partial \int_{+\tau} f_{1,1}(x_2)}{\partial t} \to A_{1,0}(x_2,\dots) + \varepsilon A_{0,1}$$

$$f_{2,2}^{0,0}(; \int_{+\tau} f_{1,1}(x_1), \int_{+\tau} f_{1,1}(x_2)) = \int_{-\infty}^{r(2)}(x_1,x_2)\int_{+\infty}^{1}\int_{+\tau}^1 f_{1,1}(x_1) f_{1,1}(x_2)$$

$$= f_{1,1}(([\int_{-\infty}^{r(2)}(x_1,x_2)\int_{+\infty}^1(x_1)]\int_{+\tau}^1(x_1)) \, \underline{x}_1; t|x_{1_0}, x_{2_0}) \times$$

$$\times f_{1,1}(([\int_{-\infty}^{r(2)}(x_1,x_2)\int_{+\infty}^1(x_2)]\int_{+\tau}^1(x_2)) \, \underline{x}_2; t|x_{1_0}, x_{2_0}) \dots (7.31)$$

Thus, by (E.4b) and (E.4c) of Appendix E:

$$\dots\dots (7.32)$$

$$\frac{\delta f_{2,2}^{0,0}}{\delta \int_{+\tau} f_{1,1}(x_1)}(; \int_{+\tau}^1 f_{1,1}(x_1) \int_{+\tau}^1 f_{1,1}(x_2)) = \delta^6(\vec{z}_1 - \vec{x}_1)\int_{+\tau}^1(x_2) f_{1,1}(\vec{z}_2; t|x_{2_0})$$

where

$$\vec{z}_1 \equiv [\int_{-\infty}^{r(2)}(x_1,x_2)\int_{+\infty}^1(x_1)] \, \vec{x}_1$$

$$\vec{z}_2 \equiv [\int_{-\infty}^{r(2)}(x_1,x_2)\int_{+\infty}^1(x_2)] \, \vec{x}_2 \qquad \dots\dots (7.33).$$

Thus, (7.30) becomes:

$$[D_{1,0} + \varepsilon D_{0,1}] f_{2,2}^{0,0}(; \mathcal{S}_{+\tau} f_{1,1} \quad \dots) =$$

$$= \left(\Omega\delta(\vec{Z}_1 - \vec{x}_1) \mathcal{S}_{+\tau}^{1} f_{1,1}(\vec{Z}_2; t | X_{2_0}) \times \right.$$

$$\times \mathcal{S}_{+\tau}^{1}(x_1) \int dx_3 [\Phi_1^r(x_1, x_3) - \varepsilon\Phi_1^a] f_{2,2}^{0,0}(x_1, x_3; f_{1,1}(x_1)..)\Big\} +$$

$$+\left(\Omega\delta(\vec{Z}_2 - \vec{x}_2) \mathcal{S}_{+\tau}^{1} f_{1,1}(\vec{Z}_1; t | X_{2_0}) \times \right.$$

$$\times \mathcal{S}_{+\tau}^{1}(x_2) \int dx_3 [\Phi_1^r(x_2, x_3) - \varepsilon\Phi_1^a] f_{2,2}^{0,0}(x_2, x_3; f_{1,1}(x_1)..)\Big)$$

$$\circ\circ\circ\circ\circ\circ\circ\circ\circ \qquad (7.34)$$

Proceeding in a similar way in the calculation of the other terms appearing in (7.24), it is found that the density correction of first order is given by:

$$f_{2,2}^{1,0}(X_2; f_{1,1}(x_1)\circ\circ\circ) + \varepsilon f_{2,2}^{0,1}(X_2, \dots) =$$

$$\circ\circ\circ\circ\circ \qquad (7.35)$$

$$= \Omega \int_0^\infty \mathcal{S}_{-\tau}^{r(2)} \mathcal{S}_{+\tau}^{1}(x_1) \mathcal{S}_{+\tau}^{1}(x_2) \times$$

$$\times \left\{ \left[\delta(\vec{Z}_1 - \vec{x}_1) f_{1,1}(\vec{Z}_2; t | X_{2_0}) \int dx_3 [\Phi_1^{r+a}(x_1, x_3)] f_{2,2}^{0,0}(x_1, x_3; f_{1,1}\circ\circ) + \right. \right.$$

$$+\delta(\vec{Z}_2 - \vec{x}_2) f_{1,1}(\vec{Z}_1; t | X_{2_0}) \int dx_3 [\Phi_1^{r+a}(x_2, x_3)] f_{2,2}^{0,0}(x_2, x_3; f_{1,1}\circ\circ) -$$

$$-\Omega\int dx_3 [\Phi_2^{r+a}(x_1, x_2, x_3) f_{3,3}^{0,0}(x_1, x_2, x_3; f_{1,1}(x_1), f_{1,1}(x_2))] \right] +$$

$$+\left[\varepsilon\Phi_1^a(x_1, x_2) \int_0^\infty \mathcal{S}_{-\tau'}^{r(2)} \mathcal{S}_{+\tau'}^{1,1} \left\{ \delta(\vec{Z}_1 - \vec{x}_1) f_{1,1}(\vec{Z}_2; t | X_{2_0}) \circ\circ\circ \right. \right.$$

$$\circ\circ\text{etc.} \text{ Same as above, only with } \Phi_1^{r+a} \text{ and } \Phi_2^{r+a}$$
$$\text{replaced by } \Phi_1^r \text{ and } \Phi_2^r, \text{respectively.} \quad \left. \left. \right\} d\tau' \right\} d\tau.$$

It is interesting to note that upon assuming that particles move independently of each other, (7.35) is identically zero.

Thus, according to the approximations already described, a density expansion of $f_{2,2}(\underline{x}_1, \underline{x}_2; t \vert \underline{x}_{1_0}, \underline{x}_{2_0})$ is provided by

$$f_{2,2}(X_2; t \vert X_{2_0}) = f_{2,2}^{[0]} + c\, f_{2,2}^{[1]} + o(c^2) \ldots\ldots \qquad (7.36)$$

with $f_{2,2}$ and $f_{1,2}$ given by (7.29) and (7.35), respectively. Clearly, however, things are quite labyrinthine. But, some useful information is obtained from this work; further reference to these equations is made at the end of the next chapter.

CHAPTER VIII

CALCULATIONS OF G_d (r,t)

In the preceding chapters, primary interest has been the derivation and solution of equations providing the evolution of the one particle conditional density, $f_{1,1}(\underline{x}_1; t|\underline{x}_{1_0})$. Unfortunately, it has been seen that the required analysis is discouragingly complicated.

Yet, even greater complication is involved in the calculation of a two particle density, $f_{2,2}$ $(\underline{x}_1,\underline{x}_2;t|\underline{x}_{1_0},\underline{x}_{2_0})$. Properly, one would start with Equation (3.23), with s = 2:

$$\frac{\partial f}{\partial t}_{2,2}(X_2;t|X_{2_0}) + (\frac{\vec{p}}{m}_1 \circ \vec{\nabla}_{q_1} + \frac{\vec{p}}{m}_2 \circ \vec{\nabla}_{q_2} + \vec{\nabla}_{q_1}\phi_{12} \circ (\vec{\nabla}_{p_1} - \vec{\nabla}_{p_2})) f_{2,2} =$$

$$= \otimes_2 \int_0^t d\tau\, L\, e^{\tau(1-\otimes_2)L_2} (1-\otimes_2)Lf_{n|1}(0)f_{2,2}(t-\tau) \quad\quad \ldots\ldots (8.1)$$

The collision integral would be expanded using methods similar to those used in Chapter 4; iteration solutions would be subsequently obtained as has been done in Chapter 5.

In this way, the zero'th term in the expansion would be taken as the solution of

$$(\partial/\partial t + \sum_{i=1}^{2}\frac{\vec{p}_i}{m}\vec{\nabla}_{q_i} + \vec{\nabla}_{q_1}\phi_{12}\circ(\vec{\nabla}_{p_1}-\vec{\nabla}_{p_2})) f_{2,2}^{[0]}(X_2;t|X_{2_0}) = 0 \quad\quad \ldots\ldots (8.2)$$

with

$$f_{2,2}^{[0]}(X_2;0|X_{2_0}) = \delta(\vec{x}_1-\vec{x}_{1_0})\, \delta(\vec{x}_2-\vec{x}_{2_0})\, .$$

i.e., to zero'th order, one considers two particles to be moving independently of the other particles of the assembly; however, they are influenced by their mutual force field.

Thus, the first step in the program would be the solution of (8.2). But, difficulties are immediately apparent because, in general, such solution remains unknown.

Suppose, however, we wish to calculate $G_d(r,t)$, defined by[**]:

$$G_d(r,t) \equiv$$
$$\equiv c \int dp_{1_0} dp_{2_0} dp_1 dp_2 dq_{1_0} dq_{2_0} \; g_2(q_{1_0}, q_{2_0}) \; \frac{e^{-\frac{\beta}{2m}(p_{1_0}^2 + p_{2_0}^2)}}{(2\pi m kT)^3} \; f_{2,2}(X_2; t \mid X_{2_0}) \qquad \ldots\ldots (8.3)$$

where $g_2(\underline{q}_{1_0}, \underline{q}_{2_0})$ is defined as in Equation (4.19). In this case it is not unreasonable to resort to a form of 'superposition' approximation, viz., assume

$$f_{2,2}(X_2; t \mid X_{2_0}) \doteq f_{1,1}(\underline{x}_1; t \mid \underline{x}_{1_0}) \, f_{1,1}(\underline{x}_2; t \mid \underline{x}_{2_0}) \qquad \ldots\ldots (8.4)$$

At least for short times, it is to be expected that $G_d(r,t)$ will not be much affected by such a simplification; close orbits, i.e., those for which (8.4) is <u>not</u> a good approximation, contribute relatively little to the calculation of (8.3) because of the presence of the weighting factor, $g_2(\underline{q}_{1_0}, \underline{q}_{2_0})$, appearing in the integral.

Hence, by (5.8), (5.13) and (8.4):

$$f_{2,2}(X_2; t \mid X_{2_0}) \doteq \Big\{ \; \delta^{q_1}(t) \delta^{q_2}(t) \delta^{p_1} \delta^{p_2} + \qquad \ldots\ldots (8.5)$$

$$+ \frac{ct^2}{2} \eta^{(2)} \Big(\delta^{q'} \delta^{q_\lambda} (\nabla_{p_l}^2 + \nabla_{p_\lambda}^2) \delta^{p_\iota} \delta^{p_\lambda} - \frac{t}{m}(\vec{\nabla}_{q_l} \delta^{q'} \cdot \vec{\nabla}_{p_\iota} \delta^{p_\iota} \delta^{q_\lambda} \delta^{p_\lambda} + \vec{\nabla}_{q_\lambda} \delta^{q_\lambda} \cdot \vec{\nabla}_{p_\lambda} \delta^{p_\lambda} \delta^{q'} \delta^{p_\iota}) + \frac{t^2}{4m^2} \delta^{p_l} \delta^{p_\lambda} (\nabla_{q_l}^2 + \nabla_{q_\lambda}^2) \delta^{q'} \delta^{q_\lambda} \Big)$$

$$+ \frac{ct^2}{2} \chi^{(2)} \Big(6\delta^{q'} \delta^{p'} \delta^{q_\lambda} \delta^{p_\lambda} - \frac{2t}{3m}(\delta^{p'} \vec{p}_{\iota} \vec{\nabla}_{q_l} \delta^{q'} \delta^{p'} \delta^{q_\lambda} + \delta^{p_\lambda} \vec{p}_{\lambda} \vec{\nabla}_{q_\lambda} \delta^{q_\lambda} \delta^{p'} \delta^{q'} + \delta^{q'} \delta^{q_\lambda} (\vec{p}_l \vec{\nabla}_{p_l} + \vec{p}_\lambda \vec{\nabla}_{p_\lambda})) \delta^{p'} \delta^{p_\lambda} \Big)$$

$$+ \text{ terms } o(\epsilon^4) \; \ldots\ldots \Big\}$$

[**]Cf. Chapter 2, above.

Consider, e.g., the zero'th term of G_d, defined by:

$$G_d^{[0]}(r,t) \equiv c \int dp_{1_o} dp_{2_o} dx_1 dp_2 dq_{2_o} g_2(q_{1_o}, q_{2_o}) \frac{e^{-\frac{\beta(p_{1_o}^2 + p_{2_o}^2)}{2m}}}{(2\pi mkT)^3} \delta q_1(t) \delta q_2(t) \delta p_1 \delta p_2$$

$$= c \int dq_{2_o} g_2(q_{1_o}, q_{2_o}) [\frac{m\beta}{2\pi t^2}]^{3/2} e^{-m\beta(q_{2_o} - q_2)^2/2t^2} \quad \ldots \ldots (8.6)$$

But, as before, notice that $[\frac{m\beta}{2\pi t}2]^{3/2} e^{-\frac{m\beta r^2}{2t^2}} = e^{\frac{t^2 \nabla^2}{2m\beta} r} \delta(r)$

Thus,

$$G_d^{[0]}(r,t) = c \int dq_{2_o} g_2(q_{1_o}, q_{2_o}) e^{-(t^2/2m\beta)\nabla_r^2} \delta(\vec{q}_{2_o} - \vec{q}_2)$$

$$= c e^{-(t^2/2m\beta)\nabla_{q_2}^2} g_2(q_{1_o}, q_2) = \quad \ldots \ldots (8.6')$$

$$= c e^{-(t^2/2m\beta)\nabla_r^2} g_2(r) \quad .$$

Next, consider

$$G_d^{[1]}(r,t) \equiv c^2 \frac{t^2}{2} \int dp_{1_o} dp_{2_o} dx_1 dp_2 dq_{2_o} \frac{e^{-\frac{\beta(p_{1_o}^2 + p_{2_o}^2)}{2m}}}{(2\pi mkT)^3} g_2(q_{1_o}, q_{2_o}) \times$$

$$\times \{ \eta^{(2)} [\delta q_1(t) \delta q_2(t) (\nabla_{p_1}^2 + \nabla_{p_2}^2) \delta p_1 \delta p_2 - $$

$$- \ldots \ldots \ldots \ldots \ldots] +$$

$$+ \frac{x}{m}^{(2)} [6\delta p_1 \delta q_1(t) \delta p_2 \delta q_2(t) - \ldots \ldots \ldots] \}$$

(see eqn. 8.5, above, for detail)

$$\ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8.7)$$

Integrate by parts re. $\underline{p}_1$ and $\underline{p}_2$ to obtain:

[1]
$$G_d(r,t) = \frac{c^2 t^2}{2} \int dq_{2_0} dq_1 dp_{2_0} dp_{1_0} \frac{e^{-\beta(p_{1_0}^2 + p_{2_0}^2)/2m}}{(2\pi mkT)^3} g_2(q_{1_0}, q_{2_0}) \times$$

$$\times [\frac{n^{(2)}}{4}(\nabla^2_{p_{1_0}} + \nabla^2_{p_{2_0}}) - \frac{\chi^{(2)}}{3m}(\vec{p}_{1_0} \vec{\nabla}_{p_{1_0}} + \vec{p}_{2_0} \vec{\nabla}_{p_{2_0}})] \delta^{q_1}(t) \delta^{q_2}(t)$$

$$= \frac{c^2 t^2}{2} \int dq_{2_0} dq_1 dp_{2_0} dp_{1_0} \frac{e^{-\beta(p_{1_0}^2 + p_{2_0}^2)/2m}}{(2\pi mkT)^3} g_2(q_{1_0}, q_{2_0}) \times$$

$$\times [\frac{n^{(2)}}{4m} - \frac{\chi^{(2)}}{3m}] \cdot [\beta(p_{1_0}^2 + p_{2_0}^2)/m - 6] \delta^{q_1}(t) \delta^{q_2}(t)$$

Further reduction yields,

[1]
$$G_d(r,t) = \frac{c^2 t^4}{2m^2} [\frac{n^{(2)}}{4} - \frac{\chi^{(2)}}{3\beta}] \int dq_{2_0} dq_1 g_2(q_{1_0}, q_{2_0})(\nabla^2_{q_1} + \nabla^2_{q_2}) \times$$

$$\times G_s^{[0]}(q_1 - q_{1_0}, t) G_s^{[0]}(q_2 - q_{2_0}, t)$$

But $\int dq_1 \nabla^2_{q_1} G_s^{[0]}(q_1 - q_{1_0})$ yields zero boundary terms; thus,

[1]
$$G_d(r,t) = \frac{c^2 t^4}{2m^2} [\frac{n^{(2)}}{4} - \frac{\chi^{(2)}}{3\beta}] \nabla^2_r e^{(t^2/2m\beta) \nabla^2_r} g_2(r) \quad \ldots \ldots \quad (8.7')$$

Hence, at least for the first two terms,

[1]
$$G_d(r,t) = c \sum_{n=0}^{\infty} t^{2n} D_R^{[n]} e^{+\nabla^2_R} g_2(\vec{R}t/(m\beta)^{1/2}) \quad \ldots \ldots \quad (8.8)$$

where the $D_R^{[n]}$ are identical to those defined previously in

the study of G_s (cf., Eq. (6.18). In fact, because

$\int d\vec{q}_1 (\vec{\nabla}_{q_1})^j G_s^{[0]}(\vec{q}_1 - \vec{q}_{1_0}) = 0$ for all $j \geq 1$, upon reflection it is

seen that (8.8) is true for all terms in the series.

Thus, re-writing (6.18) and combining with (8.8), the following result is obtained for the complete $G(r,t)$:

$$G^{cl \cdot}(r,t) = \sum_{n=0}^{\infty} t^{2n} D_R^{[n]} e^{+\nabla_R^2} G^{cl \cdot}(\frac{Rt}{[m\beta]}1/2; 0) \quad \ldots \ldots \quad (8.9)$$

where
$$G(r,0) = \delta(r) + c\, g_2(r) \quad \ldots \ldots \ldots \ldots \quad (8.10)$$

The expression given by (8.9) is formally identical to Vineyard's " convolution approximation."[10] Thus, it is seen that the basis for the latter is to be found in the assumption of superposition, (8.4).

One may now calculate the coherent scattering function. A calculation similar to the one leading to (6.22) provides:

$$S_{coh \cdot}^{cl \cdot}(k,\omega) = \sqrt{\frac{m\beta}{2\pi k^2}} e^{-m\beta\omega^2/2k^2} [\, 1 + c\, \tilde{g}_2(k,\omega)\,] \times$$

$$\times [\, 1+\frac{c\beta}{2k^2}(3-10m\beta\omega^2+m^2\beta^2\omega^4)][\, \frac{\beta\eta^{(2)}}{4} - \frac{\chi^{(2)}}{3}] +o(\epsilon^4)\ldots] \quad (8.11)$$

Hence, a propos the discussion on p. 6-13 concerning the measurement of system constants, it is now apparent how a proper measurement of the scattering cross sections will provide the desired information. For fixed momentum and energy transfer:

$$\frac{d^2\sigma}{d\Omega dE} \sim [\, \sigma_{coh}\, S_{coh}(k,\omega) + \sigma_{inc}\, S_{inc}(k,\omega)\,]$$
$$\quad \circ\circ\circ\circ\circ \quad (8.12)$$

$$\sim \sqrt{\frac{m\beta}{2\pi k^2}} \; e^{-m\beta\omega^2/2k^2} \quad [\; a_{coh}^2(\; 1+c\tilde{g}_2(k,\omega) \;) + a_{inc.}^2 \;] \times$$

$$\times [\; 1 + \frac{c\beta}{2k^2}(3-10m\beta\omega^2+ \frac{m^2\beta^2\omega^4}{k^2})(\frac{\beta\eta^{(2)}}{4} - \frac{\chi^{(2)}}{3}) \; + \; \ldots \;]$$

$\tilde{g}_2(k,\omega)$ is the Fourier transform of $g_2(r)$, and can be determined from x-ray scattering data.[45,46,47]

Of course, (8.12) is incomplete in that quantum effects are not included. Unfortunately, the counterpart of Rosenbaum's analysis[43] for the incoherent scattering function is not available and the quantum corrections to the coherent scattering function are uncertain. It has been suggested[**] that the basic correction is that previously noted, viz.,

$$S(k,\omega)= e^{\beta\hbar\omega/2} \; e^{-\beta\hbar^2 k^2/8m} \quad [\; S^{cl.}(k,\omega) + o(\hbar^2) +_{.\,.}] \quad \ldots \; (8.13)$$

However, a term by term analysis for $S_{coh.}$ is not available (see (6.23) and ff.). But, it is suspected that, as before, for small momentum and energy changes, quantum effects are small when compared with contributions to the scattering functions due to forces between particles.

Can anything more be said about the approximation made in determining $G_d(r,t)$, i.e., about the 'superposition approximation', (8.4)? Let us, for the moment, refer to the

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[**] Singwi, K.S., and Sjolander, A.[11]

zero'th term in the density expansion obtained in the pre-

vious chapter:

$$\cdots\cdots (7.29)$$

$$f_{2,2}(X_2;t|X_{2_0}) = \int_{-\infty}^{r(2)}(\underline{x}_1,\underline{x}_2) \int_{+\infty}^{1}(\underline{x}_1) \int_{+\infty}^{1}(\underline{x}_2) \ f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0}) f_{1,1}(\underline{x}_2;|\underline{x}_{2_0})$$

The action of the kinetic operators is made clear if one

notes that, acting upon any arbitrary function of X_s:

$$\int_{+\tau}^{1}(x_1) \ \cdots\cdots \int_{+\tau}^{1}(x_s) \ F(X_s;t) = \qquad \cdots\cdots (8.14)$$

$$= F(\vec{q}_1 + \frac{\vec{p}}{m}_1\tau,\vec{p}_1; \ \cdots\cdots ;\vec{q}_s + \frac{\vec{p}}{m}_s\tau,\vec{p}_s;t)$$

Hence,

$$\int_{-\tau}^{r(s)}(X_s) \int_{+\tau}^{1}(x_1) \ \cdots\cdots \int_{+\tau}^{1}(x_s) \ F(X_s;t) =$$

$$\cdots\cdots\cdots (8.15)$$

$$= F(\int_{-\tau}^{(s)}\vec{q}_1 + \frac{\tau}{m}\int_{-\tau}^{(s)}\vec{p}_1, \int_{-\tau}^{(s)}\vec{p}_1; \cdots\cdots; \int_{-\tau}^{(s)}\vec{q}_s + \frac{\tau}{m}\int_{-\tau}^{(s)}\vec{p}_s, \int_{-\tau}^{(s)}\vec{p}_s;t)$$

Note that $\vec{P}_i^{(s)}(X_s) \equiv \lim_{\tau\to\infty} \int_{-\tau}^{(s)}\vec{p}_i$ is the momentum which

the ith particle has before the occurrence of the inter-

action which results in the configuration $\{X_s\}$ at time t.

In other words, $\vec{P}_i^{(s)}(X_s)$ is the constant momentum which the

i^{th} particle has when it is infinitely far removed from the

other particles before collision; it is compatible with the

state X_s at t, which is obtained through the reduced s-body

mechanical interaction.

Similarly, $\vec{Q}_i^{(s)}(X_s) \equiv \lim_{\tau\to\infty}(\int_{-\tau}^{(s)}\vec{q}_i + \frac{\tau}{m}\int_{-\tau}^{(s)}\vec{p}_i)$ is the position at

which the ith particle would have been found at time t if

it had proceeded from infinity with momentum $\vec{P}_i^{(s)}(X_s)$ but

that as a result of the s-body interaction it is at $\underline{q}_i$,

instead.

Referring to the two particle density described by
(7.36), for almost all pairs of particles: $\vec{Q}_1(X_2) = \vec{q}_1$; $\vec{P}_1(X_2) = \vec{p}_2$; $\vec{Q}_2(X_2) = \vec{q}_2$; and, $\vec{P}_2(X_2) = \vec{p}_2$. When this is the case, terms in the density expansion of order higher than the zero'th are zero. Thus, for most pairs,

$$f_{2,2}(X_2;t|X_{2_0}) = f_{1,1}(\underline{x}_1;t|\underline{x}_{1_0})\, f_{1,1}(\underline{x}_2;t|\underline{x}_{2_0}) .$$

CHAPTER IX
SUMMARY AND COMMENTARY

The main object of this thesis has been the calculation of time-relaxed probability densities and associated correlation functions for particles moving through an equilibrium assembly of like particles.

First, an integro-differential equation (3.18) describing the temporal evolution of the probability densities was obtained from the Liouville equation. The equation is generally valid for large systems, providing there are no external fields acting on the assembly. It was assumed that the interaction between particles can be represented by additive central force potentials, and that the equilibrium probability density for the total assembly is a canonical distribution. No other assumptions were required for the derivation of the kinetic equation. In contrast to the BBGKY hierarchy, the derived equation contains all the information necessary for its solution; i.e., the kinetic equation for a reduced probability density does not contain integrals over unknown higher order densities.

Particular attention was given the kinetic equation for the one-particle density. By manipulating the collision integral appearing in that equation, the latter was put in the form

$$\frac{\partial f}{\partial t}_{1,1}(\underline{x}_1;t|\underline{x}_{1_0}) + \frac{\vec{p}_1}{m}\vec{\nabla}_{q_1} f_{1,1} = \sum_{j=0}^{\infty} \mathcal{A}^{[j]} = I \qquad \ldots\ldots (9.1)$$

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where the $\mathcal{A}^{[j]}$ successively demonstrate higher order perturbations to the evolution of $f_{1,1}$ due to the internal potential energy of the assembly. These terms may be written, figuratively, in the following functional form:

$$I = \sum_{k=1}^{\infty} \mathcal{M}_{[2k]} \int_0^t d\tau \, \frac{\tau^{(2k-2)}}{(2k-2)!} \, Op^{[k]} (p_1 ; \vec{v}_{p_1} ; \frac{\tau}{m} \vec{v}_{q_1}) \left\{ -\tau f_{1,1}^{(t-\tau)} \right\} \ldots (9.2)$$

It is apparent that the collision integral contains a "memory", i.e., it is necessary to integrate over the past history of $f_{1,1}$. $\mathcal{S}_{-\tau}$ is the streaming operator; $Op^{[k]} (p_1 ; \vec{v}_{p_1} ; \frac{\tau}{m} \vec{v}_{q_1})$ are mixed differential operators in p_1 and q_1. The constants $\mathcal{M}_{[2k]}$ are of the form:

$$\mathcal{M}_{[2k]} \sim \int d\xi_2 \ldots d\xi_{2k} \, g_{2k}(\xi_2 , \ldots , \xi_{2k}) \left(\frac{\partial^{m_{k,1}} \phi(\xi_2)}{\partial \xi^{m_{k,1}}_2} \ldots \ldots \frac{\partial^{m_{k,f}} \phi(\xi_{2k})}{\partial \xi^{m_{k,f}}_{2k}} \right) (9.3)$$ **

where ϕ is the interparticle potential and $g_{2k}(\xi_2 , \ldots , \xi_{2k})$ is related to the 2k-particle equilibrium correlation function (see 4.18, and 4.19).

It is noticed that these constants are equilibrium constants, i.e., derivatives of interparticle potentials averaged over equilibrium static correlation functions. Regarding spatial integration over interparticle potentials, there is no need to introduce any arbitrary cut-off procedures into this analysis. At small interparticle distances, $g_{2k}(\xi_2 , \ldots , \xi_{2k})$ decreases to zero faster than do the derivatives of the potentials diverge. On the other hand,

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** ....with the condition, $\sum_{j=1}^{k} \sum_{i=1}^{f} m_{j,i} = 2k$.

although for large values of ($\xi_2, \ldots, \xi_{2k}$), $g_{2k} \to 1$,
the derivatives of the potential fall off to zero fast
enough for the integral to converge. The latter is true
even for potentials of the form $\phi(\rho) \sim 1/\rho$, because we are
integrating over derivatives of the potential rather than
the potential itself (cf. 9.3).[**]

Collision integral terms through the "fourth power
of the forces" have been obtained explicitly.

The kinetic equation has been solved by an iteration
procedure:

$$f_{1,1} = f_{1,1}^{[0]} + f_{1,1}^{[1]} + f_{1,1}^{[2]} + o(\epsilon^6)$$

$$\ldots\ldots \quad (9.4)$$

where $f_{1,1}^{[0]}$ would be the only term in the expansion were
the system an ideal gas. $f_{1,1}^{[1]}$ is a first correction to
account for the presence of forces between particles and is
proportional to system constants of the type $\mathcal{M}_{[2]}$ (cf. 9.3);
$f_{1,1}^{[2]}$ is a second correction and is proportional to system
constants of the type $\mathcal{M}_{[4]}$; etc.

The time-relaxed momentum density is obtained from
the full density, (9.4), by integrating over spatial coordi-
nates. Some related correlation functions are also investi-
gated. Most interesting, however, is the demonstration by
an explicit example that calculations based upon a truncated
kinetic equation (i.e., an equation similar to (9.1), but
one which contains only a finite set of $\mathcal{J}^{[j]}$) will be

[**]For $\phi(\rho) \sim 1/\rho$, $\chi^{(2)} \equiv 0$.

incorrect if carried to an order of expansion parameters

(the $\mathcal{M}_{[2k]}$) greater than the order of the approximation

made for the collision integral.

The latter would be a trite observation were it not

that much effort is expended on the solution of kinetic

equations which are similarly only approximations. Both

the Boltzmann gas equation and the Vlasov equation are of

the latter category. [3,21]   There is undoubtedly some

point to investigating whether intrinsic limitations exist

regarding the information to be obtained from solution

of such equations.

Like the momentum density, an expansion for $G_s(r,t)$

is found in direct correspondence with the expansion ob-

tained for $f_{1,1}$ $(\underline{x}_1;t|\underline{x}_{1_0})$. As a consequence of the prior

ordering of the terms appearing in $f_{1,1}$, $G_s(r,t)$ is ex-

pressed as a series of terms which are successively less

important at high temperatures. The expansion for the

latter may be written as:

$$G_s(r,t) = \sum_{n=0}^{\infty} a_n \, t^{2n} \, D_R^{[n]} \, G_s^{[0]}(R,t) \qquad \circ\circ\circ\circ\circ\circ\circ \qquad (9.5)$$

or, alternatively,

$$G_s(r,t) = \sum_{n=0}^{\infty} a_n \, t^{2n} \, D_R^{[n]} \, e^{+\frac{1}{2} \nabla_R^2} \, \delta(R) \qquad \circ\circ\circ\circ\circ\circ\circ \qquad (9.5')$$

where $\vec{R} \equiv (m\beta/t^2)^{1/2} \vec{r}$, $G_s^{[0]}(R,t) = (m\beta/2\pi t^2)^{\frac{3}{2}} e^{-R^2/2}$ and the $D_R^{[n]}$

are purely differential operators in R (i.e., they are not

explicity functions of t). Here, too, terms in the expansion are obtained to the "fourth power of the forces" (i.e., the second order correction to an ideal gas calculation.)

The expansions for $G_s(r,t)$ have been obtained in a form demonstrating the temperature dependence of $f_{1,1}(\underline{x}_1; t|\underline{x}_{1_0})$. They are, roughly, expansions in the ratio of potential to kinetic energy of the assembly. On the other hand, they are not expansions in the time, per se.

By taking Fourier transforms of G_s, first with respect to the spatial variable and then also the time variable, one can obtain the classical approximations to, respectively, the "intermediate scattering function" and the "scattering function" for incoherent scattering of slow neutrons. For these, one obtains series in direct correspondence with the expansions for $G_s(r,t)$. Here, too, the temperature dependence of these quantities is of particular interest.

Whereas it is true that various similar expansions have already been obtained for these transformed quantities,[9,30] it is believed that the temperature dependence of the latter is more surely and explicitly demonstrated by this exposition. An additional benefit of proceeding as we have is that, because the functional form of $G_s(r,t)$ has been demonstrated by our calculations, the task of deducing meaningful information about $G_s(r,t)$ from the transforms is probably simplified

Of course, if one is seriously interested in calculating scattering cross sections, he must find some way of relating

the classical scattering functions to the correct scatter-
ing functions which are defined within the context of
quantum mechanics. Some of the schemes which have been
proposed for this purpose were examined in Chapter six.
It was concluded that they are probably valid if applied
to cross-section calculations for low momentum and energy
transfer, but they must otherwise be applied with care.
The equation giving the correct scattering function is
typically of the form:

$$\cdots\cdots \quad (9.6)$$

$$S_{inc_o}(k,\omega) = e^{\beta\hbar\omega/2} \, e^{-\beta\hbar^2 k^2/8m} \left(S_{inc_o}^{cl_o}(k,\omega,\beta) + \hbar^2 A_2(k,\omega,\beta) + \hbar^4 A_4(k,\omega,\beta) + \cdots \right)$$

where the $\{A_i\}$ are functions of k, ω and also the system
constants given by (9.3). But, $S_{incoh_o}^{cl_o}(k,\omega)$ has also been
obtained as an expansion in system constants. Comparison
of all terms appearing in (9.6) which are proportional to
system constants of type $\mathcal{M}_{[2]}$ shows that $\hbar^2 A_2(k,\omega,\beta)$ can
be neglected when compared with $S_{inc_o}^{cl_o}(k,\omega,\beta)$ only if
k and ω are small; Eq. (9.6) is correct for all k and ω,
but to apply it in general, one should retain all terms in
the expansion in $\hbar^2$ consistent with the expansion for $S_{inc_o}^{cl_o}(k,\omega)$.
The approximation,

$$S_{inc}(k,\omega) \doteq e^{\beta\hbar\omega/2} \, e^{-\beta\hbar^2 k^2/8m} \, S_{inc_o}^{cl_o}(k,\omega) \qquad \circ\circ\circ\circ\circ\circ \quad (9.7)$$

is correct only for k, ω small or β^{-1} very large. If
$S_{inc_o}^{cl_o}(k,\omega,\beta)$ is known to a given order in system constants,

then to obtain the exact cross section in a meaningful way, one must also know a large number of the $\{ A_i \}$.

Is there any point to obtaining $G(r,t)$ if one is interested only in a calculation of the cross section? The latter is defined in terms of the scattering function, whereas $G(r,t)$ has been introduced primarily to aid in relating the scattering process to the internal motion of the scattering system. To obtain the expansions obtained in this thesis, it might be easier to calculate the scattering functions from their basic definitions, rather than from $G(r,t)^{**}$.

Suppose, on the other hand, that one chooses a model Hamiltonian for the scattering system for the purpose of simplifying the calculations. Even if in this case the scattering function is calculated directly from its quantum mechanical definition, it must be acknowledged that classical considerations enter into the calculation. The choice of the model Hamiltonian is almost always determined from some prior knowledge about the gross motions of particles in such model systems and, in fact, the arguments used to justify such Hamiltonians are usually classical concepts. For example, one refers to a <u>particle</u> moving within a cluster of particles or, a <u>particle</u> trapped in a potential well or, a <u>particle</u> diffusing according to the Langevin equation, and so forth.

$**$ Remember that here, however, $G(r,t)$ was of primary interest; the cross section calculation was ancillary.

In addition to examination of expansions in powers of the forces, investigation was made of the derivation of equations pertinent to <u>density</u> expansions of $f_{1,1}$. Bogoliubov type kinetic equations were derived for $f_{1,1}$ which, in contrast to earlier derivations, are valid for systems for which inter-particle forces contain attractive as well as repelling terms.

Finally, $G_d(r,t)$ was derived from a superposition approximation for the two-particle probability density, $f_{2,2}(\underline{x}_1,\underline{x}_2;t|\underline{x}_{1_o},\underline{x}_{2_o})$. It was pointed out that this approximation is equivalent to Vineyard's "convolution approximation for $G(r,t)$.

Certainly, there are still some incomplete aspects of this research. For example, an H-theorem has not yet been established for the kinetic equations derived in chapter 3. The proof of such a theorem would be of great importance because of the general applicability of these equations.

Then, too, there is the question of the secular terms appearing in the expressions obtained for the solutions to the kinetic equation (i.e., the time-relaxed densities.) These expansions have been useful for the calculation of certain quantities pertinent to this investigation. Further-more, they are the exact expressions for short times that any approximate solution must satisfy. However, they are clearly unsatisfactory for extension over the entire time scale, and other procedures should be investigated for solution of the kinetic equations. In this regard, it might be fruitful

to employ methods recently introduced by Frieman[48] and his

collaborators.

Also, it might be interesting to investigate the deriva-

tion of the equations of hydrodynamics after starting with

similar kinetic equations for a more general one-particle

distribution. Whereas we have been particularly interested,

here, in studying the temporal evolution of probability den-

sities for particles moving through an equilibrium assembly,

analogous kinetic equations for distribution functions could

be obtained for many other non-equilibrium problems. In fact,

one can even obtain kinetic equations to provide time-

relaxed <u>correlation</u> <u>functions</u> directly.[**]

Another task yet to be performed is a more complete

investigation of the "system constants" appearing in these

expansions. Can prescriptions be devised for their calculation

similar to the diagram theories invented for the evaluation of

equilibrium distribution functions?

Let us conclude by pointing out that these calculations

are, in a broad sense, only preliminary. The equilibrium and

quasi-equilibrium (stationary state) properties of matter have

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[**] For example, for the momentum auto-correlation function,

$$\eta(t) = \langle \vec{p}_1(0) \cdot \vec{p}_1(t) \rangle ,$$

$$\partial \eta / \partial t = [\bar{\Theta} L A] \eta(t) + \bar{\Theta} \int_0^t d\tau \, e^{-\tau L(1-\Theta)} L (1-\Theta) L \, A(\bar{x}_m) \eta(t-\tau),$$

where $\bar{\Theta} \equiv \int d\bar{x}_{1_0} d\vec{x}_{1_0} f_{1\ell_0}(x_{1_0}) \vec{p}_1 \cdot \vec{p}_{1_0} X$; $\Theta \equiv A(\bar{x}_m) \bar{\Theta}$; and,

$$A(\bar{x}_m) \equiv \frac{1}{\langle p_1^2 \rangle_{\ell_0}} \cdot f_{m,n}(\bar{x}_m; 0 | \vec{x}_{1_0}) .$$

been well studied, and we are cognizant of the great successes which have been achieved in these areas. Even more exciting, though, is the thought that recent investigation into non-equilibrium problems is just the beginning of a similarly fruitful period of investigation into a more extensive but less well understood class of natural phenomena.

APPENDIX A

NOTES ON PROBABILITY THEORY[**]

1. THE NOTION OF RANDOM VARIABLES, DENSITIES, AND
   DISTRIBUTIONS

Consider a collection of entities ("sample space"), S, complete in

the sense that all possible varieties of any pertinent property or set of

properties possessed by the members of the collection are represented

by some subset of S (albeit a set of measure zero, if necessary).

A.1 Definition: A property X(·), is a "function defined on the space S

"if to every member s of S there is a real number, denoted by X(s),

which is called the value of the function X at s.

> e.g., Consider a set of cows, C, and consider the pertinent
> property to be the color of the eyes of the individual cows. If,
> for example, the number 1 is assigned to the property: blue
> eyes, 2 ⟺ red eyes, 3 ⟺ green eyes, etc., then eye-color
> (E(·)) is a function defined on the space C.

A.2 Definition: A property, X(·), is said to be a random variable

if it is a real valued function defined on a sample space on whose sub-

sets a probability function, $\mu_{Pr}(\cdot)$, has been defined. The probability

function (measure) is an a priori 'weight' assigned to the members of S.

This notion will become more familiar, below.

[**]Ref: Parzan [49], Feller, [50] Doob·[51]
    This presentation is similar to the discussion found in Parzan's
book, and is included as an aid for those readers who might be unfamiliar
with some of the terminology used in the main text, above.

A.3 <u>Definition</u>: The probability function $\text{Pr}_X(\cdot)$ of a random variable

X is a set function defined for every set of real numbers. Its value is

the "probability that X is in B".

The probability measure of X, $\text{Pr}_X(\cdot)$, is obtained from a proba-

bility function $\mathcal{M}_{\text{Pr}}(\cdot)$, defined on the sample space, by summing up the

measure of all subsets of S such that X(s) = B. i.e.,

$$\mathcal{P}_X(\mathcal{B}) = \text{``} \mathcal{P}_\lambda [\mathcal{X} \in \mathcal{B}] \text{''} = \mathcal{M}_{\mathcal{P}_\lambda} \{S : X(S) \in \mathcal{B}\} = \int_{S : \mathcal{X}(S) \in \mathcal{B}} d\mathcal{M}_{\mathcal{P}_\lambda}(S)$$

e.g., If we assigne equal measure $\mathcal{M}_{\text{Pr}}(\cdot)$, to each cow in our
sample space, C. then $\text{Pr}_E(\cdot)$ is the probability measure for a
given eye-color = $\mathcal{M}$(s: E = given eyecolor) = N_E/N, where
N_E = the number of cows having a given eyecolor, N = the total
number of members of the sample space.

However, <u>the choice of the basic probability measure is not</u>
<u>unique</u>. It is <u>an a priori</u> <u>assignment</u>, postulated for any given
problem in accord with the relevant Logic. For example,
with reference to the sample space C, one might have chosen
the probability measure to be proportional to the weight of the
cows involved. In this case, $\text{Pr}_E(\cdot)$, also, would be propor-
tional to the weight of the cows having a given eyecolor.

A.4 <u>Axioms</u>: For a measure to be a probability measure, it must
satisfy the following axioms of probability theory:

<u>Ax. 1:</u> $\mathcal{M}_{\text{Pr}}(s) \geq 0$ for every subset $s \in S$. (As a consequence,
$\text{Pr}_X(\cdot) \geq 0$ for every event.)

<u>Ax. 2:</u> $\int_{\text{all space, S}} d\mathcal{M}_{\mathcal{P}_\lambda}(S) = 1$ $\left(\Rightarrow \int_{\text{all } x} d\mathcal{P}_X(x) = 1 \right)$.

<u>Ax. 3:</u> For subsets S_1 and S_2 of S:

$$\int_{S_1 \cup S_2} d\mathcal{M}_{\mathcal{P}_\lambda}(S) = \int_{S_1} d\mathcal{M}_{\mathcal{P}_\lambda}(S) + \int_{S_2} d\mathcal{M}_{\mathcal{P}_\lambda}(S) , \quad \text{if } S_1 \cap S_2 = 0$$

A.5 <u>Definition</u>: A random variable X(·) is discrete if $Pr_X(·)$ is > 0

for at most a denumerably infinite number of points, x, and if

$\sum_{x:P_x(x)} P_x(x) = 1$. $p_X(x)$ is the probability that the observed value of the

random variable X will be equal to x.

A.6 <u>Definition</u>: The values x of a discrete r.v. for which $Pr_X(x) > 0$

are called <u>probability mass points</u>.

A.7 <u>Definition</u>: A random variable is continuous if it possesses no

probability mass points.

For a continuous r.v., the question, "what is the probability

that X = x?" has no meaning. Rather, one must ask: "What is the

probability that X is within the range B, i.e., what is $Pr_X(B)$?"

$Pr_X(B)$ can be obtained from a function $f_X(x)$ by integrating the

latter (in the Lebesgue sense) over all points x∈B, i.e.,

$$P_{r_X}(B) = P_{r_X}[X \text{ is in } B] = \int_B f_X(x) dx$$

(Note: $f_X(x) = \int_{s \in S: X(s) = x} d\mu_{P_x}(s)$).

A.8 <u>Definition</u>: $f_X(x)$, defined in the above manner, is called the

probability density function of the random variable X.

Note that $f_X(x)$ is never negative.

e.g., An example of a probability density function is the
normalized neutron density, f(E) = n(E)/n (such that $\int_{E'} f(E) dE$
is the prob. that the energy of a neutron, chosen at random from
the assembly, is in the range E'.)

A.9 <u>Definition</u>: The distribution function of a random variable, X,

denoted by $F_X(\cdot)$ is defined by

$$F_X(x) \equiv P_r[X \le x] = \int_{-\infty}^{x} f(x') \, dx'$$

(In the case of a discrete r.v., $\sum_{all\,pts,\,x' \le x} P_X(x') = F_X(x)$.

But, if integration is taken in the Lebesgue sense, then

$$F_X(x) = \int_{-\infty}^{x} f_X(x') \, dx'$$

where, for the discrete case:

$$f_X(x) = \sum_i P_i \, \delta(x - x_i) \quad ; \quad \sum P_i = 1.$$

Note that $F_X(x)$ is continuous if X is a continuous random
variable but it possesses step discontinuities if X is a discrete
r.v.)

e.g., If the probability that $X = x_o$ is 1, then

$$F_X(x) = \begin{cases} 0 & \text{if } x \le x_o \\ 1 & \text{if } x > x_o \end{cases}$$

Also, since $f_X(x) = \dfrac{d}{dx} F_X(x)$, thus $f_X(x) = \overset{Dirac}{\delta}(x - x_o)$

It is seen that $F_X(x)$ is a never decreasing function of x;

$$F(-\infty) = 0; \quad F(+\infty) = 1; \quad \int_{-\infty}^{+\infty} f(x) \, dx = 1.$$

2. MULTIVARIATE DISTRIBUTIONS AND DENSITIES, JOINTLY
    DISTRIBUTED r.v.'s

A.10 <u>Definition</u>: Two or more random variables can be defined simul-

taneously on the same sample space. In such a case, the random

variables are said to be "jointly distributed".

Consider, for example, the particular case of two random variables,

X_1 and X_2. In analogy to the previous discussion, one has

$$Pr_{X_1, X_2}(B) = \mu_{Pr} \text{ (s in S: } [X_1(s), X_2(s)] \in B)$$

for the joint probability function. It is the cumulative measure of all

points $s \in S$ such that the two dimensional phase point, $(X_1(s), X_2(s))$

associated with each s is within the set B.

A.11 Definition: The joint distribution function of the random variables

X_1 and X_2 is defined by:

$$F_{X_1, X_2}(x_1, x_2) = \mu_{Pr} \{ s \in S: (X_1 \leq x_1, X_2 \leq x_2) \} =$$

$$= Pr (X_1 \leq x_1, X_2 \leq x_2)$$

Notice that

$$\lim_{x_1 \to -\infty} F_{X_1, X_2}(x_1, x_2) = 0; \text{ similarly } \lim_{x_2 \to -\infty} F_{X_1, X_2} = 0.$$

Also, $\lim_{\substack{x_1 \to +\infty \\ x_2 \to +\infty}} F_{X_1, X_2} = 1.$

A.12 Definition: Similarly, $\lim_{x_1 \to \infty} F_{X_1, X_2}(x_1, x_2) = F_{X_2}(x_2)$ is the marginal

distribution function of the random variable X_2 corresponding to the

joint distribution F_{X_1, X_2}. (A similar definition holds for $\lim_{x_2 \to \infty} F_{X_1, X_2} = F_{X_1}(x_1)$.

A.13 Definition: In the case of continuous random variables,

$$Pr_{X_1, X_2}(B) = \iint_B f_{X_1, X_2}(x_1', x_2') \, dx_1' \, dx_2'$$

where $f_{X_1, X_2}(x_1, x_2) \equiv$ "joint probability density"

Note that $f_{X_1, X_2} \geq 0$ for all (x_1, x_2), and that $f_{X_1, X_2}(x_1, x_2) =$

$$\frac{\partial^2}{\partial x_1 \partial x_2} F_{X_1, X_2}(x_1, x_2).$$

A.14 <u>Definition</u>: The marginal probability density function of the

random variable X_1 corresponding to the joint distribution F_{X_1, X_2} is

$$f_{X_1}(x_1) = \int_{-\infty}^{+\infty} f_{X_1, X_2}(x_1, x_2) \, dx_2$$

It is seen that

$$F_{X_1}(x_1) = \int_{-\infty}^{x_1} f_{X_1}(x_1') \, dx_1' = \int_{-\infty}^{x_1} dx_1' \int_{-\infty}^{+\infty} dx_2' \, f_{X_1, X_2}(x_1', x_2')$$

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Remarks similar to these for discrete r.v.'s follow in an

obvious way. Also, generalizations to multivariate distributions of

dimension greater than 2 are easy and shall not be mentioned here.

3. INDEPENDENT RANDOM VARIABLES

Let X_1 and X_2 be jointly distributed, with individual (marginal)

densities F_{X_1} and F_{X_2}, respectively, and joint distribution F_{X_1, X_2}.

A.15 Definition: X_1 and X_2 are independent if $Pr\{X_1 \in B_1, X_2 \in B_2\} =$

$Pr\{X_1 \in B_1\} \times Pr\{X_2 \in B_2\}$ i.e., if there is no dependence between

the values taken on jointly by X_1 and X_2.

As a consequence, <u>for independent random variables</u>,

$$F_{X_1, X_2}(x_1, x_2) = F_{X_1}(x_1) \cdot F_{X_2}(x_2), \text{ and, } f_{X_1 X_2}(x_1, x_2) = f_{X_1}(x_1) \cdot f_{X_2}(x_2)$$

e.g., The space occupancies of the particles of an ideal gas
are mutually independent. Indeed, we have $f_{X_1, \ldots, X_n}(x_1, \ldots, x_n) = \prod_{i=1}^{n} f_{X_i}(x_i)$
for the ideal gas.

4. CONDITIONAL PROBABILITIES AND CONDITIONAL DENSITIES, ETC.

A.16 <u>Definition</u>: For <u>discrete</u> random variables, given two properties,

A & B, defined on the same probability space, the conditional probability

of property A, given the property B, is <u>defined as</u>:

$$\Pr\{A|B\} = \begin{cases} = \Pr\{A,B\}/\Pr\{B\} \ , & \text{if } \Pr\{B\} > 0 \\ \text{undefined} & \text{if } \Pr\{B\} = 0 \ . \end{cases}$$

For continuous r.v.'s, the above definition is going to lead to

difficulty since, if we try to define $\Pr\{A|X\} = \Pr\{A,X\}/\Pr\{X\}$,

trouble arises because $\Pr\{X = x\} = 0$. Instead:

A.17 <u>Definition</u>: The conditional probability distribution, $P_r\{A|X = x\}$,

for continuous variables, is defined by:

$$\int_B P_r(A|X=x') \, d F_X(x') \equiv P_r\left(\{Y \in A\}, \{X \in B\}\right) =$$

$$= \mu_{P_r}\{s: Y(s) \in A, X(s) \in B\} = \int_{s: Y(s) \in A, X(s) \in B} d\mu_{P_r}(s)$$

$$= \int_B P_r\{A|X=x'\} \, f_X(x') \, dx'$$

Note that $P_r\{A\} = \int_{-\infty}^{+\infty} P_r\{A|X=x\} \, d F_X(x)$. Furthermore, if A and X are

independent, $P_r\{A|x\} = P_r\{A\}$ and the above equation is trivially

satisfied.

A.18 <u>Definition</u>: The <u>conditional distribution function of Y, given X,</u>

is defined by: $F_{Y|X}(y/x) = \Pr\{Y \le y \mid X = x\}$. Consequently,

$$P_r\{X \le x, Y \le y\} = F_{X,Y}(x,y) = \int_{-\infty}^{x} F_{Y|X}(y|x') \, d F_X(x') \ .$$

A.19 Definition: The conditional probability-density function of the

random variable Y, given the random variable X, is defined by:

$f_{Y|X}(y|x) \equiv \dfrac{\partial}{\partial y} F_{Y|X}(x|y)$. We are thus led to the important relation:

$$f_{Y|X}(y|x) = f_{X,Y}(x,y) \Big/ f_X(x)$$

Proof:

In light of A.19: $\dfrac{\partial}{\partial x} F_{X,Y} = F_{Y|X}(y|x) \cdot f_X(x)$. Next, differentiating

re y: $\dfrac{\partial^2}{\partial x \partial y} F_{X,Y} = f_{X,Y} = f_{Y|X} f_X(x)$. q.e.d.

Also consider:

$$f_{X|Y}(x|y) = \int_{-\infty}^{+\infty} f_{X|Y,Z}(x|y,z') f_{Z|Y}(z'|y) dz'$$

Proof:

The "conditional probability" of realizing an event A, given that

Y = y', Z = z', is defined by the following relationship.

$$P_r\{A \text{ such that } (Y,Z) \in B\} = \iint_B P_r[A|Y=y', Z=z'] dF_{Y,Z}(y',z') =$$
$$= \iint_B P_r[A|Y=y', Z=z'] f_{Y,Z}(y',z') dy' dz'$$

it contains the entire range of Z, i.e.

But, if B is such that $\bigwedge(-\infty \leq Z \leq +\infty)$, then $P_r\{A \text{ s.t. } (Y,Z) \in B\} =$

$= P_r\{A \text{ s.t. } Y \in B'\}$ where B' = range of Y. Thus,

$$P_r\{A \text{ s.t. } Y \in B'\} = \int_{B'} dy' \int_{-\infty}^{+\infty} dz' \, P_r[A|Y=y', Z=z'] f_{Y,Z}(y',z')$$

Now, suppose that B' is the range $\{-\infty, y\}$ and A is the event that X falls

within the range $A = \{-\infty, x\}$. We thus find the following relationship

for probability distribution functions:

$$F_{X,Y}(x,y) = \int_{-\infty}^{y} dy' \int_{-\infty}^{+\infty} dz' F_{X|Y,Z}(x|y',z') f_{Y,Z}(y',z'), \text{ where } F_{X|Y,Z}(x|y',z') = P_r\{X \leq x | Y=y', Z=z'\}.$$

If we next take derivatives re x, y we obtain:

$$f_{X,Y}(x,y) = \int_{-\infty}^{+\infty} d\beta' \, f_{X|Y,Z}(x|y,\beta') \, f_{Z,Y}(\beta',y)$$

where $f_{X|Y,Z}(x|y,\beta) = \frac{\partial}{\partial x} F_{X|Y,Z}(x|y,\beta)$ = conditional probability density.

Hence, since $f_{X,Y}(x,y) = f_{X,Y}(x|y) \cdot f_Y(y)$, $\Rightarrow$

$$f_{X,Y}(x|y) = \int_{-\infty}^{+\infty} f_{X|Y,Z}(x|y,\beta') \, f_{Z|Y}(\beta'|y) d\beta' \, , \quad q.e.d.$$

5. EXPECTATIONS

Given a function of the random variable x: g(x).

A.20 <u>Definition</u>: The <u>expected value</u> of g(x), with regard to the distribution $F_X(x)$ is defined as:

$$\mathcal{E}\{g(x)\} \equiv \langle g \rangle \equiv \int_{-\infty}^{+\infty} g(x) \, dF_X(x) = \int_{-\infty}^{+\infty} g(x) \, f_X(x) \, dx$$

Alternatively:

$$\langle g \rangle = \iint_{-\infty}^{+\infty} g(x) \, f(x,y) \, dx \, dy = \iint_{-\infty}^{+\infty} g(x) \, f_{X|Y}(x|y) \, dx \, dF_Y(y)$$

Similarly, if h(x,y) is a function of the random variables X,Y:

$$\langle h \rangle = \mathcal{E}\{h(x,y)\} = \iint_{-\infty}^{+\infty} h(x,y) \, dF_{X,Y}(x,y) = \iint_{-\infty}^{+\infty} h(x,y) \, f(x,y) \, dx \, dy$$

$$= \iint_{-\infty}^{+\infty} h(x,y) \, f_{X|Y}(x|y) \, dx \, dF_Y(x)$$

Notice, if $h(x,y) = h_1(x) \cdot h_2(y)$, and if x and y are independent:

$$\langle h(x,y) \rangle = \langle h_1 \rangle \cdot \langle h_2 \rangle \, .$$

APPENDIX B

REDUCTION OF COLLISION INTEGRALS

As noted in the main text, upon expanding the collision integral

according to 4.15, one finds it convenient to write:

$$I^{(2)} = I^{(2a)} + I^{(2b)} \quad \text{with} \quad I^{(2a)} = \sum_{k=1}^{4} I_k^{(2a)} \qquad \cdots \quad (B.1)$$

according to the definitions:

$$I_1^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1 e^{+\tau_2 L_0^+} \mathcal{S}_{-\tau_2} L_0 L_0^+ f_{n|1} f_{1,1}(t-\tau_1) \quad \cdots \quad (B.2a)$$

$$I_2^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1 e^{+\tau_2 L_0^+} \mathcal{S}_{-\tau_2} L_0 L_1 f_{n|1} f_{1,1}(t-\tau_1) \quad \cdots \quad (B.2b)$$

$$I_3^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1 e^{+\tau_2 L_0^+} \mathcal{S}_{-\tau_2} L_1 L_0^+ f_{n|1} f_{1,1}(t-\tau_1) \quad \cdots \quad (B.2c)$$

$$I_4^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1 e^{+\tau_2 L_0^+} \mathcal{S}_{-\tau_2} L_1 L_1 f_{n|1} f_{1,1}(t-\tau_1) \quad \cdots \quad (B.2d)$$

$$I^{(2b)} = -\bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1 e^{\tau_2 L_0^+} \mathcal{S}_{-\tau_2} \Theta(\Xi) L L^+ f_{n|1} f_{1,1}(t-\tau_1) \quad \cdots \quad (B.2e)$$

In addition, expand

$$I_1^{(2a)} = {}^0 I_1^{(2a)} + {}^1 I_1^{(2a)} + {}^2 I_1^{(2a)} + \cdots \qquad (B.3)$$

with

$${}^0 I_1^{(2a)} = \bar{\Theta}(\Xi) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1(\Xi) \mathcal{S}_{-\tau_2} L_0(\Xi) L_0^+(\Xi) f_{n|1} f_{1,1}(t-\tau_1) \qquad (B.4a)$$

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$$^{1}I^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (\tau_2) L_1 L_0^{\dagger} \mathcal{S}_{-\tau_2} L_0 L_0^{\dagger} f_{n|1} \, f_{1,1}(t-\tau_1)$$

(B.4b)

$$^{2}I^{(2a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (\frac{\tau_2^2}{2}) L_1 L_0^{\dagger} L_0^{\dagger} \mathcal{S}_{-\tau_2} L_0 L_0^{\dagger} f_{n|1} \, f_{1,1}(t-\tau_1)$$

(B.4c)

$^{0}I_1^{(2a)}$ combines with one of the terms of $I^{(1)}$ to provide the 'basic' collision integral term Q_1 (cf., 4.32). $^{1}I_1^{(2a)} + \,^{2}I_1^{(2a)}$ are shown to yield Q_3, defined by 4.37.

The other of the nine terms ($Q_1, \ldots, Q_9$), defined by equations (4.32), (4.37),(4.40 - 4.46), are obtained in the same way. The following is an abbreviated exposition of the procedure by which these terms are obtained.

One expands

$$I_2^{(2a)} \equiv \,^{0}I^{(2a)} + \,^{1}I^{(2a)} + \cdots$$

(B.5)

with

$$^{0}I_2^{(2a)} \equiv \bar{\Theta}(\tau) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, L_1(\tau) \mathcal{S}_{-\tau_2} L_0(\tau) L_1(\tau) f_{n|1}(\tau) f_{1,1}(t-\tau_1)$$

(B.6a)

$$^{1}I_2^{(2a)} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (\tau_2) \{ L_1 L_0^{\dagger} \mathcal{S}_{-\tau_2} L_0 L_1 \} f_{n|1}(\tau) f_{1,1}(t-\tau_1)$$

(B.6b)

$$^{2}I_2^{(2a)} \equiv \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (\frac{\tau_2^2}{2}) \{ L_1 L_0^{\dagger} L_0^{\dagger} \mathcal{S}_{-\tau_2} L_0 L_1 \} f_{n|1} \, f_{1,1}(t-\tau_1)$$

(B.6c)

etc.

It is then found that (cf., Eq. (4.40), (4.41)

$$Q_2 = I_2^{(1)} + \,^{0}I_2^{(2a)} \quad ;$$

(B.7)

$$Q_4 = {}^1I_2^{(2a)} + {}^2I_2^{(2a)}$$

(B.8)

Similarly, expand

$$I^{(3)} = I^{(3a)} + I^{(3b)} + I^{(3c)} + I^{(3d)}$$

(B.9)

where

$$I^{(3a)} = \bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3\, L_1\, e^{(\tau_2-\tau_3)L_0^\dagger} \oint_{-(\tau_2-\tau_3)} L_1 e^{\tau_3 L_0^\dagger} \oint_{-\tau_3} L L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

(B.10a)

$$I^{(3b)} = -\bar{\Theta} \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3\, L_1\, e^{(\tau_2-\tau_3)L_0^\dagger} \oint_{-(\tau_2-\tau_3)} \Theta L_1 e^{\tau_3 L_0^\dagger} \oint_{-\tau_3} L L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

(B.10b)

$$I^{(3c)} = -\bar{\Theta} \int_0^t \cdots \int_0^{\tau_2} d\tau_3\, L_1\, e^{(\tau_2-\tau_3)L_0^\dagger} \oint_{-(\tau_2-\tau_3)} L_1 e^{\tau_3 L_0^\dagger} \Theta \oint_{-\tau_3} L L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

(B.10c)

$$I^{(3d)} = \bar{\Theta} \int_0^t \cdots \int_0^{\tau_2} d\tau_3\, L_1\, e^{(\tau_2-\tau_3)L_0^\dagger} \Theta \oint_{-(\tau_2-\tau_3)} L_1 e^{\tau_3 L_0^\dagger} \Theta \oint_{-\tau_3} L L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

(B.10d)

Then, (cf., (4.42)

$$Q_5 = {}^1I_3^{(2a)} + {}^0I_1^{(3a)} + {}^1I_1^{(3a)},$$

(B.11)

where $\quad {}^1I_3^{(2a)} \quad$ is obtained from (B.2c) by an obvious definition. $\quad {}^0I_1^{(3a)}$

and $\quad {}^1I_1^{(3a)} \quad$ are obtained from the expansion for $\quad I_1^{(3a)}$, viz.,

$$I^{(3a)} = {}^0I_1^{(3a)} + {}^1I_1^{(3a)} + \cdots$$

(B.12)

where

$$^0I_1^{(3a)} = \bar{\Theta}(\bar{\cdot}\bar{\cdot}) \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3\, L_1 \oint_{-(\tau_1-\tau_3)} L_1 \oint_{-\tau_3} L_0 L_0^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

(B.13a)

$$^1I_1^{[3a]} \equiv \bar{\theta}(z) \int_0^t \delta\tau_1 \int_0^{\tau_1} \delta\tau_2 \int_0^{\tau_2} \delta\tau_3 \times$$

$$\times \left[\left\{ (\tau_2-\tau_3)L_1 L_0^+ \delta_{-(\tau_2-\tau_3)} L_1 \delta_{-\tau_3} L_0 L_0^+ + \right. \right. \qquad \text{(B.13b)}$$

$$\left. \left. + \tau_3 L_1 \delta_{-(\tau_2-\tau_3)} L_1 L_0^+ \delta_{-\tau_3} L_0 L_0^+ \right\} f_{n|1} f_{1,1}(t-\tau_1) \right]$$

etc.

For $\mathcal{L}_6$ (cf. 4.43) we have:

$$\mathcal{L}_6 \equiv {}^1I_4^{[2a]} + {}^0I_2^{[3a]} + {}^1I_2^{[3a]} \qquad \text{(B.14)}$$

where ${}^1I_4^{[2a]}$ is obtained from an expansion of B.2d. ${}^0I_2^{[3a]}$ and ${}^1I_2^{[3a]}$

follow from an expansion of $I_2^{[3a]}$, defined by:

$$I_2^{[3a]} \equiv \bar{\theta} \int_0^t \delta\tau_1 \int_0^{\tau_1} \delta\tau_2 \int_0^{\tau_2} \delta\tau_3 \, L_1 e^{(\tau_2-\tau_3)L_0^+} \delta_{-(\tau_2-\tau_3)} L_1 e^{\tau_3 L_0^+} \delta_{-\tau_3} L_0 L_1 f_{n|1} f_{1,1}(t-\tau_1) \qquad \text{(B.15)}$$

Similarly, defining (cf. B.10b):

$$^{1,0}I^{[3b]} \equiv -\bar{\theta} \int_0^t \cdots \int_0^{\tau_2} \delta\tau_3 \, L_1 (\tau_2-\tau_3)L_0^+ \delta_{-(\tau_2-\tau_3)} \theta L_1 \delta_{-\tau_3} L L^+ f_{n|1} f_{1,1}(t-\tau_1) \qquad \text{(B.16)}$$

we have

$$\mathcal{L}_7 \equiv {}^1I_2^{[2b]} + {}^{1,0}I^{[3b]}$$

$$\qquad \text{(B.17)}$$

Finally, $\mathcal{L}_8 \equiv {}^0I_3^{[3a]} + {}^0I_4^{[3a]} + {}^{0,00}I^{[4a]}$

$$\qquad \text{(B.18)}$$

$$\mathcal{L}_9 \equiv {}^{0,0}I^{[3c]} + {}^{0,0,0}I^{[4b]}$$

$$\qquad \text{(B.19)}$$

with

$$^{0,0}I^{[3c]} \equiv -\bar{\Theta}\int_0^t \cdots \int_0^{\tau_2} d\tau_3 \, L_1 \, \delta_{-(\tau_2-\tau_3)} L_1 \, \mathcal{O} \, L \, L^\dagger f_{n|1} \, f_{1,1}(t-\tau_1)$$

$$\cdots\cdots (B.20)$$

$$^{0,0,0}I^{[4c]} \equiv \bar{\Theta}\int_0^t d\tau_1 \cdots \int_0^{\tau_3} d\tau_4 \left\{ L_1 \, \delta_{-(\tau_2-\tau_3)} L_1 \, \delta_{-(\tau_3-\tau_4)} L_1 \, \delta_{-\tau_4} \left\{ L L^\dagger f_{n|1} f_{1,1}(t-\tau_1) \right. \right.$$

$$\cdots\cdots (B.21)$$

$$^{0,0,0}I^{[4b]} \equiv -\bar{\Theta}\int_0^t d\tau_1 \cdots \int_0^{\tau_3} d\tau_4 \left\{ L_1 \, \delta_{-(\tau_2-\tau_3)} L_1 \, \delta_{-(\tau_3-\tau_4)} \mathcal{O} \, L_1 \, \delta_{-\tau_4} \right\} \times$$

$$\times L L^\dagger f_{n|1} \, f_{1,1}(t-\tau_1)$$

$$\cdots\cdots (B.22)$$

All terms to $\Theta(\varepsilon^4)$ are included in $\mathcal{A}_1 \rightarrow \mathcal{A}_q$.

Let us conclude by performing as an example, one of the partial

integrations somewhat more obscure than those provided in the text

(cf. Eq. 4.38 ff.). Consider,

$$^{0}I_3^{[3a]} + ^{0}I_4^{[3a]} \equiv \bar{\Theta}(\bar{\mathcal{I}})\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \int_0^{\tau_2} d\tau_3 \, L_1 \, \delta_{-(\tau_2-\tau_3)} L_1 \, \delta_{\tau_3} \, L_1 \, L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

which is to be compared with

$$^{0,0,0}I^{[4a]} \equiv \bar{\Theta}(\bar{\mathcal{I}})\int_0^t d\tau_1 \cdots \int_0^{\tau_3} d\tau_4 \, L_1 \, \delta_{-(\tau_2-\tau_3)} L_1 \, \delta_{-(\tau_3-\tau_4)} L_1 \, \delta_{-\tau_4} \, (\tfrac{-\vec{P}}{m}\cdot\vec{\nabla}_{\xi_1}) L^\dagger f_{n|1} f_{1,1}(t-\tau_1) .$$

Notice that $\delta_{-\tau} L_1 = L_1'(\tau)\delta_{-\tau}$, where $L_1'(\tau) \stackrel{def}{=} L_1 + \sum_{k\neq 1}^n -\vec{F}_{1k}\cdot\frac{\tau}{m}\vec{\nabla}_{\xi_1}$,

so that

$$^{0,0,0}I^{[4a]} = \bar{\Theta}\int_0^t d\tau_1 \cdots \int_0^{\tau_3} d\tau_4 \, L_1 \left[L_1'(\tau_2-\tau_3) \right] \left[L_1'(\tau_3-\tau_4) \right] \delta_{-\tau_4} \, (\tfrac{-\vec{P}}{m}\cdot\vec{\nabla}_{\xi_1}) L^\dagger f_{n|1} f_{1,1}(t-\tau_1) .$$

Integrate by parts over τ_4 and then τ_3 :

$$^{0,0,0}I^{[4a]} = \bar{\Theta}\int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 (\tfrac{\tau_2^2}{2}) L_1 \left\{ L_1'^2 + \tfrac{1}{3}\sum -\vec{F}_{1k}\cdot\tfrac{\tau_2}{m}\vec{\nabla}_{\xi_1} L_1 + \tfrac{2}{3} L_1 \sum -\vec{F}_{1k}\cdot\tfrac{\tau_2}{m}\vec{\nabla}_{\xi_1} + \right.$$

$$+ \tfrac{\tau_2^2}{4m}(\sum -\vec{F}_{1k}\cdot\vec{\nabla}_{\xi_1})^2 \left\} \delta_{-\tau_2} (\tfrac{-\vec{P}}{m}\cdot\vec{\nabla}_{\xi_1}) L^\dagger f_{n|1} f_{1,1}(t-\tau_1) .$$

Next, integrate by parts over τ_2,

$$^{0,0,0}I^{[4a]} = \theta \int_0^t d\tau_1 \frac{\tau_1^2}{2} L_1 \left[L_1^2 + \frac{1}{3}\sum -\vec{F}_{1k}\cdot\frac{\tau_1}{m}\vec{\nabla}_{q_1} L_1 + L_1 \frac{2}{3}\sum_{k\neq 1} -\vec{F}_{1k}\cdot\frac{\tau_1}{m}\vec{\nabla}_{q_1} + \right.$$

$$\left. + \frac{\tau_1^2}{4m^2}(\sum \vec{F}_{1k}\cdot\vec{\nabla}_{q_1})^2 \right] \delta_{-\tau_1} L^\dagger f_{n|1} f_{1,1}(t-\tau_1)$$

$$-\theta \int_0^t d\tau_1 \int_0^{\tau_1} d\tau_2 \, \tau_2 L_1 \left[L_1^2 + \frac{\tau_2}{2m}\sum -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1} L_1 + \frac{\tau_2}{m} L_1 \sum -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1} + \right.$$

$$\left. + \frac{\tau_2^2}{2m}(\sum -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1})^2 \right] \delta_{-\tau_2} L^\dagger f_{n|1} f_{1,1}(t-\tau_1).$$

But, as can be easily verified, the last terms is just the negative of

$^0I_3^{[3a]} + {}^0I_4^{[3a]}$. Thus, we define one of the 'basic' collision integrals

(B.18).

$$\ell_8 \equiv {}^0I_3^{[3a]} + {}^0I_4^{[3a]} + {}^{0,0,0}I^{[4a]} =$$

$$= \bar\theta \int_0^t d\tau_1 \frac{\tau_1^2}{2} L_1 \left[L_1^2 + \frac{\tau_1}{3m}\sum_{k\neq 1} -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1} L_1 + \frac{2}{3} L_1 \tau_1 \sum_{k\neq 1} -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1} + \right.$$

$$\left. + \frac{\tau_1^2}{4m^2}(\sum_{k\neq 1} -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1})^2 \right] (L^\dagger + \frac{\tau_1}{m}\sum_{k\neq 1} -\vec{F}_{1k}\cdot\vec{\nabla}_{q_1}) \delta_{-\tau_1} f_{n|1} f_{1}(t-\tau_1)$$

.

APPENDIX C

RELATIONSHIPS BETWEEN SYSTEM CONSTANTS

We shall prove that $\chi^{(4)} = 3\chi^{(2,2)}$; it is expeditious to evaluate

these coefficients in spherical coordinates. Thus,

$$\chi^{(4)} = \int d^3\vec{q}\ g_2(|\vec{q}|)\ \frac{\partial^4}{\partial q_x^4}\ \varphi(|\vec{q}|) =$$

$$= \int_0^\infty d\rho \int_0^{2\pi} d\theta \int_0^\pi d\varphi\ \rho^2 \sin\varphi\ g_2(\rho) \times$$

$$\times \left\{ \frac{\partial^4 \varphi}{\partial \rho^4}'\left(\frac{\partial\rho}{\partial x}\right)^4 + 6\frac{\partial^3\varphi}{\partial\rho^3}\left(\frac{\partial\rho}{\partial x}\right)^2\frac{\partial\rho}{\partial x^2} + 3\frac{\partial^2\varphi}{\partial\rho^2}\left(\frac{\partial\rho}{\partial x^2}\right)^2 + \right. \quad\cdots\ (C.1)$$

$$\left. + 4\frac{\partial^2\varphi}{\partial\rho^2}\frac{\partial\rho}{\partial x}\frac{\partial^3\rho}{\partial x^3} + \frac{\partial\varphi}{\partial\rho}\frac{\partial^4\rho}{\partial x^4} \right\}$$

Hence, since $x = \rho \sin\varphi\cos\theta$; $y = \rho\sin\varphi\sin\theta$; $z = \rho\cos\varphi$:

$$\chi^{(4)} = \int_0^\infty d\rho \int_0^{2\pi} d\theta \int_0^\pi d\varphi\ \rho^2\sin\varphi\ g_2(\rho) \times \left\{ \frac{\partial^4\varphi}{\partial\rho^4}[\sin^4\varphi\cos^4\theta] + \right.$$

$$+ \frac{6}{\rho}\frac{\partial^3\varphi}{\partial\rho^3}\sin^2\varphi\cos^2\theta[1 - \sin^2\varphi\cos^2\theta] +$$

$$+ \frac{3}{\rho^2}\frac{\partial^2\varphi}{\partial\rho^2}[1 - 2\sin^2\varphi\cos^2\theta + \sin^4\varphi\cos^4\theta] +$$

$$+ \frac{12}{\rho^2}\frac{\partial^2\varphi}{\partial\rho^2}\sin^2\varphi\cos^2\theta[\sin^2\varphi\cos^2\theta - 1] +$$

$$\left. + \frac{1}{\rho^3}\frac{\partial\varphi}{\partial\rho}\{-3[1 - 6\sin^2\varphi\cos^2\theta + 5\sin^4\varphi\cos^4\theta]\} \right\}.$$

Next, performing the integration over θ and φ, one obtains

$$\chi^{(4)} = \frac{\pi}{15} \int_0^\infty d\rho\ \rho^2\ g_2(\rho)\left\{ 12\frac{\partial^4\varphi}{\partial\rho^4} + 48\frac{1}{\rho}\frac{\partial^3\varphi}{\partial\rho^3} \right\} \quad\cdots\ (C.1')$$

In the same way, one shows:

$$\chi^{(2,2)} = \frac{\pi}{15} \int_0^\infty d\rho \; \rho^2 \; g_2(\varphi) \left\{ 4 \frac{\partial^4 \varphi}{\partial \rho^4} + \frac{16}{\rho} \frac{\partial^3 \varphi}{\partial \rho^3} \right\} \quad \ldots, (C.2)$$

It is quite straightforward to show the validity of the other relation-

ships stated on page 4-20. Their proofs are essentially no different

from the one here described.

APPENDIX D

CALCULATIONAL AIDS TO CHAPTER 6

Table D-1: Some Useful Integrals

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t^3}{m^3} \vec{p}_1 \cdot \vec{\nabla}_{\xi_1} \nabla_{\xi_1}^2 \delta^6 = -\frac{\beta}{m} \frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 G_s^{(0)}(r,t) \quad **$$

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t^4}{m^4} \nabla_{\xi_1}^2 \nabla_{\xi_1}^2 \delta^6 = \frac{\beta^2}{m^2} \frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 G_s^{(0)}(r,t)$$

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t}{m} \vec{p}_1 \cdot \vec{\nabla}_{\xi_1} \delta^6 = -\frac{t^2}{m\beta} \nabla_r^2 G_s^{(0)}(r,t)$$

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t^2}{m^2} (\vec{p}_1 \cdot \vec{\nabla}_{\xi_1})^2 \delta^6 = \left(\frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 + \frac{2t^2}{m\beta} \nabla_r^2 \right) G_s^{(0)}(r,t)$$

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t}{m} p_1^2 \vec{p}_1 \cdot \vec{\nabla}_{\xi_1} \delta^6 = -\frac{m}{\beta} \left(\frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 + \frac{5t^2}{m\beta} \nabla_r^2 \right) G_s^{(0)}(r,t)$$

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t^2}{m^2} p_1^2 \nabla_{\xi_1}^2 \delta^6 = \left(\frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 + \frac{3t^2}{m\beta} \nabla_r^2 \right) G_s^{(0)}(r,t)$$

**Proof:

$$\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \frac{t^3}{m^3} \vec{p}_1 \cdot \vec{\nabla}_{\xi_1} \nabla_{\xi_1}^2 \delta(\vec{\xi}_1 - \vec{\xi}_{1o} - \frac{\vec{p}_1 t}{m}) = -\int d^3p_1 \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \vec{p}_1 \cdot \vec{\nabla}_{p_1} \nabla_{p_1}^2 \delta^6 =$$

$$= \int d^3p_1 [3 - \beta/m \, p_1^2] \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}} \nabla_{p_1}^2 \delta^6 =$$

$$= \int d^3p_1 \, \delta^6 \left\{ 3\nabla_{p_1}^2 - \beta/m [6 - 7\beta/m \, p_1^2 + (\beta/m)^2 p_1^{2^2}] \right\} \frac{e^{-\beta p_1^2/2m}}{(2\pi mk_BT)^{3/2}}$$

$$= -\beta/m \left\{ 15 - 10m\beta v^2/t^2 + m^2\beta^2 v^4/t^4 \right\} G_s^{(0)}(r,t)$$

$$= -\beta/m \left\{ \frac{t^4}{m^2\beta^2} \nabla_r^2 \nabla_r^2 G_s^{(0)}(r,t) \right\} \qquad \text{Q.E.D.}$$

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Table D-2: Contributions to $G_s^{(2)}(r,t)$

Term in Collsn Integral	Corresponding Contribution to $G_s^{(2)}(r,t)$
$t^3 \frac{m}{\beta}\nabla_{p_1}^2 f_{11}^{(0)}(t)$	$\frac{t^4}{60}\left(\frac{t^2}{m\beta}\nabla_r^2\right)G_s^{(0)}(r,t)$
$\frac{t^4}{m}\frac{m}{\beta}\nabla_{p_1 q_1}^2$	$\frac{t^4}{30}\left(\frac{t^2}{m\beta}\nabla_r^2\right)G_s^{(0)}$
$\frac{t^5}{m^2}\frac{m}{\beta}\nabla_{q_1}^2$	$\frac{t^4}{6}\left(\frac{t^2}{m\beta}\nabla_r^2\right)G_s^{(0)}$
$t^3\,\vec{p}_1\cdot\vec{\nabla}_{p_1}$	$-\frac{t^4}{20}\left[\frac{t^2}{m\beta}\nabla_r^2+15\right]G_s^{(0)}$
$\frac{t^4}{m}\vec{p}_1\cdot\vec{\nabla}_{q_1}$	$-\frac{t^4}{5}\left(\frac{t^2}{m\beta}\nabla_r^2\right)G_s^{(0)}$
$t^3\left(\vec{p}_1\cdot\nabla_{p_1}\right)^2$	$\frac{t^4}{4}\left[9+\frac{23}{15}\frac{t^2}{m\beta}\nabla_r^2+\frac{1}{15}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\frac{t^4}{m}\vec{p}_1\cdot\vec{\nabla}_{p_1}\,\vec{p}_1\cdot\vec{\nabla}_{q_1}$	$t^4\left[\frac{2}{3}\frac{t^2}{m\beta}\nabla_r^2+\frac{1}{30}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\frac{t^4}{m}\vec{p}_1\cdot\vec{\nabla}_{q_1}\,\vec{p}_1\cdot\vec{\nabla}_{p_1}$	$t^4\left[\frac{13}{15}\frac{t^2}{m\beta}\nabla_r^2+\frac{1}{30}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$t^3\,p_1^2\nabla_{p_1}^2$	$t^4\left[\frac{3}{2}+\frac{1}{4}\frac{t^2}{m\beta}\nabla_r^2+\frac{1}{60}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\frac{t^4}{m}\,p_1^2\nabla_{p_1 q_1}^2$	$t^4\left[\frac{1}{2}\frac{t^2}{m\beta}\nabla_r^2+\frac{1}{30}\frac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$t^3\,\vec{p}_1\cdot\vec{\nabla}_{p_1}\nabla_{p_1}^2$	$-\frac{\beta}{m}t^4\left[\frac{1}{12}\frac{t^2}{m\beta}\nabla_r^2+\frac{t^4}{140\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$

Table D-2 (Cont.)

Term in Collsn Integral	Corresponding Contribution to $G_s^{121}(r,t)$
$\dfrac{t^4}{m}\,\vec{p}_1\cdot\vec{\nabla}_{p_1}\nabla^2_{p_1\zeta_1}$	$-\beta/m\,t^4\left[\dfrac{2}{15}\dfrac{t^2}{m\beta}\nabla_r^2 + \dfrac{t^4}{105\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^5}{m^2}\,\vec{p}_1\cdot\vec{\nabla}_{\zeta_1}\nabla^2_{p_1\zeta_1}$	$-\beta/m\,t^4\left[\dfrac{1}{6}\dfrac{t^2}{m\beta}\nabla_r^2 + \dfrac{t^4}{42\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$t^3\nabla^2_{p_1}\nabla^2_{p_1}$	$\left(\beta/m\right)^2 t^4\left[\dfrac{1}{280}\dfrac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^4}{m}\nabla^2_{p_1}\nabla^2_{p_1\zeta_1}$	$''$
$\dfrac{t^5}{m^2}\nabla^2_{p_1}\nabla^2_{\zeta_1}$	$\left(\beta/m\right)^2 t^4\left[\dfrac{1}{168}\dfrac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^5}{m^2}\nabla^2_{p_1\zeta_1}\nabla^2_{p_1\zeta_1}$	$''$
$\dfrac{t^6}{m^3}\nabla^2_{p_1\zeta_1}\nabla^2_{\zeta_1}$	$\left(\beta/m\right)^2 t^4\left[\dfrac{1}{56}\dfrac{t^4}{m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$t^3\nabla^2_{p_1}\,\vec{p}_1\cdot\vec{\nabla}_{p_1}$	$-\beta/m\,t^4\left[\dfrac{t^2}{20\,m\beta}\nabla_r^2 + \dfrac{t^4}{140\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^4}{m}\nabla^2_{p_1}\,\vec{p}_1\cdot\vec{\nabla}_{\zeta_1}$	$-\beta/m\,t^4\left[\dfrac{t^4}{105\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^4}{m}\nabla^2_{p_1\zeta_1}\,\vec{p}_1\cdot\vec{\nabla}_{p_1}$	$-\beta/m\,t^4\left[\dfrac{t^2}{20\,m\beta}\nabla_r^2 + \dfrac{t^4}{105\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$
$\dfrac{t^5}{m^2}\nabla^2_{p_1\zeta_1}\,\vec{p}_1\cdot\vec{\nabla}_{\zeta_1}$	$-\beta/m\,t^4\left[\dfrac{t^4}{42\,m^2\beta^2}\nabla_r^2\nabla_r^2\right]G_s^{(0)}$

APPENDIX E

THE FUNCTIONAL CALCULUS

In the derivation of kinetic equations appearing in Chapter 7, notions of the functional calculus play an important role. For this reason it is probably helpful to consider some aspects of functionals and their derivatives.

1. "Z is a functional of the function x(t) in the interval (a,b) when it depends on all the values taken on by x(t) when t varies in the interval (a,b)."[**] Thus, the functional is a generalization of the concept of a function of many variables.

Ordinarily, one writes a function of the parameters α, β, ... in the following form: $Z(\alpha, \beta, ...)$. Changing the notation, Z can also be written as: $Z(u_\alpha, u_\beta, ...)$. Now, suppose the set $\{u_\alpha, u_\beta, ...\}$ is a continuous set of infinitely many points in the interval (a,b). The set of variables $\{u_\alpha, u_\beta, ...\}$ can be represented by the function u(t), $t \in (a,b)$. In this way, Z is a functional of u(t), and is written as $Z\left(\overset{b}{\underset{a}{u(t)}}\right)$. Similarly, one can consider quantities which are functionals of more than one function, say, u(t) and v(t) and which are, also, functions of parameters y_1, y_2, ... Such a functional might be written in the following form:

$$F(y_1, y_2, \cdots \mid u(t), v(t)))_,$$

_____

[**]Volterra,[52] Chapter 1, Section 1.

2.   With regard to derivatives, too, the theory of the calculus of

functionals is a direct generalization of the theory of the calculus of

functions of many independent variables. For ordinary functions, the

partial derivative $\dfrac{\partial f}{\partial u_i}$ is related to the total differential through

$df = \sum_i \dfrac{\partial f}{\partial u_i} du_i$. In the theory of functionals, the summation becomes

the integral, $\displaystyle\int \dfrac{\delta F}{\delta u(x)}\, \delta u(x)\, dx = \epsilon \int \dfrac{\delta F}{\delta u(x)}\, \eta(x)\, dx$ and leads to the

following definition:** $F'[u(t); \xi]$, defined as the first derivative

of the functional F with respect to the function u(t) at the point ξ , is

determined by the following relationship:

$$\int_a^b F'[u(t); \xi]\, \eta(\xi)\, d\xi = \lim_{\epsilon \to 0}\left\{ \frac{F[u(t)+\epsilon\eta(t)] - F[u(t)]}{\epsilon} \right\}$$

$$= \int_a^b \frac{\delta F}{\delta u(\xi)}\, \eta(\xi)\, d\xi$$

Another definition, involving somewhat more rigor, is stated as

follows. In the neighborhood of a value x_0, let y(x) be given a continuous

increment Θ(x) which does not change sign, and such that $|\Theta(x)| < \epsilon$

for $x_0 - h \leq x \leq x_0 + h$ and Θ(x) = 0 for x otherwise. Form the limit $\dfrac{\Delta F}{\sigma}$

where $\Delta F = F[y(x) + \Theta(x)] - F[y(x)]$ and $\sigma = \int_a^b \Theta$ (x) dx. If $\dfrac{\Delta F}{\epsilon h} < M$

and if $\dfrac{\Delta F}{\sigma}$ approaches (uniformly) a limit as ϵ and h approach zero in an

arbitrary manner, then the limit is defined as the functional derivative

of F [y(x)] at the point x_0: $F'[y(x); x_0]$. Hence, the definition is

analogous to the definition of the ordinary partial derivative:

** ibid., chapt.I, sec. II.

$$\frac{\partial f}{\partial y_i} = \lim_{h \to 0} \frac{\Delta_i f}{h} = \lim_{h \to 0} \left[\frac{f(y_1, \ldots, y_i + h, \ldots, y_n) - f(y_1, \ldots, y_n)}{h} \right].$$

We note that $F'[y(x); x_0]$ is a functional of $y(x)$ and x_0.

3. In general, by applying successively the rule for $\dfrac{\delta G}{\delta u(y)}$ to the

functionals $G = \dfrac{\delta F}{\delta u(y)}, \dfrac{\delta^2 F}{\delta u(y_1)\delta u(y_2)}, \ldots\ldots,$ etc., one can show, as

a logical consequence, that the appropriate defining relationship for the

n^{th} functional derivative of F is:

$$\frac{d^n}{d\varepsilon^n} \left[F[y(t) + \varepsilon \eta(t)] \right]_{\varepsilon=0} =$$

$$= \int_a^b \int_a^b \ldots \int_a^b F^{(n)}[y(t); \xi_1, \ldots, \xi_n] \eta(\xi_1) \ldots \eta(\xi_n) d\xi_1 \ldots d\xi_n$$

4. Let us now make use of the definition of the functional derivative

to derive some relations which shall be useful in the ensuing discussion.

a) Suppose $F[u] = \int a(x) u(x) dx.$ Then $\Delta F = F[u(x) + \varepsilon \eta(x)] -$

$-F[u(x)] = \varepsilon \int a(x) \eta(x) dx + \Theta(\varepsilon^2)$ so that the definition,

$\lim\limits_{\varepsilon \to 0} \Delta F / \varepsilon = \int \dfrac{\delta F}{\delta u(x)} \eta(x) dx$ implies: $\dfrac{\delta F}{\delta u(x)} = a(x)$.

b) Suppose $F[u] = u(y).$ Therefore, $\dfrac{F[u+\varepsilon\eta] - F[u]}{\varepsilon} = \eta(y) = \int \dfrac{\delta F}{\delta u(x)} \eta(x) dx.$

Hence, $\dfrac{\delta F}{\delta u(x)} = \dfrac{\delta u(y)}{\delta u(x)} = \delta^{dirac}(x-y)$.

c) Product Differential Rule for Functionals:

Suppose $F = A[u(x)] \cdot B[u(x)]$, where A and B are both

regular homogeneous functionals of degree 1[**], viz., $A[u(x)] =$

$= \int a(x)\, u(x)\, dx$ and $B[u(x)] = \int b(y)\, u(y)\, dy$. In this case,

$$\Delta F = F[u+\varepsilon\eta] - F[u] = \iint a(x)\, b(y)\left\{(u(x)+\varepsilon\eta(x))(u(y)+\varepsilon\eta(y)) - u(x)\, u(y)\right\}dx\, dy$$

$$= \varepsilon \iint a(x)\, b(y)\left[\eta(x)\, u(y) + \eta(y)\, u(x)\right]dx\, dy + \Theta(\varepsilon^2) =$$

$$= \varepsilon \iint \left[a(x)\, b(y) + a(y)\, b(x)\right]\eta(x)\, u(y)\, dx\, dy + \Theta(\varepsilon^2).$$

$$\therefore \frac{\delta F}{\delta u} = \frac{\delta A[u] \cdot B[u]}{\delta u} = \int \left[a(x)\, b(y) + a(y)\, b(x)\right] u(y)\, dy =$$

$$= \frac{\delta A(u)}{\delta u} \cdot B[u] + A[u] \frac{\delta B[u]}{\delta u}.$$

$$q.e.d.$$

d) Suppose $F_n[u(x)]$ is a regular homogeneous functional of

degree n, i.e., $F_n[u(x)] = \int_{..} \int a(x_1,\ldots,x_n)\, u(x_1)\ldots u(x_n)\, dx_1..dx_n$

and, in addition, the kernel $a(x_1,\ldots,x_n)$ is symmetric with respect

to permutation of its n variables.

Then, $\Delta F_n = F_n[u+\varepsilon\eta] - F_n[u] = \varepsilon\int_{..}\int a(x_1,\ldots x_n)\left[\{\eta(x_1)u(x_2)\ldots u(x_n)\} + \ldots\right.$

$$\left. + \ldots + \{u(x_1)\ldots\eta(x_n)\}\right]dx_1\ldots dx_n$$

$$= \varepsilon\int_{..}\int \left[\sum_{j=1}^{n} a(x_1,\ldots,x_n)\right]\eta(x_1)u(x_2)\ldots u(x_n)\, dx_1\ldots dx_n + \Theta(\varepsilon^2)$$

Hence, due to the symmetric property of the kernel, a, the first functional derivative is

$$\frac{\delta F_n}{\delta u(x_1)} = n \int \ldots \int a(x_1, \ldots, x_n) u(x_2) \ldots u(x_n) dx_2 \ldots dx_n .$$

Repeated differentiation yields, for the sth functional derivative:

$$\frac{\delta^s F_n}{\delta u(x_1) \ldots \delta u(x_s)} = \frac{n!}{(n-s)!} \int \ldots \int a(x_1, \ldots, x_n) u(x_{s+1}) \ldots u(x_n) dx_{s+1} \ldots dx_n$$

$$q.e.d.$$

APPENDIX F

THE BBGKY HIERARCHY

By successive integration over the coordinates of the particles

of the assembly, the Liouville equation can be transformed into a

hierarchy of coupled integro-differential equations, each of which pro-

vides the temporal evolution of the s particle probability density in terms

of the s + 1st density.

For an isolated system for which the internal potential energy

can be considered to be the sum of two-body interactions, the Liouville

equation may be written as:

$$\frac{\partial f_{n,n}}{\partial t} = \left[H_n^0 + \sum_{i<j}^{n} \varphi_{ij} ; f_{n,n} \right] \qquad \qquad \cdots \cdots \text{(F.1)}$$

where $H_n^0 = \sum_{i=1}^{n} p_i^2/2m$ is the Hamiltonian of motion and $\sum_{i<j} \varphi_{ij}$

is the internal potential energy of the assembly. Let the n-particle

density be designated as $f_{n,n}(X_n;t| x_{1o})$, as a reminder that the sys-

tem is symmetric under interchange of designation of any pair of

particles, <u>except</u> a pair in which one of the members is particle num-

ber 1.[**]

Integrate the Liouville equation over the coordinates $x_{-s+1}, \ldots, x_{-n}$.

One obtains:

[**] In other words, all particles of the assembly are assumed to be of the
same type; however, by focusing attention on particle #1, the initial
probability $f_{n,n}(X_n;o|x_{1o})$ is not symmetric under interchange of the
variable x_1 with any other x_j. On the other hand, $f_{n,n}(X_n;o|x_{1o})$
is invariant under interchange of the designation of all other particles;
$f_{n,n}(X_n;t|x_{1o})$ will therefore have a similar symmetry.

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$$\frac{\partial f_{s,s}(\vec{X}_s;t|\vec{x}_{10})}{\partial t} = [H_s^0 + \sum_{i<j}^{ss} \varphi_{ij} \; ; \; f_{s,s}] +$$

$$+ \int d\kappa_{s+1}..d\kappa_n \left[\sum_{i=1}^{s} \sum_{j=s+1}^{n} \varphi_{ij} \; ; \; f_{n,n}(\vec{X}_n;t|\vec{x}_{10}) \right] \qquad \overline{} \cdots \quad (F.2)$$

where $f_{s,s}(\vec{X}_s;t|\vec{x}_{10})$ is defined by Eq. (3.2) of the text. To derive

Eq. (F.2) we have noted that $\iint d\rho_i \, d\rho_j \left[\varphi_{ij} \; ; \; f_{n,n} \right] = 0$

and that, also, $\int d q_i \left[\rho_{i/2m}^2 \; ; \; f_{n,n} \right] = 0$.

Now, because of the symmetry properties of $f_{n,n}(\underline{X}_n; t|\underline{x}_{1_0})$,

the previous equation yields the hierarchy:

$$\frac{\partial f_{s,s}(\vec{X}_s;t|\vec{x}_{10})}{\partial t} - [H_s^0 + \sum_{i<j}^{ss} \varphi_{ij} \; ; \; f_{s,s}] =$$

$$= (n-s) \int d\kappa_{s+1} \left[\sum_{i=1}^{s} \varphi_{i,s+1} \; , \; f_{s+1,s+1} \right] \qquad \cdots \cdots \; (F.3)$$

On the other hand, suppose we had specified the initial positions

of _two_ of the particles. Then, in contrast to the usual form of the

equations of the hierarchy (F.3), the following set would be obtained:

$$\frac{\partial f_{1,1}(\vec{x}_1;t|\vec{x}_{10},\vec{x}_{20})}{\partial t} + \frac{\vec{p}_1}{m} \cdot \vec{\nabla}_1 \, f_{1,1}(\vec{x}_1;t|\vec{x}_{10},\vec{x}_{20}) =$$

$$= \int d\vec{x}_2 [\varphi_{1,2} \; , \; f_{2,2}(\vec{x}_1,\vec{x}_2;t|\vec{x}_{10},\vec{x}_{20})] + \qquad \cdots \cdots \; (F.4a)$$

$$+ (n-2) \int d\vec{x}_3 [\varphi_{1,3} \; , \; f_{2,2}(\vec{x}_1,\vec{x}_3;t|\vec{x}_{10},\vec{x}_{20})]$$

$$\frac{\partial f_{1,1}(\vec{x}_2;t|\vec{x}_{10},\vec{x}_{20})}{\partial t} + \underset{\sim}{\vec{p}_2} \cdot \vec{\nabla}_{\vec{x}_2} f_{1,1}(\vec{x}_2;t|\vec{x}_{10},\vec{x}_{20}) =$$

$$= \int dx_1 \left[\varphi_{1,2} ; f_{2,2}(\vec{x}_1,\vec{x}_2;t|\vec{x}_{10},\vec{x}_{20}) \right] + \qquad \cdots \qquad \text{(F.4b)}$$

$$+ (N-2) \int dx_3 \left[\varphi_{2,3} ; f_{2,2}(\vec{x}_2,\vec{x}_3;t|\vec{x}_{10},\vec{x}_{20}) \right]$$

$$\frac{\partial f_{s,s}(\vec{x}_s;t|\vec{x}_{10},\vec{x}_{20})}{\partial t} - \left\{ H_s^o + \sum_{i<j}^{ss} \varphi_{ij} ; f_{s,s}(\vec{x}_s;t|x_{10},x_{20}) \right\} =$$

$$= (N-s) \int dx_{s+1} \left[\sum_{i=1}^{s} \varphi_{i,s+1}, f_{s+1,s+1}(\vec{x}_{s+1};t|x_{10},x_{20}) \right) \qquad \text{(F.4c)}$$

$$s \geq 2 ; (1,2) \in \{s\}$$

Both sets, (F.3) and (F.4) are pertinent to the main text of this analysis.

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