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 \( \mu \)-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 double expansion in \( c \) and \( \mathcal{E}c \), where \( c \) is the density, and \( \mathcal{E} \) is a coupling constant.
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 understanding 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 probability 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 densities for locating particles moving within an equilibrium assembly. A particular example of these functions is $G(r,t)$, the probability density for finding a particle in the neighborhood of a point of configuration 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. Chapter two 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 chapter three, 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 chapter four. 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 consistent with the expansion of the collision integral, is developed in chapter five. 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 $\mu$-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 chapter six, 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 chapter seven Bogoliubov type kinetic equations\(^3\) are developed to provide density 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.

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

\*\* 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 chapter nine.

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 extension of the theory to systems with attractive forces, while requiring some new calculation, is quite straightforward. However, when one tries to obtain expressions for the two particle densities, modifications are necessary because 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 statistical 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. The particular methods used in this thesis were chosen simply because they seemed best for the particular problem at hand. This point is discussed at greater 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 analogous 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: \(^1,6,7\)

\[
\frac{2^2 \sigma}{\Omega \hbar} = \frac{1}{4\pi} \frac{K'}{K_0} \left( a_{coh}^2 S_{coh}(\vec{k}', \omega) + a_{inc}^2 S_{inc}(\vec{k}, \omega) \right) \quad \ldots (2.1)
\]

In the above, \(E_0\) is the energy of the incident neutron; \(E'\) is the energy of the scattered neutron; \(K_0\) and \(K'\) are the associated wave-numbers; \(\omega = \hbar^{-1}(E_0 - E')\); \(\vec{k} = \vec{k}'\); 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:

\[
S_{coh}(k, \omega) \equiv \left[ \frac{1}{dt} \right] \frac{1}{d\vec{k}} e^{-i[\omega t - \vec{k} \cdot \vec{r}]} G(r, t) \quad \ldots (2.3a)
\]

and

\[
S_{inc}(k, \omega) \equiv \left[ \frac{1}{dt} \right] \frac{1}{d\vec{k}} e^{-i[\omega t - \vec{k} \cdot \vec{r}]} G_s(r, t) \quad \ldots (2.3b)
\]
G(r,t) and G_s(r,t) are defined by:

\[ G(r,t) = \frac{1}{n} \left\langle \sum_{k=1}^{N} \int \delta(\mathbf{r} + \mathbf{q}_k(0) - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{q}_j(t)) \, d\mathbf{r}' \right\rangle \tag{2.4a} \]

and

\[ G_s(r,t) = \frac{1}{n} \left\langle \sum_{j} \int \delta(\mathbf{r} + \mathbf{q}_j(0) - \mathbf{r}') \delta(\mathbf{r}' - \mathbf{q}_j(t)) \, d\mathbf{r}' \right\rangle \tag{2.4b} \]

n = the number of particles in the scattering assembly.

q_k(0) and q_j(t) are the positions of the k\textsuperscript{th} nucleus at t = 0, and of the j\textsuperscript{th} nucleus at time t, respectively.

The expectation values denoted by \( \langle \ldots \ldots \rangle \) 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:

\[ G(r,t) = \text{the probability density for finding a particle in the neighborhood of } r \text{ at time } t, \text{ given that there was a particle at } r = 0 \text{ at } t = 0; \tag{2.5a} \]

\[ G_s(r,t) = \text{the probability density for finding a particle at } r \text{ at time } t, \text{ given that the same particle was at } r = 0 \text{ at } t = 0. \tag{2.5b} \]
It is quickly seen that, in the interpretation of classical mechanics, 2.5a follows from 2.4a. Viz., by definition,

\[ G(r,t) = \frac{1}{n} \left\langle \sum_{k, q_{k_0}} \int d\tilde{r} \left[ \delta(\tilde{r} + \tilde{q}_{k}(0) - \tilde{r}') \delta(\tilde{r}' - \tilde{q}_{j}(t)) \right] \right\rangle \]

\[ = \frac{1}{n} \sum_{k, q_{k_0}} \int d\tilde{r} \left[ \delta(\tilde{r} + \tilde{q}_{k}(0) - \tilde{r}') \delta(\tilde{r}' - \tilde{q}_{j}(t)) \right] \]

But, the classical joint expectation of any quantity, 
\[ \langle J_{1}(X_0)J_{2}(X_0) \rangle \]

is defined by

\[ \langle J_{1}(X)J_{2}(X_0) \rangle = \int dx_0 \int dx J_{1}(X)J_{2}(X_0) f(x_0) f(x_0 | x_0) \]  \hspace{1cm} (2.6)

where \( J(X) \) is a function of the phase variable \( X = (\tilde{x}_1, ..., \tilde{x}_s) \).

\( f(x_0) \) is the probability density for \( X \) at \( t = 0 \); \( f(x_0 | x_0) \) is the conditional density for \( X \subset t \), given that at \( t = 0, X_0 \).

Thus,

\[ G(r,t) = \frac{1}{n} \sum_{k, q_{k_0}} \int d\tilde{r}' \int dq_{k_0} dq_{j} \delta(\tilde{r} + \tilde{q}_{k}(0) - \tilde{r}')\delta(\tilde{r}' - \tilde{q}_{j}(t)) f(\tilde{q}_{j} | \tilde{q}_{k_0}) f(\tilde{q}_{k_0}) \]

\[ = \frac{1}{n} \sum_{k, q_{k_0}} \int d\tilde{r}' \int dq_{k_0} \delta(\tilde{r} + \tilde{q}_{k}(0) - \tilde{r}') f(\tilde{r}' | \tilde{q}_{k_0} ; t) \frac{1}{\Omega} \]

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\(^{**}\), \( f_0(q_{k_0}) = \frac{1}{\Omega} \), where \( \Omega \)

is the volume occupied by the assembly. Next, performing the integration over \( r' \):

\(^{**}\)Here, we assume also that the scattering system is isotropic.
\[ G(r,t) = \frac{1}{n} \sum_{q_{k_0}} \int_{q_{k_0}}^{q_{k_0} + \Delta q_{k_0}} f_{j,k}(\vec{r} + \vec{q}_{k_0} | \vec{q}_{k_0}; t) / \Omega \]

But, \( f(\vec{r} + \vec{q}_{k_0} | \vec{q}_{k_0}; t) = f(\vec{r} | 0; t) \) . Recognizing this, and summing over \( k \) and \( j \) after performing the integration over \( q_{k_0}^{+} \).

\[ G(r,t) = f_{k,k}^{\text{self}}(r|0; t) + (n-1) f_{j,k}^{\text{distinct}}(r|0; t) , \]

In the above equation, \( f_{k,k}^{\text{self}}(r|0; t) \) is the probability density for finding the \( k^{th} \) 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 \( j^{th} \) particle at \( r \) @ time \( t \), given that the \( k^{th} \) designated particle \( (j \neq k) \) was located at \( r = 0 \) @ \( t = 0 \).

Thus,

\[ G_s(r,t) = f_{k,k}^{\text{self}}(r|0; t) \] \hfill (2.7a)

Frequently, there is also defined:

\[ G_d(r,t) = (n-1) f_{d}^{\text{distinct}}(r|0; t) \] \hfill (2.7b)

---

**Anticipating, somewhat, we note that**

\[ G_d(r,0) = c g_2(r) \]

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 for the purpose of relating the exact cross section to scattering functions, $S(k, \omega)$, determined from the 'classical' G functions. Clearly, there is some advantage to proceeding 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 $\Gamma$-space.

Thus, we wish to find some way of calculating $f_{s,s}(X_s; t | X_{s_0})$ ** which, when multiplied by $dx_1 \ldots dx_s$, is the $**X_s$ is the six-$s$ dimensional vector, $(x_1, \ldots, x_s)$. $x_1$ is the 6-dimensional vector, $(q_1, p_1)$.
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 \(x_{10}, \ldots, x_{s_0}\). \(f_{s,s}(X_s; t|X_{s_0})\) 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.,

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

\(H_n(X_n)\) 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.,

\[
\{ H, f_{n,n} \} = \sum_{i\in\mathcal{N}} \{ q_i, H \} \frac{\partial}{\partial p_i} f_{n,n} - \{ p_i, H \} \frac{\partial}{\partial q_i} f_{n,n}.
\]

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 directed towards obtaining kinetic equations for "distribution functions" 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 calculations 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-differential 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:

\[
\frac{\partial f_{s,s}}{\partial t} = \left[ H_s, f_{s,s} \right] = (n-s) \int d\hat{x}_{s+1} \left[ \sum \phi(q_j - \hat{q}_{s+1}); f_{s+1,s+1} \right]
\]

\(\ldots \ldots \) (2.9)

Unfortunately, this is an almost empty scheme, because to determine the \(s^{th}\) order distribution one must know, first, higher order distributions which are themselves to be determined from similarly open equations.

Of course, one might try to find some way of terminating the chain of kinetic equations at low order. Commonly employed is the "superposition approximation", which consists of assuming that the \(s+1^{st}\) order distribution is proportional to products of \(s\) order distributions. E.g., to terminate the BBGKY hierarchy at second order, it is assumed that

**...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.** \( ^{3,12} \)

For example, Bogoliubov \( ^{3} \), 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 determinanistic 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

** On the other hand, it has been shown that the superposition 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,

\[ \hat{f}_{s_s}(X_s;t) \equiv \frac{1}{\tau} \int_{0}^{\tau} \int \cdots \int dx_{s+1} \cdots dx_n \ f_{n_n}(X_n;t+\lambda), \]

defined for small but finite \( \tau \). 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 has indicated that these assumptions imply a lack of correlations between particles before collision, an assumption akin to the Strosszahltansatz of Boltzmann.)**

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

Prigogine and collaborators\textsuperscript{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 investigated. An elaborate diagram scheme, analogous to those used in the quantum theory of fields, has been developed to expedite 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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, 
\[ \Pr = \frac{1}{\mathbb{R}^n} \int dq_1 \cdots dq_n, \]  
and manipulating the Liouville equation in a clever way, Zwanzig derived \(^2,^7\) the following equation for the one particle non-equilibrium momentum density:

\[
\frac{\partial f_{0,1}(p_1; t)}{\partial t} = \int d^p_{2 \cdots n} (PrL) \int ds e^{-L(1-Pr)L} f_{0,n}(p_1, \ldots, p_n; t-s) + \]
\[
+ Pr L e^{-L(1-Pr)L} \int d^p_{n+1} f_{n,n}(X_n; 0). \]

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

** 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 transforms 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 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 or Schofield.
A central problem of irreversible statistical mechanics has been the derivation of kinetic equations necessary for the description of the temporal behavior of pertinent reduced probability densities. Here, this question is discussed in detail for the particular case of time-relaxed probability densities in equilibrium assemblies. Interest in these functions is not only intrinsic; as has been indicated in the previous chapter, various quantities of physical importance 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 systems, 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 in his studies of the approach to equilibrium.

Let it be agreed that

\[
\begin{align*}
\mathcal{F}_{n,n} ( \gamma_1, \ldots, \gamma_n; \lambda_1, \ldots, \lambda_n; t, \lambda_0, \ldots, \lambda_{so}, \lambda_{so}, \ldots, \lambda_{so} ) & \equiv \\
\mathcal{F}_{n,n} ( X; t; X ) & \equiv (3.1)
\end{align*}
\]
will represent the conditional probability density for finding a specified isolated n-particle system in the neighborhood of a point \((\hat{q}_1, \ldots, \hat{q}_n, \hat{p}_1, \ldots, \hat{p}_n)\approx X_n\) of \(\Gamma\)-space, at time \(t\), given that at \(t = 0, X_s = X_{s_0}\). (\(X_s\) designates a point in a pertinent \(6s\) dimensional reduced phase space.)

Marginal densities** are obtained from \(f_{n,n}(X_n;t|X_{s_0})\) in the following manner:

\[
f_{a,b}(\hat{q}_1, \ldots, \hat{q}_a; \hat{p}_1, \ldots, \hat{p}_b; t|X_s) = \int \int \cdots \int d_{a+1}q_{a+1} \cdots d_{b+1}q_{b+1} f_{n,n}(X_n;t|X_s).
\]

is the marginal conditional density, with respect to \(f_{n,n}(X_n;t|X_{s_0})\), for finding the set of position coordinates \(\{q_1, \ldots, q_n\}\) and momentum coordinates \(\{p_1, \ldots, p_n\}\) in the neighborhood of the point \((q_1, \ldots, q_a, p_1, \ldots, p_a)\) of the appropriate reduced \(\Gamma\)-space, at time \(t\), given that at \(t = 0, X_s = X_{s_0}\).

It is noted that \(f_{a,b} \geq 0\) and that

\[
\int d_{a+1}q_{a+1} \cdots d_{b+1}q_{b+1} f_{a,b}(\hat{q}_1, \ldots, \hat{q}_a; \hat{p}_1, \ldots, \hat{p}_b; t|X_s) = 1
\]

for all \(a, b\).

As is well known, once the initial state \(f_{n,n}(X_n;0|X_{s_0})\) is specified, \(f_{n,n}(X_n; t|X_{s_0})\) is determined for all time by the Liouville equation. The latter may be written in the following convenient form:

\[
\frac{\partial}{\partial t} f_{n,n}(X_n; t|X_{s_0}) = L f_{n,n}(X_n; t|X_{s_0}) \quad \ldots \ldots \quad (3.3)
\]

** 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,

\[
L_0 = - \sum_{i=1}^{n} \frac{\dot{q}_i}{p_i} \cdot \hat{v}_i \tag{3.4a}
\]

\[
L_1 = \frac{1}{2} \sum_{j \neq k} \sum_{i=1}^{n} \frac{\partial V(|q_i - q_j|)}{\partial q_j} \cdot \left( \frac{\dot{q}_j}{p_j} - \frac{\dot{q}_k}{p_k} \right) \tag{3.4b}
\]

\[
L_2 = \sum_{i=1}^{n} \sum_{l=1}^{n} \frac{\partial u^{[i]}}{\partial q_i} \cdot \hat{v}_i \tag{3.4c}
\]

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 \( i \)th and \( j \)th particles and \( u^{[i]} \) is the external potential acting upon the \( i \)th 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, \( f_{1,1}(P_1, q_1; t | P_{1o}, q_{1o}) \), defined as the probability density for finding particle \# 1 in the neighborhood of the phase point \( (q_1, P_1) \) at time \( t \), given that it was at \( (q_{1o}, P_{1o}) \) 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:

\[ \mathcal{O} \equiv f_{n|1}(x_2, \ldots, x_n; 0|x_1) \int \cdots \int d^6x_2 \cdots d^6x_n \ldots \quad (3.5) \]

where \( f_{n|1}(0) \) designates the probability density at \( t = 0 \) for finding the n-1 particle subsystem in the neighborhood of phase point \((x_2, \ldots, x_n)\), given that the coordinates of particle #1 are \( x_1 = (\mathcal{E}_1, \mathcal{Q}_1) \).

Note that, once given \( f_{n,n}(x_1, \ldots, x_n; 0) \), 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 \( \mathcal{O} \) is a projection operator; i.e.,

\[ \mathcal{O}^{2} F_{n}(X; t) = \mathcal{O} F_{n}(X; t) \], 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:

\[ \mathcal{O} \frac{\partial f_{n|1}}{\partial t} (X; t|x_1; \mathcal{O}) = \mathcal{O} L \left( \mathcal{O} f_{n,n} + (1-\mathcal{O}) f_{n,n} \right) \ldots \quad (3.6) \]

\[ (1-\mathcal{O}) \frac{\partial f_{n,n}}{\partial t} = (1-\mathcal{O}) L \left( \mathcal{O} f_{n,n} + (1-\mathcal{O}) f_{n,n} \right) \ldots (3.7) \]

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

\[ (1-\mathcal{O}) f_{n,n} = \int_{0}^{t} ds \, e^{s(1-\mathcal{O}) L(1-\mathcal{O}) L_{0}} f_{n|1}(0) f_{1,1}(x_1; t-s|x_1; \mathcal{O}) + e^{t(1-\mathcal{O}) L(1-\mathcal{O})} f_{n,n}(X; 0|x_1; \mathcal{O}) \]

\[ \ldots \quad (3.8) \]
Placing (3.8) into (3.6), one obtains:

\[
\frac{d}{dt} \mathbb{S}_{\perp, n, n} (X_n; t \mid X_0) = \mathcal{G} \mathbb{S}_{\perp, n, n} + \int_{t}^{+} dt \mathcal{G} \mathbb{S}_{\perp, n, n} \mathcal{L} (1-\Phi) \mathcal{L} \mathbb{S}_{\perp, n, n} f_n (t-\tau) + \mathcal{G} \mathbb{S}_{\perp, n, n} \mathcal{L} (1-\Phi) \mathbb{S}_{\perp, n, n} (X_n; 0 \mid X_0) \quad (3.9)
\]

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 equilibrium assembly of like particles) the initial condition for the full n - particle density, conditioned upon the positions of a designated subset of s particles, is given by:

\[
f_{n,p}^n (X_n; 0 \mid X_s) = \frac{e^{-\beta V(q_1^0, \ldots, q_s^0, q_{s+1}^0, \ldots, q_n^0)} e^{-\frac{1}{2m} \sum_{i=1}^{n} p_i^2}}{Z_{q_n}} \left( \frac{\prod_{i=1}^{s} \delta(q_i^0 - q_{i,}\delta(p_i^0, - q_{i,}^0))}{(2\pi mkT)^{3n/2}} \right) \delta_{eq} (q_{1,}^0, \ldots, q_{s,}^0) \quad (3.10)
\]

Here,

\[
Z_{q_n} = \int dq_1 \ldots dq_n e^{-\beta V(q_1, \ldots, q_n)} \quad (3.11)
\]

and

\[
f_{eq} (q_1, \ldots, q_s) = \int dq_1^0 \ldots dq_n^0 dp_1 \ldots dp_n f_{eq}^n (X_n) = \frac{e^{-\beta \sum_{i=1}^{n} p_i^2/2m}}{(2\pi mkT)^{3n/2}} \int dq_1 \ldots dq_n e^{\beta V(q_1, \ldots, q_n)}/Z_{q_n} \quad (3.12)
\]

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 \( x_i = (q_i, p_i) \)

**i.e., set \( L_2 = 0 \). This condition will be relaxed later.
It is certainly true that \( f_{n,n} (x;0|x_n) = \prod_{i=1}^{n} \delta(x_i - x_i^0) \).

But, the quantities of interest here are of the form:

\( f_{n,n} (X;0|X_{s_0}) \), i.e., the probability density for finding the system in the neighborhood of \( X_n \) given the exact position of the subset of particles \#1's \((1 + s)\) 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:**

\[
\begin{align*}
  f(X|Y) &= \int_{X} f(X|Y,Z) f(Z|Y) \, dz' \\
  &= \int_{X} \int_{X} f(X|Y,Z) \, dz' \\
  &= \int_{X} \int_{X} f(X|Y,Z) \, dz' \\
  &= \int_{X} \int_{X} f(X|Y,Z) \, dz'
\end{align*}
\]

The generalization of this relationship leads us to the conclusion:

\[
\begin{align*}
  f(X;0|X_{s_0}) &= \int_{X} \int_{X} f(X;0|X_{s_0}) \, f(X_{s+1};...;x_n|X_{s_0}) \\
  &= \int_{X} \int_{X} f(X;0|X_{s_0}) \, f(X_{s+1};...;x_n|X_{s_0})
\end{align*}
\]

But, because

\[
\begin{align*}
  f_{X|Y}(x|y) &= f(X|Y)/f(Y)
\end{align*}
\]

we have

\[
\begin{align*}
  f_{X|Y}(x|y) &= f[X(X_{s_0})]/f[X_{s_0}]
\end{align*}
\]

Therefore:

\[
\begin{align*}
  f_{n,n} (X;0|X_{s_0}) &= \\
  &= \int_{X} \int_{X} \delta(x - x_i) \... \delta(x - x_i) \prod_{i=1}^{n} \delta(x_i - x_i^0) \, f[X_{s+1};...;x_n|X_{s_0}]
\end{align*}
\]

**For proof of this statement refer to appendix A.
In particular, as a special case of (3.10):

$$f_{n,n} (x_0 | x_{1o}) = \frac{e^{-\beta V(q_1, \ldots, q_n)}}{Z_n / \Omega_n} \frac{\beta \mu^2_{i,2}}{2m} \delta(q_{1l} - q_{1o}) \delta(p_{1l} - p_{1o})$$

Note how this differs from \( f(0) \), the latter being given by:

$$f_{n|l} (x_2 \ldots n; x_0 | x_{1o}) = \frac{e^{-\beta V(q_1, \ldots, q_n)}}{Z_n / \Omega_n} \frac{\beta \mu^2_{i,2}}{2m} \frac{3(n-1)/2}{(2\pi mkT)^{3(n-1)/2}}$$

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

$$\Theta f_{n,n} (x_0 | x_{1o}) = f_{n|l} (x_2 \ldots n; x_0 | x_{1o}) \cdot f(x_0 | x_{1o}) = f_{n,n} (x_0 | x_{1o})$$  \( \ldots (3.15) \)

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

\((1-\Theta) f_{n,n} (x_0 | x_{1o}) = 0\). In this way, the simplification of the kinetic equation has been initiated.

Further simplification ensues upon noting that:

$$\Theta L \Theta f_{n,n} = f_{n|l} \left\{ \frac{-\beta}{m} \cdot \check{q}_1 \right\} f_{l,l} (x_1; t | x_{1o})$$  \( \ldots (3.16) \)

This statement is true because

1) \( \Theta L \Theta f_{n,n} = \Theta (\frac{-\beta}{m} \cdot \check{q}_1) \Theta f_{n,n} = f_{n|l} (\frac{-\beta}{m} \cdot \check{q}_1) f_{l,l} (x_1; t | x_{1o}) \)

which follows due to the fact that, in the limit

\(\Omega \rightarrow \infty\), \( \int d\check{q}_2 \ldots d\check{q}_n \) \( \check{q}_i \) yields boundary terms which

\( \rightarrow 0 \) for \( i \neq 1; \)

2) \( \Theta L \Theta f_{n,n} = 0 \) if \( f_{n|l} (x_2 \ldots n; x_0 | x_{1o}) \)

is an even function of the variables \( (\check{q}_{1i} - \check{q}_{1o}), i = 2, 3, \ldots, n \).

This is due to the fact a typical contribution will be
proportional to 
\[ \int d\xi_2 \ldots d\xi_n \tilde{F}_{1j} \left( |q_j - q_1| \right) \frac{\partial}{\partial p_j} |1 f_{1,1} \]
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 ourselves only with particles moving through equilibrium assemblies. Other non-equilibrium problems might be attacked this way (e.g., upon the assumption of binary isotropic interactions, (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 because 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,
\[ \int d\xi_2 \ldots d\xi_n \tilde{F}_{12}(q_2 - q_2) \frac{\partial}{\partial p_1} |1 f_{1,1} = \frac{1}{\Omega} \int d\xi_2 \tilde{F} \frac{\partial}{\partial p_1} g_2(q_2 - q_1) f_{1,1} \]
where \( \Omega \) 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 total contribution from these terms will \( \propto \Omega^{\frac{N}{n}} = \Omega^{\frac{1}{3}} \)
Thus, in the limit \( \Omega \to \infty \), \( n \to \infty \), \( n/\Omega = c \), \( c \) = constant, such contributions become vanishingly small.
general, the full knowledge of the initial probability density will be unknown. On the other hand, at least \( f_{n,1}(x_1;0) \) must be known for the problem to have a meaning.

A good guess would have to be made for \( f_{n,1}(x_2, \ldots, x_n;0|x_1) \).

Let us remember that to obtain the simplifications 3.15 and 3.16 the absence of external fields was required (cf. p. 34). 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

\[
\mathcal{Q} \mathcal{L} \mathcal{G} f_{n,n} = f_{n,1}(0) \left\{ \frac{\mathbf{p}_1}{m} \cdot \mathbf{v}_1 + \frac{\partial \mathbf{u}^{\text{ext}}}{\partial \mathbf{q}_1} \cdot \mathbf{v}_1 \right\} f_{1,1}(x_1;t|x_1;0)
\]
\[ f_{1,1}(P_1, Q_1; t| P_{10}, Q_{10}) \] may now be written

\[
\frac{3f}{\tau t,1,1}(x,\tau t| x, l_0) + \frac{m}{2} q_1 f_{1,1} =
\]

\[
= \mathcal{O} \int_0^t L e^{(1-\mathcal{O})L} f_{n|1}(0) f_{1,1}(x_{1|t-\tau} , x_{1|l_0})
\]

In the above equation,

\[(3.19) \quad \mathcal{O} \equiv \int d\hat{x}_2, \ldots, d\hat{x}_n
\]

(In other words, \( \mathcal{O} = f_{n|1}(0) \mathcal{O} \) and \( f_{1,1}(x_{1|t}, x_{1|l_0}) = \mathcal{O} f_{n|n}(x_{n|t}, x_{n|l_0}) \))

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

$$\mathcal{Q}_s = \int f_{\frac{n}{s}}(x_{s+1}, \ldots, x_n; 0|x_1, \ldots, x_s) \prod_{i=1}^{s} dx_{s+i} \ldots dx_n \quad \ldots \quad (3.20)$$

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

$$\mathcal{Q}_s f_{\frac{n}{n}}(0) = f_{\frac{n}{n}}(0) \quad \Rightarrow \quad (1 - \mathcal{Q}_s) f_{\frac{n}{n}}(0) = 0.$$ 

In analogy to 3.16, we have:

$$\mathcal{Q}_s \mathcal{L} \mathcal{Q}_s f_{\frac{n}{n}} = f_{\frac{n}{s}} \int dx_{s+1} \ldots dx_n \left[ \sum_{i=1}^{s} \sum_{m \neq i} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} \right] f_{\frac{n}{s}}(0) f_{\frac{s}{s}} =$$

$$= f_{\frac{n}{s}}(0) \int dx_{s+1} \ldots dx_n \left[ \sum_{i=1}^{s} \sum_{m \neq i} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} \right] f_{\frac{n}{s}} f_{\frac{s}{s}}(t)$$

where

$$\hat{D}_{i,j} = \left( \frac{1}{2} \frac{\partial^2}{\partial x_i \partial x_j} \right) \quad \ldots \quad (3.22)$$

This follows because

$$\mathcal{Q}_s \mathcal{L} \mathcal{Q}_s f_{\frac{n}{n}} = f_{\frac{n}{s}} \int dx_{s+1} \ldots dx_n \left[ \frac{1}{2} \sum_{i=1}^{s} \sum_{m \neq i} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} \right] f_{\frac{n}{s}}(0) f_{\frac{s}{s}} =$$

$$= f_{\frac{n}{s}}(0) \left[ \frac{1}{2} \sum_{i=1}^{s} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} \right] f_{\frac{s}{s}}(t)$$

where $$\int dx_{s+1} \ldots dx_n \left[ \sum_{i=1}^{s} \sum_{m \neq i} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} \right] f_{\frac{n}{s}} = 0$$ by virtue of integration over an odd function. We have, in the above argument, noticed that

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

As a result, the kinetic equation describing the evolution of the s-particle density in the absence of external forces is given by

$$\frac{\partial f}{\partial t} = \mathcal{S}_s \left( X_s ; t | X_s \right) + \sum_{i=1}^{s} \frac{1}{2} q_i \hat{\mathcal{F}}_{ij} \hat{\mathcal{D}}_{ij} f_{\frac{s}{s}} =$$

$$= \mathcal{Q}_s \int dt \mathcal{L} e^{\tau (1 - \mathcal{Q}_s)} L f_{\frac{n}{s}}(0) f_{\frac{s}{s}}(x; t - \tau | X_s)$$

$$= \mathcal{Q}_s \left[ H_s f_{\frac{s}{s}} \right] =$$
In particular, for particles moving through an equilibrium assembly:

\[
    f_{n|s}(0) = \frac{\Omega_s e^{-\beta V(q_1, \ldots, q_n)}}{Z_q n_s(q_1, \ldots, q_n)} \prod_{i=s+1}^{\infty} f(p_i) \quad \cdots \quad (3.24)
\]

where

\[
    g_s(q_1, \ldots, q_n) = \Omega_s \int dq_{s+1} \cdots dq_n \frac{e^{-\beta V(q_1, \ldots, q_n)}}{q_n} \quad \cdots \quad (3.25)
\]

Also,

\[
    f_{s,s}(x_s; 0|x_s) = \prod_{i=1}^{s} \delta(q_i - q_{i_0}) \delta(p_i - p_{i_0}) \quad \cdots \quad (3.26)
\]

As has already been indicated, \( G_q(r,t) \) is related to \( f_2,2(x_1, x_2; t|x_{1_0}, x_{2_0}) \). 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:

\[
    Q = \frac{1}{\Omega^{n-s}} \int dq_{s+1} \cdots dq_n \quad \cdots \quad (3.27)
\]

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:
\[
\frac{\partial}{\partial t} + \sum_{l \geq 1} \frac{e^{2i}}{l^2} \dot{q}_l = \sum_{l \geq 1} \dot{q}_l u_{\text{ext}} \cdot \dot{v}_l + \sum_{l \geq 1} \frac{e^{2i}}{l^2} \dot{q}_l \phi \cdot \dot{v}_l \int_{s_0}^{t} L f_{s,s}^{(X_s:t|X_{s_0})} = \int_{s_0}^{t} \tau(1-Q) L f_{s,s}^{(X_s:t|X_{s_0})} + \int_{s_0}^{t} \frac{e^{2i}}{l^2} \phi \cdot \dot{v}_l \int_{s_0}^{t} \tau(1-Q) L f_{s,s}^{(X_s:t|X_{s_0})}
\]

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

\[
f_{s,n}^{(x_1,\ldots,x_n,p_1,\ldots,p_n)} \rightarrow \prod_{l=1}^{\infty} f_{\text{eq}}(p_l)
\]

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

\[
f_{n,n}^{\text{eq}}(x_1,\ldots,x_n) = e^{-\beta \frac{P^2}{2m}} \frac{Z_n}{Z_n^{(\text{ext})}} e^{-\frac{1}{2m} \sum_{l=1}^{\infty} \delta(x_l-x_{10})} e^{-\beta \frac{U}{kT}}
\]

then

\[
f_{n,n}^{\text{eq}}(x_1,\ldots,x_n) = e^{-\beta \frac{U}{kT}} e^{-\frac{1}{2m} \sum_{l=1}^{\infty} \delta(x_l-x_{10})} e^{-\frac{1}{2m} \sum_{l=1}^{\infty} \delta(x_l-x_{10})} e^{-\beta \frac{U}{kT}}
\]

where

\[
f_{s,s}^{\text{eq}}(x_1,\ldots,x_n) = \prod_{l=1}^{\infty} f_{\text{eq}}(x_l) e^{-\beta \frac{P^2}{2m}} \frac{Z_n}{Z_n^{(\text{ext})}} e^{-\frac{1}{2m} \sum_{l=1}^{\infty} \delta(x_l-x_{10})} e^{-\beta \frac{U}{kT}}
\]
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, \textit{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 \( f_{s,s}(x_s; t \mid x_{s_0}) \).

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 \( f_{1,1} \):

\[
\sum_{n=1}^{t} \int_{L}^{n} t(1-Q) f_{n}(t|0) f_{1,1}(x_1; t| x_{1_0}) = \quad \ldots \quad (3.29)
\]

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 "specific" densities because the arguments \( \dot{q}_1, \ldots, \dot{q}_a, \dot{p}_1, \ldots, \dot{p}_b \) pertain to designated members of the assembly.*

Closely related are Bogoliubov's "distribution functions"**, which are defined by:

\[
F_{s-s}(X_{s_1}^{t}, \ldots, X_{s_n}^{t} | X_{r_0}^{t}) \equiv \int_{s_1}^{t} \ldots \int_{s_n}^{t} f_{s}(X_{s}^{t})
\]

it is clear that they are related to our density functions by:

\[
f_{s_1} \ldots f_{s_n}(X_{s}^{t} | X_{r_0}^{t}) = \frac{1}{n^s} F_{s}(X_{s}^{t} | X_{r_0}^{t})
\]

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

\[
f_{gen}^{s}(x_{s_1}^{t}, \ldots, x_{s_n}^{t} | x_{r_0}^{t}) = \frac{n!}{(n-s)!} \int_{x_{s_1}}^{t} \ldots \int_{x_{s_n}}^{t} f_{s}(X_{s}^{t})
\]

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 particles. However, in our study, where attention is focused

*See, e.g.; Hill, p. 182; Vineyard, pp. 2, 51.

**Bogoliubov, 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, \( n(\mathbf{r}; t | \mathbf{q}_{1_0}) \), defined as the expected number of particles in the neighborhood of \( \mathbf{r} \) at time \( t \), given that particle designated \( \#1 \) was at \( \mathbf{q}_{1_0} \) at \( t = 0 \). In order to do so, one takes the expectation of the density operator defined by \( N(X_n) \equiv \sum_{\mathbf{r}-\mathbf{q}_1} \delta(\mathbf{r}\mathbf{-q}_1) \)

i.e.,

\[
n(\mathbf{r}; t | \mathbf{q}_{1_0}) \equiv \langle \mathbf{\delta}(\mathbf{r}\mathbf{-q}_{1_0}) \rangle = \int d\mathbf{\bar{r}}_1 \ldots d\mathbf{\bar{r}}_n \left[ \sum_{i=1}^{n} \delta(\mathbf{\bar{r}}_i\mathbf{-q}_{1_0}) \right] f_{n,n}(\mathbf{X}; t | \mathbf{q}_{1_0})
\]

\[
= \int d\mathbf{\bar{r}}_1 f_{1,0}(\mathbf{\bar{r}}_1; t | \mathbf{q}_{1_0}) \delta(\mathbf{\bar{r}}_1\mathbf{-q}_{1_0}) \sum_{i=2}^{n} \int d\mathbf{\bar{r}}_i f_{1,0}(\mathbf{\bar{r}}_i; t | \mathbf{q}_{1_0}) \delta(\mathbf{\bar{r}}_i\mathbf{-q}_{1_0})
\]

\[
= f_{1,0}(\mathbf{\bar{r}}; t | \mathbf{q}_{1_0}) + (n-1) f_{1,0}^{\text{distinct}}(\mathbf{\bar{r}}; t | \mathbf{q}_{1_0})
\]

where \( f_{1,0}(\mathbf{\bar{r}}; t | \mathbf{q}_{1_0}) \) is the probability density for finding a particle at \( \mathbf{r} \) (configuration space) at time \( t \), given that it was located at \( \mathbf{q}_{1_0} \) at \( t = 0 \); \( f_{1,0}^{\text{distinct}}(\mathbf{\bar{r}}; t | \mathbf{q}_{1_0}) \) is the probability density for finding a specified particle at \( \mathbf{r} \) at time \( t \), averaged over the initial position of the particle, given only that a different specified particle was at \( \mathbf{q}_{1_0} \) 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

\[
n(\mathbf{\bar{r}}; t | 0) = \frac{1}{n} \sum_{j=1}^{n} \int d\mathbf{\bar{r}}' \delta(\mathbf{\bar{r}}+\mathbf{\bar{r}}_k(0)-\mathbf{\bar{r}}') \delta(\mathbf{\bar{r}}'-\mathbf{\bar{r}}_j(t)) = G(\mathbf{\bar{r}}, t)
\]
for a system composed of identical particles. \( G_s = f_{1,0}^{self}(r; t | 0) \)
and \( G_d(r, t) = (n-1) f_{1,0}^{dist}(r; t | 0) \). **

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

\[
n(r, t) = \int \mathbf{x}_n n \mathbf{n}_n(X_n; t) N(X_n) = n f_{1,0}(r, t).
\]

For example, for a system in equilibrium, \( f_{1,0} = 1/\Omega \), so that

\[
n(r, t) = n/\Omega = c = \text{the macroscopic density.}
\]

**Anticipating somewhat, \( f_{1,0}^{self}(\mathbf{q}_1; t | \mathbf{q}_{1_0}) \) and \( f_{1,0}^{dist}(\mathbf{q}_2; t | \mathbf{q}_{1_0}) \) may be explicitly calculated from

\[
f_{1,0}(\mathbf{x}_1; t | \mathbf{x}_{1_0}) \text{ and } f_{2,2}(\mathbf{x}_2; t | \mathbf{x}_{2_0}) \]

by

\[
f_{1,0}^{self}(\mathbf{q}_1; t | \mathbf{q}_{1_0}) = \int \mathbf{p}_0 \mathbf{p}_1 \frac{e^{-\beta \mathbf{p}^2/2m}}{(2\pi m k T)^3} f_{1,1}(\mathbf{p}_1, \mathbf{q}_1; t | \mathbf{p}_{1_0}, \mathbf{q}_{1_0})
\]

\[
f_{1,0}^{dist}(\mathbf{q}_2; t | \mathbf{q}_{1_0}) = \int \mathbf{q}_2 \mathbf{q}_{1_0} \frac{f_0(\mathbf{p}_1, \mathbf{p}_{1_0}; \mathbf{q}_2, \mathbf{q}_{1_0}) f_{2,2}(\mathbf{x}_2; t | \mathbf{x}_{2_0})}{(2\pi m k T)^3} \]

\[
= \frac{1}{\Omega} \int \mathbf{x}_2 \mathbf{q}_{2_0} \frac{e^{-\beta (\mathbf{p}_1^2 + \mathbf{p}_{1_0}^2)}}{(2\pi m k T)^3} f_{2,2}(\mathbf{x}_2; t | \mathbf{x}_{2_0})
\]
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, \( f_{1,1}(x_1; t/x_0) \). 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 \((q_1', p_1')\) at time \(t\), given that it was located at \((q_{0}, p_{0})\) at time \(t = 0\), is provided by the solution of equation 3.18:
\[
\frac{\partial f_{1,1}(q_1, p_1; t | q_{10}, p_{10})}{\partial t} + \frac{p_1}{m} \cdot q_1 \cdot f_{1,1}(q_1, p_1; t | q_{10}, p_{10}) = \quad \ldots \ldots \quad (4.1)
\]

\[
t = \Theta \int_0^t e^{-\tau L(1-\Theta)} L(1-\Theta) L f_n(1^n) f_1,1(q_1, p_1; t-\tau | q_{10}, p_{10})
\]

with initial condition:

\[
f_{1,1}(q_1, p_1; 0 | q_{10}, p_{10}) = \delta(q_1-q_{10}) \delta(p_1-p_{10})
\]

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

\[
\Theta = \int dq_2 \cdots dq_n dp_2 \cdots dp_n \quad \ldots \ldots \quad (4.2a)
\]

\[
\int_{1^n} (X_n) = e^{-S(q_1, \ldots, q_n)} \prod_{i=1}^{n} f(p_i) \quad \ldots \ldots \quad (4.2b)
\]

\[
\Theta = f_n(X_n) \Theta \quad \ldots \ldots \quad (4.2c)
\]

\(L\) 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 interaction between particles can be described as the sum of central pair potentials.

Frequently, the six dimensional variable \(x\) shall appear in the following analysis to denote \((q,p)\). 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:

\[ X \equiv (x_1, \ldots, x_n) \]

Let us focus our attention on the collision integral of the kinetic equation. Making repeated use of the following well-known* identity

\[
e^{-\tau L_0(1-\theta)} L_1(1-\theta) = e^{-\tau' L_0(1-\theta)} L_1(1-\theta) e^{\tau' L(1-\theta)}
\]

the integral term of eqn. 4.1 becomes...

\[
I = \int_0^t dt_1 \int_0^{\tau_{1}} L_0(1-\theta) L(1-\theta) L f_{n|1} f_{1,1} (x_1; t-t_1| x_{10}) +
\]

\[
+ \int_0^t dt_1 \int_0^{\tau_{1}} L_0(1-\theta) L_2(1-\theta) L(1-\theta) L f_{n|1} f_{1,1} (t-t_1| x_{10})
\]

\[
+ \int_0^t dt_1 \int_0^{\tau_{1}} L_0(1-\theta) L_3(1-\theta) L(1-\theta) L f_{n|1} f_{1,1} (t-t_1| x_{10})
\]

\[\text{..........................}
\]

\[\text{................ (4.4)}\]

*See, e.g., Van Hove \textsuperscript{34}, Bernard and Callen \textsuperscript{35}. 4.3 can be verified by noticing that it holds for \( \tau = 0 \) and also, the differentials re. \( \tau \) 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:  \[ \bar{\Theta} e^{\tau L_0 (1-\Theta)} = \bar{\Theta} \quad \ldots \ldots \quad (4.5) \]

(Proof:  \[ \bar{\Theta} e^{\tau L_0 (1-\Theta)} = \bar{\Theta} \left[ 1 + \tau L_0 (1-\Theta) + \frac{\tau^2}{2!} L_0 (1-\Theta) L_0 (1-\Theta) + \ldots \right] \]

But, because \( \bar{\Theta} \bar{\varphi}_{\bar{q}_i} \), \( i \not= 1 \) yields boundary terms which \( \rightarrow 0 \) as the volume of the system \( \Omega \rightarrow \infty \),

\[ \bar{\Theta} L_0 (1-\Theta) = \bar{\Theta} \left( \frac{\bar{\varphi}_m}{m} \bar{\varphi}_{\bar{q}_1} \right) (1-\Theta) = - \frac{\bar{\varphi}_m}{m} \bar{\varphi}_{\bar{q}_1} \bar{\Theta} (1-\Theta) \]

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

In a similar way, it is quickly seen that

\[ \bar{\Theta} L_n^0 (1-\Theta) = 0 \text{ for } n \geq 0 ; \quad \bar{\Theta} e^{\tau L_0 (1-\Theta)} = 0. \quad \ldots \ldots \quad (4.6) \]

As a consequence of (4.6) we have the following

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

(Proof:

\[ e^{\tau L_0 (1-\Theta)} = 1 + e^{\tau L_0 (1-\Theta)} + \frac{\tau^2}{2!} L_0 (1-\Theta) L_0 (1-\Theta) + \ldots \]

\[ = 1 + e^{\tau L_0 (1-\Theta)} + \frac{\tau^2 L_0^2 (1-\Theta)}{2!} + \ldots \]

\[ = [ e^{\tau L_0 (1-\Theta)} + \Theta ] \]

\[ \text{q.e.d.} \]

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

\[ (1-\Theta) \Theta = 0 ; \quad L_1 (1-\Theta)[e^{\tau L_0 (1-\Theta)} + \Theta] = L_1 (1-\Theta)e^{\tau L_0 (1-\Theta)} \]
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:

\[
I^r = \tilde{\Theta} \int_0^t \int_0^{\tau_1} \ldots \int_0^{\tau_r} L_1[e^{-(\tau_2 - \tau_3) L_0 (1-\Theta)} L_1[e^{-(\tau_3 - \tau_4) L_0 (1-\Theta)}] \ldots L_1[e^{-(\tau_r - \tau_{r+1}) L_0 (1-\Theta)}] L_1[e^{L_0 (1-\Theta)} L f(n_1 n_1 f(t - \tau_1)] \ldots \ldots \ldots (4.9)
\]

Let us continue with the simplification of (4.9).

Notice, in these expressions, the appearance of terms:

\[
(1-\Theta) L f(n_1 n_1 f(t - \tau_1) \text{ and } \frac{Z \delta_q^2}{\delta q_n^2} \text{ for } \delta_q^2 \delta_p n_1 n_1 \text{ and } \delta_q^2 \delta_p q_1 \delta_q^2 \delta_p q_1 \text{ for } \delta_p n_1 n_1 \text{ and } \delta_p q_1 \delta_p q_1 \text{ because } V(q_1, \ldots, q_n) \text{ is an even function of the spatial separations between particles, whereas } L_1 \text{ is an odd function of these variables (see the discussion following 3.15).}
\]

Also,

\[
[\tilde{\Theta} L_0 f(n_1 n_1 f(n_1 n_1 f(t - \tau_1) = \ldots \ldots \ldots (4.10)
\]

Hence,

\[
(1-\Theta) L f(n_1 n_1 f(t - \tau_1) = \ldots \ldots \ldots (4.10)
\]

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

\[
\begin{align*}
\hat{q}_i &\leftrightarrow \tilde{q}_i; \quad \hat{q}_i \leftrightarrow (\hat{q}_i - \tilde{q}_i), \quad i \neq 1 \ldots \ldots (4.11a)
\end{align*}
\]

which implies

\[
\begin{align*}
\hat{q}_1 &\rightarrow (\hat{q}_1 - \frac{n}{q_1^2} \hat{f}_i); \quad \hat{q}_1 \rightarrow \hat{q}_1, \quad i \neq 1 \ldots \ldots (4.11b)
\end{align*}
\]
The Jacobian of the transformation is unity.

Under this transformation, the operators appearing in 4.9 become

$$L(n) + L(\xi) = L_0(\xi) + L_1(\xi)$$

(4.12)

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

$$L_0(\xi) = \sum_{i=1}^{n} \frac{\partial}{\partial x_i} \cdot \phi_i$$

$$L_1(\xi) = \sum_{i=1}^{n} \frac{\partial}{\partial x_i} \cdot \phi_i - \sum_{j=1}^{n} \frac{\partial}{\partial p_j} \cdot \phi_j$$

(4.13)

It is noted that $f_{n|1}(\xi)$ is not a function of $q_1$.

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

$$[ L(\xi) f_{n|1}(\xi) + f_{n|1}(\xi) (\frac{\partial}{\partial x_i} \cdot \phi_i)] f_{1,1}(x_1; t - \tau_1 | x_{10}) =$$

$$= L^\dagger(\xi) f_{n|1}(\xi) f_{1,1}(x_1; t - \tau_1 | x_{10})$$

(4.10)

where

$$L^\dagger(\xi) = L_0^\dagger(\xi) + L_1(\xi)$$

(4.13)

and

$$L_0^\dagger(\xi) = - \sum_{i=1}^{n} \frac{\partial}{\partial x_i} \cdot \phi_i$$

In summary, finally, the kinetic equation for $f_{1,1}$

$(x_1; t/x_{10})$ may be written as:
\[
\frac{\partial f_{1,1}}{\partial t} + \sum_{m} p_{m} q_{1,1}(x_{1,1} \mid x_{1,0}) = \int_{1}^{\infty} l_{1}(x_{1,1} \mid x_{1,0})
\]

(4.14)

with,
\[
l_{1}(r) = \bar{O}(z) \int_{0}^{t} d\tau_{1} \int_{0}^{\tau_{1}} d\tau_{2} \ldots \int_{0}^{\tau_{n}} d\tau_{n} L_{1}(z) \times 
\]

(4.15)*

\[
\times [e^{\tau_{2} - \tau_{3}} L_{0}^{\dagger}(z)] L_{1} \times 
\times [e^{\tau_{3} - \tau_{4}} L_{0}^{\dagger}(1 - \theta)] L_{1} \times \ldots \times [e^{\tau_{r} - \tau_{r+1}} L_{0}^{\dagger}(1 - \theta)] L_{1} \times 
\times L_{1} [e^{\tau_{r+1} - \tau} L_{0}^{\dagger}(1 - \theta)] L_{1} f_{n | 1}(z) f_{1,1}(x_{1,1} \mid x_{1,0}) 
\]

\[
\bar{O}(z)
\]

is the streaming operator (Taylor's series operator):
\[
\bar{O}(z) = e^{-\frac{z}{m_{1}}} q_{1}
\]

(4.16)

having the property that, when acting upon a function of

\[ q_{1}, p_{1}, \text{ and } t: \]

\[
\bar{O}(z) fcn(q_{1} ; p_{1} ; t) = fcn(q_{1} - \frac{p_{1} \tau}{m_{1}} ; p_{1} ; t) \]

(4.16a)

\[
\bar{O}(z)
\]

is defined by:
\[
\bar{O}(z) = \int \! d\xi_{2} \ldots d\xi_{n} \int \! d\phi_{2} \ldots d\phi_{n}
\]

(4.17)

there being obvious similar definitions for \[ O(z) \]

and \[ f_{n | 1}(z) \]

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

* \[
l_{1}(z) = \bar{O}(z) \int_{0}^{t} L(z) L^{\dagger}(z) f_{n | 1}(z) f_{1,1}(x_{1,1} \mid x_{1,0})
\]

(4.15)
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 \( f_{1,1} (x_1; t/x_{1_0}) \).

What, however, are the criteria for determining the relative contribution of various terms in the collision integral series? The identification of the necessary expansion parameters is, of course, one of the desired results of this study. In this regard, it can be asserted \textit{a posteriori} that further reduction of the interaction terms will demonstrate the intrinsic importance of constants of the following form:

\[
\int d\xi_2 \ldots d\xi_k g_k(\xi_2, \ldots, \xi_k) \left[ \frac{\partial}{\partial \xi_2} \phi(\xi_2) \frac{\partial}{\partial \xi_3} \phi(\xi_3) \ldots \frac{\partial}{\partial \xi_k} \phi(\xi_k) \right] \ldots (4.18)
\]

where \( \phi(\xi) \) is the pair potential energy expressed as a function of the distance between particles and,

\[
g_k(\xi_2, \ldots, \xi_k) = \frac{\Omega^{k-1} \int d\xi_2 \ldots d\xi_k e^{-BV(\xi_2, \ldots, \xi_k)}}{\int d\xi_2 \ldots d\xi_k e^{-BV(\xi_2, \ldots, \xi_n)}} \ldots (4.19)
\]

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 interactions. 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 $\rho \to 0$ and/or the temperature $T \to \infty$, the $g_k$ are well approximated by

$$
g_k = \frac{n_{k-1} e^{-\beta V(\xi_1, \ldots, \xi_k)}}{\int d\xi_1 \cdots d\xi_k e^{-\beta V(\xi_1, \ldots, \xi_k)}} \quad \ldots \quad (4.19)
$$

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

$$
M \equiv \sum_{\gamma} \sum_{\nu} m_{j, \gamma, \nu} \quad \ldots \quad (4.20)
$$

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. However, 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,

$$
\int \left[ e^{-\beta \phi(\xi) / \xi} \hat{\phi}(\xi) \cdot \frac{\partial \hat{\phi}(\xi)}{\partial \xi} \right] d^3 \xi = \frac{1}{\beta} \int d^3 \phi \ e^{-\beta \phi} \beta \hat{\phi} \quad \ldots \quad (4.19')
$$

(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 \( I_{1}^{[1]} \). From 4.15:

\[
I_{1}^{[1]} = \bar{\sigma}(\bar{\phi}) \int_{0}^{t} d\tau L(\bar{f}) L^\dagger(\bar{f}) \ f_{n}|_{1}(\bar{f}) \ f_{1,1,1}(x_{1,1}, t-\tau | x_{1,0}) \ .... \quad (4.20)
\]

It is convenient to break the integral into two parts, \( I_{1}^{[1]} \) and \( I_{1}^{[2]} \), defined by:

\[
I_{1}^{[1]} = \bar{\sigma}(\bar{\phi}) \int_{0}^{t} d\tau L(\bar{f}) L_{0}^\dagger(\bar{f}) \ f_{n}|_{1}(\bar{f}) \ f_{1,1,1}(t-\tau) \ .... \quad (4.20')
\]

\[
I_{1}^{[2]} = \bar{\sigma}(\bar{\phi}) \int_{0}^{t} d\tau L(\bar{f}) L_{1}(\bar{f}) \ f_{n}|_{1}(\bar{f}) \ f_{1,1,1}(t-\tau) \ .... \quad (4.20'')
\]

\( I_{1}^{[1]} \) can be quickly simplified. \( \bar{\sigma}(\bar{\phi}) \bar{\phi}_{1} \) yields boundary terms in \( \bar{\phi}_{1} \), which are zero in the limit that the volume of the assembly grows large, so that from
4.20'a it is seen that:

\[ I_{1}^{[1]} = \tilde{\Phi}(\Xi) \int_{0}^{t} d\tau \left[ L_{1}(\Xi) \frac{\mathbf{p}_{1}}{m}, \mathbf{v}_{1} \right] L_{0}^{\dagger}(\Xi) f_{n|1}(\Xi) f_{1,1}(t-\tau) \]

But, for the same reason, \( \tilde{\Phi}(\Xi)L_{0}^{\dagger}(\Xi) f_{n|1}(\Xi) = 0 \). Hence,

\[ I_{1}^{[1]} = \tilde{\Phi}(\Xi) \int_{0}^{t} d\tau L_{1}(\Xi)L_{0}^{\dagger}(\Xi) f_{n|1} f_{1,1}(t-\tau) \]. Writing the explicit form of the Liouville operators:

\[ I_{1}^{[1]} = \tilde{\Phi}(\Xi) \int_{0}^{t} d\tau \left[ \frac{1}{2} \sum_{i,j} \hat{r}_{ij}^{\dagger}(n_{j}^{i} - \mathbf{v}_{j}^{i}) + \sum_{i,j} \hat{r}_{ij}^{\dagger} \mathbf{v}_{j}^{i} - \hat{R}_{ij}^{\dagger} \mathbf{v}_{j}^{i} \right] f_{n|1} f_{1,1}(t-\tau) \]

But, because \( \hat{r}_{kj} \) is an odd function in the variables \( \xi_{k} - \xi_{j} \)

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

and, whereas \( \tilde{\Phi}(\Xi) \mathbf{v}_{j}^{i} \dagger \) is 0 for \( k \neq 1 \):

\[ I_{1}^{[1]} = \tilde{\Phi}(\Xi) \int_{0}^{t} d\tau \left[ \mathbf{r}_{1}^{\dagger}(\xi_{1}), \mathbf{v}_{1}^{i} \right] \left[ -\left( \mathbf{r}_{1}^{\dagger} \mathbf{v}_{1}^{i} + \mathbf{v}_{1}^{i} \mathbf{r}_{1}^{\dagger} \right) \xi_{1}^{i} \right] f_{n|1}(\Xi) f_{1,1}(t-\tau) \]

Since all particles are alike, and because \( \tilde{\Phi}(\Xi) \mathbf{p}_{j}^{i} f_{n|1}(\Xi) = 0 \)

(because integration is over an odd function of \( \mathbf{p}_{j}^{i} \)), we finally have:

\[ I_{1}^{[1]} = c x(2) \int_{0}^{t} d\tau L_{1}(\Xi) \left[ \frac{3}{m} + \frac{\mathbf{p}_{1}^{i}}{m} \mathbf{v}_{1}^{i} \right] f_{1,1}(t-\tau|\mathbf{x}_{10}) \]

\[ \ldots \] \hspace{1cm} (4.21)

where

\[ x(2) \equiv \lim_{\Omega \to \infty} \int_{\Omega} d^{3} \xi \frac{1}{2} g_{2}(\xi) \frac{\partial^{2}}{\partial \xi^{2}} \phi(|\xi|) \]

\[ \ldots \] \hspace{1cm} (4.22)

In a similar way, \( I_{2}^{[1]} = \tilde{\Phi}(\Xi) \int_{0}^{t} d\tau L_{2}(\Xi) f_{n|1} f_{1,1}(t-\tau) \)

But, \( \tilde{\Phi}(\Xi) \left[ \frac{\mathbf{p}_{1}^{i}}{m} \mathbf{v}_{1}^{i} \right] L_{2}(\Xi) f_{n|1} f_{1,1}(t-\tau) = 0 \) because the \( \tilde{\Phi} \) integration is over an odd function of the variables \( \xi_{i} - \xi_{j} \).

The latter observation is a special case of the following Lemma: If \( Q = \tilde{\Phi}(\Xi)[L_{1}(\Xi)L_{0}(\Xi)\ldots L_{1}(\Xi)L_{0}^{\dagger} \ldots L_{1}(\Xi)L_{0}^{\dagger} \ldots] f_{n|1}(\Xi) \) 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,
\[ I_{2}^{[1]} = \bar{\eta}(\varepsilon) \int_{0}^{t} d\tau L_{1}(\varepsilon) L_{1}(\varepsilon) f_{n|1} f_{1,1}(t-\tau) \]

or, finally,
\[ I_{2}^{[1]} = c \eta \int_{0}^{t} \nu^{2} f_{n|1} f_{1,1}(t-\tau) \]

with
\[ \eta \equiv \int d^{2}\xi \frac{g_{1}(\xi)}{F_{2}^{2}(\xi)} \]

In summary, the first collision integral has been re-
duced to a form involving simple and well known operators,

viz:
\[ I_{2}^{[1]} = c \int_{0}^{t} \left( x_{m}^{(2)}(3+p_{1}^{2} + \nu^{2} p_{1}) \right) f_{n|1} f_{1,1}(t-\tau) \]

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

Now, consider the second collision integral. From 4.15,
it is seen that $I_{2}^{[2]}$ can be written as the sum of two terms,
defined by:
\[ I_{2}^{[2a]} = \bar{\eta}(\varepsilon) \int_{0}^{t} d\tau_{1} L_{1} \nu^{2} L_{0}^{\dagger}(\varepsilon) \]
\[ I_{2}^{[2b]} = -\bar{\eta}(\varepsilon) \int_{0}^{t} d\tau_{2} L_{1} \nu^{2} L_{0}^{\dagger}(\varepsilon) \]

Considering the first of these contributions, it is con-
venient to further designate
\[ I_{2}^{[2a]} = \sum_{i=1}^{4} I_{i1}^{[2a]} \]

with
\[ I[2a]_1 = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( e^{-\tau_2 L_0^+} \beta - \tau_2 L_0 L_0^+ \right) f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.28a) \]

\[ I[2a]_2 = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( L_1 e^{-\tau_2 L_0^+} \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.28b) \]

\[ I[2a]_3 = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( e^{-\tau_2 L_0^+} \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.28c) \]

\[ I[2a]_4 = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( L_1 e^{-\tau_2 L_0^+} \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.28d) \]

It is immediately obvious that \( I[2] \) is rather involved; to continue with the reduction of the collision integrals, we proceed as follows.

Consider \( I[2a]_1 \) (4.28a). The exponential operator

\[ e^{\tau_2 L_0^+} \]

may be expanded

\[ e^{\tau_2 L_0^+} = 1 + \tau_2 L_0^+ (\xi) + \frac{\tau_2^2 L_0^2(\xi) L_0^+(\xi)}{2} + \ldots \quad (4.29) \]

so that

\[ I[2a]_1 = 0_{[2a]} I[2a]_1 + I[2a]_1 + 1_{[2a]} I[2a]_1 + 2_{[2a]} I[2a]_1 + \ldots, \quad \text{where} \]

\[ 0_{[2a]} = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( e^{-\tau_2 L_0^+} \right) f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.30a) \]

\[ 1_{[2a]} = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( L_1 e^{-\tau_2 L_0^+} \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.30b) \]

\[ 2_{[2a]} = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( L_1 \left( \tau_2 L_0^2 \right) \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.30c) \]

\[ 3_{[2a]} = \bar{\Theta} \int_0^t \int_0^{\tau_i} d\tau_1 \left( L_1 \left( \tau_2^2 L_0^3 \right) \right) \beta - \tau_2 L_0 L_0^+ f_{n|1,1}(t-\tau_1) \quad \ldots \quad (4.30d) \]

and so forth.
Writing the Liouville operators explicitly, \( O_{1}^{[2a]} \) is seen to be:

\[
O_{1}^{[2a]} = \tilde{\mathcal{O}}(\xi) \int_{0}^{t} d\tau_{2} \int_{0}^{t} d\tau_{1} \left( \begin{array}{cc}
\frac{1}{2} \sum_{i} x_{i} \cdot \vec{\theta}_{1}^{i} \frac{1}{2} \sum_{i} x_{i} \cdot \vec{\theta}_{1}^{i} \times \\
- \frac{1}{2} \left( \vec{\theta}_{1}^{i} \cdot \vec{\theta}_{1}^{i} \right) + \sum_{i} \vec{\theta}_{1}^{i} \cdot \vec{\theta}_{1}^{i}
\end{array} \right) \tilde{\mathcal{O}}(\xi)_{n} f_{1,1}(t-\tau_{1})
\]

However, since \( F_{1j}(\xi_{i}-\xi_{j}) \) is an odd function of the variable \( (\xi_{i}-\xi_{j}) \), whereas \( f_{n,1}(\xi) \) is an even function of this variable, and whereas the \( \tilde{\mathcal{O}} \) operator integrates over these variables, upon a little reflection it is seen that the only non-zero terms in \( O_{1}^{[2a]} \) are

\[
O_{1}^{[2a]} = \tilde{\mathcal{O}}(\xi) \int_{0}^{t} d\tau_{1} \int_{0}^{t} d\tau_{2} \left( \begin{array}{cc}
- \frac{1}{2} \sum_{i} x_{i} \cdot \vec{\theta}_{1}^{i} \times \\
- \frac{1}{2} \left( \vec{\theta}_{1}^{i} \cdot \vec{\theta}_{1}^{i} \right)
\end{array} \right) \tilde{\mathcal{O}}(\xi)_{n} f_{1,1,1}(t-\tau_{1})
\]

But, \( \tilde{\mathcal{O}}(\xi) \) integrates over in the above equation yields

\[
O_{1}^{[2a]} = \tilde{\mathcal{O}}(\xi) \int_{0}^{t} d\tau_{1} \left( \begin{array}{cc}
- \frac{1}{2} \sum_{i} x_{i} \cdot \vec{\theta}_{1}^{i} \times \\
- \frac{1}{2} \left( \vec{\theta}_{1}^{i} \cdot \vec{\theta}_{1}^{i} \right)
\end{array} \right) \tilde{\mathcal{O}}(\xi)_{n} f_{1,1,1}(t-\tau_{1}) - 
\]

\[\cdots \cdots \text{(4.31)}\]

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 \( \mathcal{Q}^{(1)} \):

\[
\mathcal{Q}^{(1)}_{1} = I_{1}^{[1]} + O_{1}^{[2a]} = c \chi^{(2)} \int_{0}^{t} d\tau_{1} \left[ \frac{3}{m} \vec{p}_{1} \cdot \vec{\theta}_{1}^{i} \times \right] \tilde{\mathcal{O}}(\xi)_{n} f_{1,1,1}(t-\tau_{1})
\]

\[\text{and } \tilde{\mathcal{O}}_{-\tau_{1}} \text{ commute.}\]  \[\cdots \cdots \text{(4.32)}\]

As we shall see, \( \mathcal{Q}^{(1)}_{1} \) 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: $\int_{1_1}^{2a}$. 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:

$$\int_{1}^{2a} \cdot \mathcal{S}(\xi) \int_{0}^{\tau_2} \int_{0}^{\tau_1} (\xi_j \dot{p}_{j} \cdot \dot{\xi}_j)^{3} \times$$

$$\times \frac{f_{n \mid 1}(\xi)}{\beta} \frac{f_{n \mid 1}(t-\tau_1)}{\beta} \frac{f_{n \mid 1}(t-\tau_1)}{\beta} \ldots \quad (4.33)$$

Consider $\mathcal{G}(\xi)(-F_{x}(\xi) \frac{3}{\beta} \frac{(\dot{p}_{j} - \dot{p}_{1})}{\beta} \frac{3}{\beta} \frac{f_{n \mid 1}(\xi)})$. The requirement that $\mathcal{G}$ act upon an even function of $\xi$ leaves only the following non-zero terms:

$$\mathcal{G}(\xi)(-F_{x}(\xi) \frac{3}{\beta} \frac{(\dot{p}_{j} - \dot{p}_{1})}{\beta} \frac{3}{\beta} \frac{f_{n \mid 1}(\xi)}) + 3(\dot{p}_{j} - \dot{p}_{1})^{2} \frac{3}{\beta} \frac{f_{n \mid 1}(\xi)}{\beta} \frac{3}{\beta} \frac{f_{n \mid 1}(\xi)}{\beta} \frac{3}{\beta} \frac{f_{n \mid 1}(\xi)}{\beta}$$

However, $\mathcal{G}(\xi)$ must act upon an even function of $\dot{p}_{j}$. Thus, the above expression is:
\[ \tilde{\Theta}(\xi)[-F_{x}\frac{\partial}{\partial x}] \left( (-3[p^2_{1}+p^2_{2}]p_{1} \frac{\partial}{\partial p_{1}} - 3[p^2_{1}+p^2_{2}]p_{1} \frac{\partial}{\partial x}) + \frac{3(p^2_{1}+p^2_{2})(-1-p_{1})}{y} \frac{\partial}{\partial y} \frac{\partial}{\partial x} + \frac{3(p^2_{1}+p^2_{2})(-1-p_{1})}{x} \frac{\partial}{\partial x} \frac{\partial}{\partial p_{1}} \right) f_{n|1} \]

\[ = \tilde{\Theta}(\xi)F_{x} \left( \frac{\partial}{\partial x} \frac{\partial}{\partial p_{1}} f_{n|1}(\xi) \right) \]

\[ + \frac{3(m+p^2_{1})(1+p_{1})}{y} \frac{\partial}{\partial y} \frac{\partial}{\partial x} \frac{\partial}{\partial p_{1}} f_{n|1}(\xi) \]

Next, adding the similar contributions from \( F_{y} \) and \( F_{z} \) and noting that:

\[ \tilde{\Theta}(\xi)F_{x} \frac{\partial}{\partial x} \frac{\partial}{\partial y} f_{n|1}(\xi) = \tilde{\Theta}(\xi)F_{x} \frac{\partial}{\partial x} \frac{\partial}{\partial z} f_{n|1}(\xi) \]

we obtain for \( 1_{1}[2a] \):

\[ 1_{1}[2a] = -c/m \chi^{(4)} \int_{0}^{t_{2}} \int_{0}^{t_{1}} (-t_{2})(3(m+p^2_{1})+3(m-p^2_{1})+2p^2_{1}) \phi_{1}(t-t_{1}) \]

\[ -3c/m \chi^{(2,2)} \int_{0}^{t_{2}} \int_{0}^{t_{1}} (-t_{2})(2m+p_{1}p_{2})+2p^2_{1} \phi_{2}(t-t_{1}) \]

where the system constants are defined by

\[ \chi^{(4)} = \int d^{3} \xi g_{2}(\xi) \frac{\partial^{4}}{\partial \xi^{4}} \phi(\xi) \]

and

\[ \chi^{(2,2)} = \int d^{3} \xi g_{2}(\xi) \frac{\partial^{4}}{\partial \xi^{4} \partial y^{2}} \phi(\xi) \]

It is easily deconstrasted that \( 1_{1}[2a] \) is closely related to \( 2_{1}[2a] \).
Note that, in light of the Lemma 4.23, 4.30c can be written:

$$2_{I}^{[2a]} = \int_{0}^{t} \int_{0}^{r_{1}} d\tau_{1} \int_{0}^{r_{2}} L_{1} \frac{r_{2}^{2}}{2} L_{0}^{+} L_{0}^{+} \frac{q_{1} \left( -\frac{p_{1}}{m}, \nu_{1} \right)}{q_{1}} L_{0}^{+} f_{n} f_{1,1}^{l}(t-\tau_{1}) \quad \ldots (4.36)$$

But, integrate the above expression by parts to obtain:

$$2_{I}^{[2a]} = \int_{0}^{t} L_{1} \frac{r_{2}^{2}}{2} L_{0}^{+} L_{0}^{+} f_{n} f_{1,1}^{l}(t-\tau_{1}) - 1_{I}^{[2a]}$$

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

$$Q_{3} = 1_{I}^{[2a]} + 2_{I}^{[2a]}$$

$$= \frac{c_{3}}{m} x^{(4)} \int_{0}^{t} d\tau_{1} \frac{r_{2}^{2}}{2} \left( 3 \left( \frac{3m}{\beta} + p_{1}^{2} \right) + \frac{3}{\beta} \left( \frac{3mp_{1}^{2} + p_{1}^{3}}{\beta} \right) \frac{\partial}{\partial p_{1}} \right) f_{n} f_{1,1}^{l}(t-\tau_{1})$$

$$+ \frac{3c_{3}}{m} x^{(2,2)} \int_{0}^{t} d\tau_{1} \frac{r_{2}^{2}}{2} \left( 2 \left( \frac{3m + p_{1}^{2} \beta}{\beta} \right) + 2p_{1}^{2} + p_{1}^{2} \left( \frac{\beta}{\beta} p_{1} \right) \right) f_{n} f_{1,1}^{l}(t-\tau_{1})$$

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

$$\int_{0}^{t} d\tau_{1} \frac{r_{2}^{2}}{2} \left( \frac{15m}{\beta} + 5p_{1}^{2} + \frac{5m}{\beta} p_{1} \frac{\partial}{\partial p_{1}} + p_{1}^{2} \frac{\partial}{\partial p_{1}} \right) f_{n} f_{1,1}^{l}(t-\tau_{1}) \quad \ldots (4.37)$$

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

Next, one considers $3_{I}^{[2a]}$. 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 terms contributing 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:

\[
\int_0^t \cdots (4.38)
\]

\[
\tau_1 \cdots \left( \frac{3}{m} \frac{p_1}{q_1} \right) \int_{\tau_1}^{t} f_{1,1}(t - \tau_1)\]

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

\[
I = \sum_{k=1}^{9} D_k + o(M^5)
\]

(4.39)

where: **

\[
D_1 = \frac{c_{\eta}}{m^2} \int \left( \frac{3}{m} \frac{p_1}{q_1} \right) \int_{\tau_1}^{t} f_{1,1}(t - \tau_1) \]

(4.32)

\[
D_2 = \frac{c_{\eta}}{m^2} \int \left( \frac{3}{m} \frac{p_1}{q_1} \right) \int_{\tau_1}^{t} f_{1,1}(t - \tau_1) \]

(4.40)

\[
D_3 = \frac{c_{\eta}}{m^2} \int \left( \frac{3}{m} \frac{p_1}{q_1} \right) \int_{\tau_1}^{t} f_{1,1}(t - \tau_1) \]

(4.37)

\[
D_4 = \frac{c_{\eta}}{m^2} \int \left( \frac{3}{m} \frac{p_1}{q_1} \right) \int_{\tau_1}^{t} f_{1,1}(t - \tau_1) \]

(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.

\[
\begin{align*}
\mathcal{Q}_{5,1} &= \frac{t}{m^3} \chi^{(4,xx)} \left[ \int \tau^2 \left( \frac{(5m + p_1^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 20 + \frac{4p_1}{3m} p_1 \frac{m}{1} q_1 + 4p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 + \frac{4p_1}{m} q_1 + 4p_1 \frac{m}{1} q_1 + 4p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 \right) f(t) \right] \\
\mathcal{Q}_{5,1} &= \frac{t}{m^3} \chi^{(4,xx)} \left[ \int \tau^2 \left( \frac{(3m + p_1^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 12 + 10p_1 \frac{m}{1} q_1 + 8p_1 \frac{m}{1} q_1 \right) f(t) \right] \\
\mathcal{Q}_{5,1} &= \frac{t}{m^3} \chi^{(4,xy)} \left[ \int \tau^2 \left( \frac{(2m + p_1^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 6 + 5p_1 \frac{m}{1} q_1 + 2p_1 \frac{m}{1} q_1 \right) f(t) \right] \\
\mathcal{Q}_{5,1} &= \frac{t}{m^3} \chi^{(4,yy)} \left[ \int \tau^2 \left( \frac{(18 + 9p_1^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 2 + 2p_1 \frac{m}{1} q_1 + 2p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 \right) f(t) \right]
\end{align*}
\]

\[
\begin{align*}
\mathcal{Q}_{6,1} &= \frac{t}{m^4} \chi^{(4,xx)} \left[ \int \tau^2 \left( \frac{(33 + 20p_1^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 3p_1 \frac{m}{1} q_1 + 2p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 \right) f(t) \right] \\
\mathcal{Q}_{6,1} &= \frac{t}{m^4} \chi^{(4,xy)} \left[ \int \tau^2 \left( \frac{(6 + 6q_v^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 3p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 \right) f(t) \right] \\
\mathcal{Q}_{6,1} &= \frac{t}{m^4} \chi^{(4,yy)} \left[ \int \tau^2 \left( \frac{(6q_v^2 + 14q_v^2)}{3} \left( 3q_v^2 + 4q_v^2 \right) + 2p_1 \frac{m}{1} q_1 \frac{m}{1} q_1 \right) f(t) \right]
\end{align*}
\]
\[ \mathcal{J}_{1,1} = -c^2 \chi^{(2)} \left[ 2 \int_{0}^{\tau} \frac{1}{2} \left[ \frac{3+\not{p}}{m} \frac{\not{v}}{p_1} \right] \left( \not{r} \frac{3+\not{p}}{m} \frac{\not{v}}{p_1} + 2\tau \frac{\not{p}}{p_1} \frac{\not{v}}{q_1} \right) + \right. \\
\left. + \eta^{(2)} \left[ \frac{v^2}{p_1} + \frac{5\tau v^2}{q_1} + \frac{2\tau^2 v^2}{q_1} \right] \right] \mathcal{J}_{1,1}(t-\tau) \]

\[ \mathcal{J}_{8,1,1} = c^{[\psi_3]} + c^{[\mu]} \left[ \int_{0}^{\tau} \frac{1}{2} \left( \frac{3v^2}{p_1} + \frac{5\tau v^2}{q_1} + \frac{3\tau^2 v^2}{q_1} \right) \right] \mathcal{J}_{1,1}(t-\tau) \]

\[ \mathcal{J}_{9,1,1} = c^{[\psi_4]} + c^{[\psi]} \left[ \int_{0}^{\tau} \frac{1}{2} \left( \frac{9+3\tau v^2}{p_1} + \frac{1}{p_1} \right) \right] \mathcal{J}_{1,1}(t-\tau) \]

\[ \mathcal{J}_{1,1} = -c^2 \int_{0}^{\tau} \frac{1}{2} \left( \frac{v^2}{p_1} + \frac{3\tau v^2}{q_1} + \frac{2\tau^2 v^2}{q_1} \right) \mathcal{J}_{1,1}(t-\tau) \]

\[ \mathcal{J}_{1,1} = -c^2 \int_{0}^{\tau} \frac{1}{2} \left( \frac{v^2}{p_1} + \frac{5\tau v^2}{q_1} + \frac{2\tau^2 v^2}{q_1} \right) \mathcal{J}_{1,1}(t-\tau) \]

Finally:

\[ \mathcal{J}_{9,1,1} = -c^2 \int_{0}^{\tau} \frac{1}{2} \left( \frac{v^2}{p_1} + \frac{3\tau v^2}{q_1} + \frac{2\tau^2 v^2}{q_1} \right) \mathcal{J}_{1,1}(t-\tau) \]

The system constants appearing in \( \mathcal{J}_{1} \) through \( \mathcal{J}_{9} \) 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): \( \mathcal{J}_{1} \) and \( \mathcal{J}_{2} \) are the first order
terms in the expansion; $\mathcal{L}_3$ through $\mathcal{L}_9$ 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:

\[
I = \mathcal{M}_{[2]} \int_{0}^{t} dt \ 0_p^{[1]} (p_1;^+_1 \vec{v}_{1 \ m} q_1) \delta_{-\tau} f_{1,1}(t-\tau)
\]

\[
+ \mathcal{M}_{[4]} \int_{0}^{t} dt \ \frac{t^2}{2!} 0_p^{[2]} (p_1;^+_1 \vec{v}_{1 \ m} q_1) \delta_{-\tau} f_{1,1}(t-\tau)
\]

\[
+ \mathcal{M}_{[6]} \int_{0}^{t} dt \ \frac{t^4}{4!} 0_p^{[3]} (p_1;^+_1 \vec{v}_{1 \ m} q_1) \delta_{-\tau} f_{1,1}(t-\tau)
\]

\[
+ \ldots \ldots \ldots \ldots
\]

\[
= \sum_{k=1}^{2k} \mathcal{M}_{[2k]} \int_{0}^{t} dt \ \left( \frac{(2k-2)}{(2k-2)!} \right) 0_p^{[k]} (p_1;^+_1 \vec{v}_{1 \ m} q_1) \delta_{-\tau} f_{1,1}(t-\tau)
\]

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

Notice the manner in which the powers of $\tau$ in the integrals increase directly with increasing powers of $M$. Terms in the $0_p^{[k]}$ which do not contain derivatives re. spatial coordinates do not contain the time $\tau$ 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 $\left( \tau / m \right)$.
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 simple 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 calculations to assemblies for which interparticle forces are characterized by a hard repelling core plus short range attracting well (cf. fig. 5.2, p. 71, below.) In this case the system constants are roughly proportional to powers of \( \varepsilon_0 \), where \( \varepsilon_0 \) 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 reciprocal of the appropriate coupling constant.

For example, consider the system constants \( \eta^{(1)} \) and \( \eta^{(1 \times \gamma)} \) (cf. table 4.1), evaluated for a repulsive coulomb potential, \( \varphi(\rho) \sim +e/\rho \). If one approximates \( g_2(\rho) \) by \( g_2(\rho) \approx -\int \frac{d\rho}{e^{(3\gamma(\rho))}} \), it is quite easily shown that \( \eta^{(1 \times \gamma)} \propto \frac{1}{(e^2\beta)^2} \eta^{(1)} \). 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

\[ \alpha = \frac{1}{\omega^2} \frac{c}{m(e^2 c) \rho^2} \]

where \( \omega \) is the frequency of the incident radiation, and \( \rho \) 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 successively higher order. Suppose we make the following approximation for \( g_\alpha(\rho) \) (corresponding to an infinitely strong repulsive core).

\[
\tilde{g}_2(r) = \begin{cases} 
\beta \rho \alpha & r < r_0 \\
\exp(-\beta \rho \alpha) & r > r_0 
\end{cases}
\] (4.48)

Then, for example,

\[
\frac{\langle n_\mu(n_x) \rangle}{\langle n(n) \rangle} = \frac{e^{2 \beta \rho \alpha}}{\langle n(n) \rangle} \left( \int \frac{d^3 q}{2!} \frac{\tilde{g}_2(q)}{1 + e^{\beta \rho \alpha q^2}} \right) \approx \mathcal{O}(\epsilon_0^2)
\]

where \( \epsilon_0 \) 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 \( \eta^{(c)} \) with those proportional to \( \beta^2 \frac{\langle n_\mu(n_x) \rangle}{\langle n(n) \rangle} \), one finds that the pertinent expansion parameter is effectively \( \beta \epsilon_0 \).
Table 4-1: Definitions of system constants appearing in the collision integral expansion.

<table>
<thead>
<tr>
<th>Expression</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi^{(2)}$</td>
<td>$\int d^3 \xi \ g_2 (</td>
</tr>
<tr>
<td>$\chi^{(4)}$</td>
<td>$\int d^3 \xi \ g_2 (</td>
</tr>
<tr>
<td>$\chi^{(2,2)}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi (\xi)}{\partial \xi_x^2 \partial \xi_y^2}$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{yy}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi \partial \phi}{\partial \xi_x^2 \partial \xi_y^2}$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{xx}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \left( \frac{\partial^2 \phi}{\partial \xi_x^2} \right)^2$</td>
</tr>
<tr>
<td>$\chi^{(2)}_{xy}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \left( \frac{\partial^2 \phi}{\partial \xi_x \partial \xi_y} \right)^2$</td>
</tr>
<tr>
<td>$\chi^{(4)}$</td>
<td>$\int d^3 \xi \ d^3 \xi \ g_3 (\xi_2, \xi_3) \frac{\partial^2 \phi (\xi_2) \partial^2 \phi (\xi_3)}{\partial \xi_2^2 \partial \xi_3^2}$</td>
</tr>
<tr>
<td>$\chi^{(4,xx)}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi (\xi)}{\partial \xi_x^2} \frac{F(\xi)}{x}$</td>
</tr>
<tr>
<td>$\chi^{(4,xy)}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi (\xi)}{\partial \xi_x \partial \xi_y} \frac{F(\xi)}{x \ y}$</td>
</tr>
<tr>
<td>$\chi^{(4,xx)}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi (\xi)}{\partial \xi_x^2} \frac{F(\xi)}{x \ y}$</td>
</tr>
<tr>
<td>$\chi^{(4,xy)}$</td>
<td>$\int d^3 \xi \ g_2 (\xi) \frac{\partial^2 \phi (\xi)}{\partial \xi_x \partial \xi_y} \frac{F(\xi)}{x \ y}$</td>
</tr>
</tbody>
</table>

Relationships between system constants:

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

b) $\psi^{(4,xx)} = 2 \psi^{(4,xy)}$

c) $n^{(4,xx)} = 3 n^{(4,xy)}$

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

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

(see appendix C for proof).
CHAPTER V

SOLUTION OF THE KINETIC EQUATION FOR $f_{1,1}(x_1; t|x_{1_0})$;

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 $f_{1,1}(x_1; t|x_{1_0})$. 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 $f_{1,1}(x_1; t|x_{1_0})$ 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

$$f_{1,1}(x_1; t|x_{1_0}) = f_{1,1}^{[0]} + f_{1,1}^{[1]} + f_{1,1}^{[2]} + \ldots \ldots$$

$$= \sum_{i=1}^{\infty} f_{1,1}^{[i]}$$

...(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 $f_{1,1}^{[i]}$ 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, $f = \frac{e^{-\frac{\mathbf{p}_1^2}{2m\mathbf{k}T}}}{(2\pi m k T)^{3/2}}$, whereas the zero'th order term in our case is a time dependent six dimensional delta function in $\mu$-space.

It is evident that the zero'th term of the solution for $f_{1,1}^{[0]}$ is given by:

$$\frac{\partial f_{1,1}^{[0]}}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{q}_1} f_{1,1}^{[0]} = 0 \quad \text{(5.2)}$$

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

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

$$\frac{\partial f_{1,1}^{[1]}}{\partial t} + \frac{\mathbf{p}_1}{m} \cdot \nabla_{\mathbf{q}_1} f_{1,1}^{[1]} = \mathcal{L}_1(f_{1,1}^{[0]}) + \mathcal{L}_2(f_{1,1}^{[0]}) = \mathcal{O}_{1,1}^{[0]}(t-t')$$

$$= \int_0^t d\tau \left[ \frac{\mathbf{v}_1}{m} (\mathbf{v}_2 + \mathbf{v}_1) + \mathbf{v}_1 \cdot \mathbf{v}_2 + \mathbf{v}_1 \cdot \mathbf{v}_2 \right] \mathcal{O}_{1,1}^{[0]}(t-\tau)$$

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

**Enskog 36
the second order correction is provided by:
\[
\frac{\partial^2 f^{[2]}}{\partial t \partial p_{\perp}} + \frac{\partial}{\partial p_{\perp}} \frac{\partial}{\partial q_{\perp}} f^{[2]} = \ldots \ldots (5.4)
\]

with initial condition \( f^{[2]}(q_{\perp},0) = 0 \), 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:
\[
\mathcal{L}_s[ G(t) ] \equiv \int_0^\infty dt \, G(t) \, e^{-st} \ldots \ldots (5.5)
\]

For our purposes, the Fourier transform is defined by
\[
\mathcal{F}_k \left[ g(q_{\perp}) \right] \equiv \frac{1}{(2\pi)^{3/2}} \lim_{\Omega \to \infty} \int_{\Omega} d^3q_{\perp} \, g(q_{\perp}) \, e^{ik \cdot q_{\perp}} \ldots \ldots (5.6)
\]

which, by the (Plancherel) Fourier Integral theorem converges in the mean to
\[
\frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{+\infty} d^3q_{\perp} \, g(q_{\perp}) \, e^{ik \cdot q_{\perp}}
\]

It is quickly seen that, in accord with these definitions,
\[
\mathcal{F}_k \mathcal{L}_s f^{[0]} = \frac{e^{-ik \cdot q_{\perp}}}{(2\pi)^{3/2}} \frac{1}{s - ik \cdot p_{\perp}} \delta(p_{\perp} - p_{\perp}) \ldots \ldots (5.7)
\]

Inversion of the transform provides
\[
f^{[0]}(q_{\perp}, t | q_{\perp}, 0) = \delta(q_{\perp} - q_{\perp}) \delta(p_{\perp} - p_{\perp}) \ldots \ldots (5.8)
\]
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:

$$
\frac{f^{[1]}_{1,1}}{f^{[0]}_{1,1}} = \frac{1}{(s-ik\cdot p_1)} \left[ \mathcal{J} \left( f^{[0]}_{1,1} + \mathcal{J} \left( f^{[0]}_{1,1} \right) \right) \right] \quad \cdots (5.9)
$$

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

$$
\mathcal{J} \left( f^{[0]}_{1,1} \right) = f^{[0]}_{1,1}(t) \quad \cdots \cdots \quad (5.10)
$$

so that (replacing 4.32, 4.40)

$$
\mathcal{J} (f^{[0]}_{1,1}) + \mathcal{J} (f^{[0]}_{1,1}) = \frac{c}{p_1} \left( \nu_2 + \frac{v^2}{2m} \right) \mathcal{J} (f^{[0]}_{1,1}) \quad \cdots (5.11)
$$

i.e., the integration in the collision integral becomes merely a simple integration of a polynomial in $\mathcal{J}$.

Consider a typical calculation with 5.11 and 5.9. One has

$$
\frac{1}{(s-ik\cdot p_1)} \frac{1}{p_1} \mathcal{J} (f^{[0]}_{1,1}) = \nu_2 (s-ik\cdot p_1)^2 \delta(p_1 - p_1^o) \quad \cdots (5.12)
$$

Therefore

$$
\frac{1}{(s-ik\cdot p_1)^{1/2}} \frac{1}{p_1} \mathcal{J} (f^{[0]}_{1,1}) = \frac{1}{2} \delta^{(t)} (t) v^2 \delta_p \quad \cdots (5.12)
$$

where

$$
\delta_p = \delta(p_1 - p_1^o) \quad ; \quad \delta^{(t)} (t) = \frac{1}{(s-ik\cdot p_1)} \rho \quad \cdots (5.12)
$$

$$
\mathcal{J} (t^n) = \frac{\Gamma(n+1)}{n+1} = n^n \quad \cdots \cdots \quad (5.12)
$$

\* 

\*
In this way it is straight-forward determined that:

\[
\begin{align*}
\mathcal{f}_{1,1}(\gamma_1; t | \gamma_{10}) &= \cdots \cdots \quad (5.13) \\
&= ct^2 \left( \eta \left[ \delta^q(t) \gamma^2 \delta^p - \frac{t}{m} \hat{\gamma}_{10} \right] \delta^q \delta^p + \frac{t^2}{4m} \delta^p \gamma^2 \delta^q(t) \right) \\
&\quad + \chi \left( \delta^q \delta^p - \frac{2t}{3m} \delta^p \hat{\gamma}_{10} \right) \delta^q + \delta^q(t) \delta^p \hat{\gamma}_{10} \delta^p \right) 
\end{align*}
\]

Proceeding as before, one might calculate the explicit expressions for \( f_{1,1}^2 \). 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 \( f_{1,1}^2 \) due only to the first two terms of the r.h.s. of 5.4.

From 4.40, 4.32, and 5.13:

\[
\begin{align*}
\mathcal{L}_1(\mathcal{f}_{1,1}^1) + \mathcal{L}_2(\mathcal{f}_{1,1}^1) &= c^2 \int_0^t \frac{dt}{\eta} \left[ \delta^q(t) \gamma^2 \delta^p - \frac{t}{m} \hat{\gamma}_{10} \right] \delta^q \delta^p + \frac{t^2}{4m} \delta^p \gamma^2 \delta^q(t) \\
&\quad + \chi \left( \delta^q \delta^p - \frac{2t}{3m} \delta^p \hat{\gamma}_{10} \right) \delta^q + \delta^q(t) \delta^p \hat{\gamma}_{10} \delta^p \right) \\
&= c^2 \left[ \delta^q(t) \gamma^2 \delta^p - \frac{t}{m} \hat{\gamma}_{10} \right] \delta^q \delta^p + \frac{t^2}{4m} \delta^p \gamma^2 \delta^q(t) \\
&\quad + \chi \left( \delta^q \delta^p - \frac{2t}{3m} \delta^p \hat{\gamma}_{10} \right) \delta^q + \delta^q(t) \delta^p \hat{\gamma}_{10} \delta^p \right)
\end{align*}
\]

(footnote continued on bottom of next page. . .)
knowledge of $f_{1,1}(x_1; t | x_{1o})$. Thus, rather than oppress the reader with a detailed accounting of the second term, $f^{[2]}_{1,1}$, we proceed to calculate the dynamical quantities of primary interest by methods which circumvent the complete calculation of the $\nu$-space density. The remainder of this chapter concerns the calculation of momentum space densities and associated expectation values and correlation functions. Specifically, we shall obtain: $\langle p_1(t) | p_1(0) \rangle$, the momentum time-relaxed density; $\langle p_1(t) | \hat{p}_1(0) \rangle$, which is the expected value of the momentum at time $t$, given the value of the momentum at $t = 0$; $\langle \hat{p}_1(t) | \hat{p}_1(0) \rangle$ the momentum autocorrelation function; and, $\langle p_1(0)p_1(t_1)p_1(t_2)p_1(t_3) \rangle$, which is a four-time momentum correlation function to be related to the neutron scattering cross-sections in a later chapter.

(footnote continued from previous page)

$$
\begin{align*}
&= \frac{2^3 \pi^3}{6} \left\{ \eta^{(2)}_{\nu^2} + \chi^{(2)}_{\nu^2} [3 + \frac{3}{2}] \right\} \left\{ \eta^{(2)}_{\nu^2} \left[ \delta q^2 + \delta p + \delta q^2 + \frac{3}{4m} \delta q^2 \right] + \frac{3}{20m^2} \delta q^2 \right\} \\
&\quad + \chi^{(2)}_{\delta q^2} + \left[ \frac{3}{m} \delta q^2 + \delta q^2 + \delta q^2 + \frac{3}{2} \delta q^2 \right] \\
&\quad + \frac{3}{12} \eta^{(2)}_{\nu^2} \left[ \delta q^2 + \delta q^2 + \delta q^2 + \delta q^2 + \delta q^2 + \frac{3}{8} \delta q^2 \right] \\
&\quad + \chi^{(2)}_{\delta q^2} + \left[ \frac{3}{m} \delta q^2 + \delta q^2 + \delta q^2 + \frac{3}{15} \delta q^2 \right]
\end{align*}
$$

It is apparent that these contributions to the inhomogeneous term of 5.4 are discouragingly lacking in simplicity. The corresponding contributions to $f^{[2]}_{1,1}$ 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.

Proceeding with this program, it is clear from the discussions of chapter III that the momentum time-relaxed density may be obtained from \( f_{1,1}(x_1; t \mid x_{1o}) \) by integrating over configurational coordinates. The probability density for finding particle \#1 with momentum in the neighborhood of \( p_1 \), at time \( t \), given that at \( t = 0 \) the particle had momentum \( p_{1o} \), is defined by:

\[
\phi(p_{1}; t \mid p_{1o}) = \int d^3q_{1o} d^3q_1 f_{1,1}(x_1; t \mid x_{1o}) f_{eq}(q_{1o} \mid p_{1o}) \tag{5.14}
\]

where \( f_{eq}(q_{1o} \mid p_{1o}) \) is the equilibrium probability density for finding the particle located at \( q_{1o} \), given that it has momentum \( p_{1o} \). Of course, in an isolated homogeneous system, \( f_{eq}(q_{1o} \mid p_{1o}) \) is independent of \( p_{1o} \); in fact, it is given by

\[
f_{eq}(q_{1o} \mid p_{1o}) = \frac{1}{\Omega} \text{, where } \Omega = \text{ volume of the system.}
\]

Thus,

\[
\phi(p_{1}; t \mid p_{1o}) = \frac{1}{\Omega} \int d^3q_{1o} d^3q_1 f_{1,1}(x_1; t \mid x_{1o}) \tag{5.14'}
\]

Let us expand \( \phi \) in a series in direct correspondence with the iteration series for \( f_{1,1} \). Thus,

\[
\phi(p_{1}; t \mid p_{1o}) = \sum_{i=0}^{\infty} \phi^{[i]}(p_{1}; t \mid p_{1o}) \tag{5.15}
\]
where
\[ (\mathbf{P}_1; t | \mathbf{P}_{10} ) = \mathbb{1} \int \frac{d^3 q}{4 \pi} \frac{d^3 q}{4 \pi} f^{(i)}_{1, l} (x_1; t | x_{10} ) \ldots \ldots (5.16) \]

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:
\[ 0 (\mathbf{P}_1; t | \mathbf{P}_{10} ) = \delta (\mathbf{P}_1 - \mathbf{P}_{10} ) \ldots \ldots (5.17) \]

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:
\[ 0 (\mathbf{P}_1; t | \mathbf{P}_{10} ) = \frac{c t^2}{2} \left[ n^{(2)} \mathbf{P}_1 + \chi^{(2)} \left( 3 \mathbf{P}_1 + \mathbf{P}_{10} \right) \right] \phi^{(0)} (\mathbf{P}_1; t | \mathbf{P}_{10} ) \ldots \ldots (5.18) \]

In principle, one might calculate the higher order corrections in this manner. Observe, however, that \( \phi \) 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:
\[ 0 \frac{\phi}{\delta t} = \mathbb{1} \int \frac{d^3 q}{4 \pi} \frac{d^3 q}{4 \pi} \left[ \phi^{(0)} + \eta^{(2)} \mathbf{P}_1 \right] \phi^{(0)} \ldots \ldots (5.19) \]

which clearly has the solution given by 5.18.###

In the same way, the contributions to \( \phi^{(2)}_{(\mathbf{P}_1; t | \mathbf{P}_{10} )} \) are

** See, e.g., Arsac, Schwartz

### Since, as initial condition for 5.19, we know that \( \phi^{(0)} (0) \equiv 0 \) for all \( \mathbf{P}_1, \mathbf{q}_1 \).
determined directly from 5.4. For example, the contribution due to $\mathcal{D}_1 f_{[1]}^{(1)} + \mathcal{D}_2 f_{[1]}^{(1)}$ is found to be:

\[
\phi_{\eta_1 \eta_2}^{[2]} = c^2 \int_0^t d\tau_1 \int_0^\tau_1 d\tau_2 \left[ \frac{\eta_1^2}{p_1^2} + \frac{\eta_2^2}{p_2^2} + \frac{3}{m} (3+\vec{p}_1 \cdot \vec{p}_2) \right] \delta^{(4)}(\vec{p}_1 - \vec{p}_0) 
\]

\[
= \frac{c^2 t^4}{24} \left[ \frac{\eta_1^2}{p_1^2} + \frac{\eta_2^2}{p_2^2} + \frac{3}{m} (3+\vec{p}_1 \cdot \vec{p}_2) \right] \delta^{(4)}(\vec{p}_1 - \vec{p}_0) 
\]

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 $\phi^2 (\vec{p}_1, t | \vec{p}_0) \phi$ |
|----------------|---------------------------------------------------------------|
| $J_1(f_{1,1}) + J_2(f_{1,1})$ | $\frac{2c^4}{24} \left[ \frac{n(2)\gamma^2}{p_1} + \frac{x(2)}{m} (3+\vec{p}_1 \cdot \vec{p}_1) \right] \phi^2 \phi$ |
| $J_3(f_{1,1})$ | $\frac{ct^4}{24m^3} \left[ \frac{15m}{\beta} + \frac{5p_1^2}{\beta} + \frac{5m}{\beta} \vec{p}_1 \cdot \vec{p}_1 + p_1^2 \vec{p}_1 \cdot \vec{p}_1 \right] \phi^2 \phi$ |
| $J_4(f_{1,1})$ | $\frac{ct^4}{24m^3} \left[ -10 + 5m \vec{v}^2 + \frac{1p_1^2}{3} \vec{p}_1 \cdot \vec{p}_1 - 2\vec{p}_1 \cdot \vec{v} \cdot (1-\vec{p}_1 \cdot \vec{p}_1) \right] \phi^2 \phi$ |
| $J_5(f_{1,1})$ | $\frac{ct^4}{24m^2} \left[ \frac{24}{\beta} \left( 5 \vec{v}^2 + 20 + 4\vec{p}_1 \cdot \vec{v} \cdot (3 + \vec{p}_1 \cdot \vec{p}_1) \right) \phi^2 \phi + \frac{22}{\beta} \left( 3 \vec{v}^2 + 6 + 5\vec{p}_1 \cdot \vec{v} \cdot (3 + \vec{p}_1 \cdot \vec{p}_1) \right) \phi \phi \phi \phi \right]$ |
| $J_6(f_{1,1})$ | $\frac{ct^4}{24m^2} \left[ \vec{v} \cdot \vec{v} + \vec{v} \cdot \vec{v} \right]$ |
| $J_7(f_{1,1})$ | $\frac{2c^4}{24m} \left[ \left( 3 + \vec{p}_1 \cdot \vec{v} \right) \left( \frac{x(2)}{m} (3 + \vec{p}_1 \cdot \vec{v}) \right) + \frac{n(2)\gamma^2}{p_1} \phi \right.$ |

(continued on next page)
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

\[
\frac{df_{1,1}}{dt} + \frac{\hat{v}_{1}}{m} \cdot \hat{v}_{1} f_{1,1} = c \int_{0}^{t} d\tau \left[ \frac{\chi(2)(3+\hat{v}_{1} \cdot \hat{v}_{1})}{m} + \eta(2)(\frac{\hat{v}_{1}^{2} + \tau}{p_{1}^{2} \cdot \hat{v}_{1} \cdot \hat{v}_{1}}) \right] \int_{t-\tau}^{t} f(t-\tau) f(t) \, dt.
\]

then only the first term in table 5.1 would have appeared as the contribution to \( \phi_{[2]}^{[2]}(p_{1}, t | p_{1,0}) \). 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; \( \phi_{[1]}^{[1]}(f_{1,1}^{[1]}), \phi_{[2]}^{[2]}(f_{1,1}^{[2]}) \) contribute terms exactly
cancelled by $\{ 7^{(f_{1,1})_x} + 9^{(f_{1,1})_x} \}$ contributions!! It is suspected that examination of the higher order terms of $\psi(p_1; t | p_{1o})$ 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 distribution 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 $< \dot{p}_1(t) | \dot{p}_1(0) >$, the expected value of the momentum of a particle at $t$, given that the particle's initial momentum was $p_{1o}$. By definition,

$$< \dot{p}_1(t) | \dot{p}_1(0) > = \int d^3p_1 \dot{p}_1 \psi(p_1; t | p_{1o})$$ .................................. (5.21)

It has already been demonstrated that the terms appearing in $\psi(p_1; t | p_{1o})$ are of the form $p_{1i}^m \delta(p_1 - p_{1o})$. Appealing to the definition, 5.21, it is noticed that only those terms of $\psi$ for which $m \geq n-1$ contribute to

$$< \dot{p}_1(t) | \dot{p}_1(0) >$$ . This simplifies matters considerably and, by a straightforward calculation, one obtains:

$$< \dot{p}_1(t) | \dot{p}_1(0) > = \dot{p}_{1o} + \frac{t^2}{2m} [c x^{(2)} \dot{p}_{1o}] + .................................. (5.22)$$

$$+ \frac{t^4}{4! m^2} \left( c^2 \chi^{(4)} + c [(2 \chi^{(2)} + 4 \chi^{(2)}) + 5 \chi^{(3)} + 10 \chi^{(4)}] p_{1o} - \chi^{(5)} \frac{t^2}{2} \dot{p}_{1o} \right) +$$

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

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = \int d^3p_1 d^3p_1 \rho_1^3 p_1^3 p_1^0 \phi(\vec{p}_1, t; \vec{p}_1, 0) \tag{5.23}$$

or, alternatively, (recognizing that the system of interest is an equilibrium assembly):

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = \int d^3p_1 d^3p_1 \rho_1^3 p_1^3 p_1^0 \left[ \frac{-\beta p_1^2}{2m p_0} \right] \frac{1}{(2\pi m k T)^3} \phi(\vec{p}_1, t; \vec{p}_1, 0) \tag{5.24}$$

However, it is clear that from the latter expression:

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = \int d^3p_0 \frac{-\beta p_0^2}{2m p_0} \frac{1}{(2\pi m k T)^3/2} \vec{p}_0 \cdot < \vec{p}_1(t) \cdot \vec{p}_0 > \tag{5.24'}$$

Thus, referring to 5.22, the following iteration is obtained for $< \vec{p}_1(t) \cdot \vec{p}_1(0) >$:

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > = < \vec{p}_0^2 >_{eq} \left\{ 1 - \frac{ct^2}{2m} \chi^{(2)} + \frac{ct^4}{4! m^2} \chi^{(4)} + \frac{ct}{12m^2} \left[ \gamma \chi^{(4)} - 5 \chi^{(2)} + 2 \chi \right] + \ldots \right\} \tag{5.25}$$

In the above expression, $< \vec{p}_0^2 >_{eq} = 3m/\beta = \int d^3p_0 p_0^2 e^{\frac{-\beta p_0^2}{2m}}$ 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.,

$$< \vec{p}_1(t) \cdot \vec{p}_1(0) > \approx \frac{-At^2}{2} \begin{array}{l}3m/\beta e^{3m/\beta e^{\frac{-\beta p_0^2}{2m}}}
\end{array} \tag{5.26}$$

**e.g., Rice, De Gennes
with

$$A \equiv \frac{c_1^{(2)}}{m}$$  \hspace{1cm} (5.26')

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

$$\lim_{t \to \infty} \langle \vec{p}_1(t) \cdot \vec{p}_1(0) \rangle = 0$$  \hspace{1cm} (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 \(\chi^{(4)}\) by

$$\chi^{(2)}.$$  \hspace{1cm} (5.26)

Certainly, in the high temperature limit

where

$$g_2(\xi) = \frac{\Omega}{\int d^3 \vec{e} \ e^{i\vec{e} \cdot \vec{q}}}, \quad g_3(\xi_1, \xi_2, \xi_3) = \frac{\Omega^3}{\int d^3 \vec{e}_1 \cdot \int d^3 \vec{e}_2 \cdot \int d^3 \vec{e}_3 \ e^{i\vec{e}_1 \cdot \vec{q}_1 + i\vec{e}_2 \cdot \vec{q}_2 + i\vec{e}_3 \cdot \vec{q}_3}}$$

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 \(|\xi_3| < r^*\), \(\beta^2 \phi(\xi_2) \cdot \beta^2 \phi(\xi_3) = 0\) so that integration over much of the excluded region of hyperspace provides zero contribution to \(\chi^{(4)}\), anyhow. Thus:

$$\chi^{(4)} = \Omega^2 \int d^3 \xi_2 \cdot d^3 \xi_3 \cdot e^{-\beta V(\xi_2, \xi_3)} \left[ \frac{\partial^2 \phi(\xi_2)}{\partial \xi_{2m}^2} \frac{\partial^2 \phi(\xi_3)}{\partial \xi_{3n}^2} \right] \approx \ldots \ldots$$  \hspace{1cm} (5.28)

In light of 5.28, it is noticed that the term of order
\[(c t^2 \chi^{(2)})^2\] which actually occurs in \[\langle p_1(t)p_1(0)\rangle\] is the third term in a Taylor's series expansion of \[\cos\left(\frac{c\chi t^2}{m}\right)^{1/2}\], rather than being the appropriate term of the series expansion of 5.26. For very dense systems, for which as a first approximation one may neglect terms of \(o(ct^n)\) compared with terms \(o(c^2 t^n)\), one obtains only the cosine term, viz.,

\[\langle \dot{p}_1(t)\dot{p}_1(0)\rangle = \cos A t^{1/2} \quad \ldots \quad (5.29)\]

This result is satisfying in that it demonstrates the existence 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, \[\langle \dot{p}_1(t)\dot{p}_1(0)\rangle\] probably has, in a rough way, the form of a damped oscillation (cf. fig 5-1.) However, 5.25 does not contain enough information to demonstrate this hypothesis explicitly.

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

\[\langle \dot{p}_1(t)\dot{p}_1(0)\rangle = \cos A t^{1/2} e^{-Bt^4} \quad \ldots \quad (5.30)\]

where

\[B = \frac{c}{12m^2} \left[ 5n +5\chi \left( \frac{\zeta}{r_{\zeta}a} \right) + \frac{\zeta}{r_{\zeta}a} +2\chi \left( \frac{\zeta}{r_{\zeta}a} \right) \right] \quad \ldots \quad (5.30')\]

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 $\langle \hat{p}_1(t) \hat{p}_1(0) \rangle$ for longer times requires an expansion to higher powers of the interaction parameters.

![Graph](image)

**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 potential and its first two derivatives are plotted as a function of $\rho$, the intermolecular separation distance.
Fig. 5-2: Typical intermolecular 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:

\[
\chi^{(2)} = \int d^3\xi \frac{g_2(\xi) 2^2 \phi(\xi)}{\frac{\partial^2}{\partial \phi^2}} = \frac{4\pi}{3} \int_0^\infty d\rho \rho^2 g_2(\rho) \left[ \frac{\partial^2 \phi}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \phi}{\partial \rho} \right]
\]

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 \( g_2(\xi) = \Omega e^{-\beta (\xi)} \int e^{-\beta (\xi)} d\xi \). Then, simple integration provides the relationship \( \chi^{(2)} = \beta \eta^{(2)} \) where

\[
\eta^{(2)} = \int d^3\xi \frac{g_2(\xi)}{x(\xi)} \left( \frac{x(\xi)}{\xi} \right)^2 (\text{see table 4-1, p. 60})
\]

The latter is obviously a positive quantity. In general, \( \chi = \int d^3\xi \frac{g_2(\xi) \partial \phi \partial \phi}{\frac{\partial^2}{\partial \xi^2} \frac{\partial^2}{\partial \xi^2}} = \beta \tilde{\eta}^{(2)} \), where \( \tilde{\phi} \) is a fictitious potential defined by \( g_2(\xi) = e^{-\beta \tilde{\phi}(\xi)} \) (see fig. 5.3.) We see that \( \tilde{\phi} \) has essentially the same form as \( \phi \). \( \eta^{(2)} \) 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 \( \Omega e^{-\beta (\xi)} \int e^{-\beta (\xi)} d\xi \) the following useful relationships between system constants (cf. table 4-1) may be obtained.
Previously, it has been shown that, in limit $T \to \infty$,

$$
\chi^{(2)} = \beta \eta^{(2)} 
\tag{5.31}
$$

In addition, it is easy to show:

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

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

$$
\chi^{2,xx} = \frac{\beta^2 \mu}{3} (4xx)(4xx) \quad ; \quad \chi^{2,xy} = \beta \psi^{(4,xy)}(4xy) \quad \ldots \ldots \tag{5.34a, b, c, d}
$$

$$
\chi^{2,xy} + 2 \chi^{2,yy} = \beta^2 \mu - 3 \eta \quad = \chi^{2,xx} \quad \ldots \ldots \tag{5.34d}
$$

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

$$
B = \frac{c}{12 m^2} \left[ \chi^{2,xx} + 2 \chi^{2,xy} \right] \quad \ldots \ldots \tag{5.35}
$$

Certainly, then, in the high temperature limit, because $\chi^{2,xx}$ and $\chi^{2,xy}$ 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:

\[ \langle p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) \rangle = \iiint \frac{d^3p_0...d^3p_3}{x_0...x_3} \phi(p_0,t_0;...;p_3,t_3) \]

i.e. the joint expectation of the xth component of the momentum of a particle at \( t_0, t_1, t_2, t_3 \). \( \phi(p_0,t_0;p_1,t_1;p_2,t_2;p_3,t_3) \) is the joint probability density for finding a specified particle with momentum \( \vec{p}_3 \) at \( t = t_3, \ldots \), \( \vec{p}_0 \) 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.,

\[ f(x_{s_0}, t_0; \ldots; x_{s_r}, t_r) = \int d[x_{n_0}(x_{n_r})] \]

\( x_{n_0} = x_{s_0}, \ldots, x_{n_r} = x_{s_r} \).

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

\[ f(x_{s_0}, t_0; \ldots; x_{s_r}, t_r) = \int d[x_{s_0}] \ldots \int d[x_{s_r}] f(x_{n_0}, t_0; \ldots; x_{n_r}, t_r) = \]

\[ = \int d[x_{s_0}] \ldots \int d[x_{s_r}] f(x_{s_0}) \delta(x_{n_0} - e^{-(t_1-t_0)}l_{x_{s_0}}) \ldots \delta(x_{n_r} - e^{-(t_r-t_0)}l_{x_{s_r}}) \]

**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

\[
< p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) > = \ldots \ldots (5.37)
\]

\[
= \int d\vec{p}_0 \ldots d\vec{p}_3 \left[ p_0 \begin{array}{c} x_1 \\ x_2 \\
end{array} p_2 \begin{array}{c} x_1 \\ x_2 \\
end{array} \right] \phi(\vec{p}_3, t_3-t_2 | \vec{p}_2) \times \\
\times \phi(\vec{p}_2, t_2-t_1 | \vec{p}_1) \times \phi(\vec{p}_1, t_1-t_0 | \vec{p}_0)
\]

It can be seen from the memory term of 3.18 that \( f_{1,1} \) \((x_1; t | x_{1,0})\) 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:

\[
\langle p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) \rangle = \quad \text{......... (5.38)}
\]

\[
= \int \cdots d\phi_3 \cdots d\phi_1 \left[ p_1 \cdots p_3 \right] \left( \delta(\phi_3 - \phi_2) \delta(\phi_2 - \phi_1) \delta(\phi_1 - \phi_0) + \right.
\]

\[
+ \delta(\phi_3 - \phi_2) \delta(\phi_2 - \phi_1) c(t_1 - t_0)^2 \left[ \eta^{(2)} + \chi^{(1)} (3+\phi_1 \phi_1) \right] \delta(\phi_1 - \phi_0) + \right.
\]

\[
+ \delta(\phi_3 - \phi_2) c(t_2 - t_1)^2 \left[ \eta^{(2)} + \chi^{(1)} (3+\phi_2 \phi_2) \right] \delta(\phi_2 - \phi_1) \delta(\phi_1 - \phi_0) + \right.
\]

\[
+ c(t_3 - t_2)^2 \left[ \eta^{(2)} + \chi^{(1)} (3+\phi_3 \phi_3) \right] \delta(\phi_3 - \phi_2) \delta(\phi_2 - \phi_1) \delta(\phi_1 - \phi_0) + \right.
\]

\[
+ o("\text{fourth power in the forces}") \right) ;
\]

\[
(t_0 < t_1 < t_2 < t_3)
\]

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

\[
\langle p_1(t_0)p_1(t_1)p_1(t_2)p_1(t_3) \rangle = \quad \text{......... (5.39)}
\]

\[
= \frac{3m^2}{\beta^2} \left( 1+c \frac{\chi^{(2)}}{2m} \right) [ -t_3^2 + 2t_3 t_2 - \frac{7t_2^2}{3} + \frac{8t_2 t_1}{3} - \frac{7t_1^2}{3} + 2t_1 t_2 - t_0 ]
\]

\[
+ \text{.................}
\]

\[
= \frac{3m^2}{\beta^2} \exp - c \frac{\chi^{(2)}}{2m} [ t_3^2 - 2t_3 t_2 + \frac{7t_2^2}{3} - \frac{8t_2 t_1}{3} + \frac{7t_1^2}{3} - 2t_1 t_2 + t_0^2 ]
\]

** e.g. Balescu 42
\frac{3m^2}{\beta^2} \text{ 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\textsuperscript{31,32}. Upon assuming a linear relationship for the current produced by an external electric field of frequency $\omega$, the dielectric constant is found to be given by**

$$
\varepsilon(\omega) = 1 + \frac{4\pi}{2\beta} \lim_{\lambda \to 0} \int \frac{dt}{E} e^{-(\lambda+i\omega)t} \sum_{i, j, i', j'} \sum_{n, m, n', m'} <p_{i}(\omega)p_{j}(t)\rangle \cdots (5.40)
$$

** also here assuming a zero external magnetic field. Egn. 5.40 can be modified for more general relationships between current and applied fields.
The summation is over all charge carriers of the assemblage.

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

$$\varepsilon(\omega) = 1 + \frac{4\pi}{3\omega^3} \frac{\rho_e}{m_e} \langle \frac{\mathbf{p}(0)}{\mathbf{p}(t)} \mathbf{e} \rangle$$  \hspace{1cm} (5.41)

In the above equation, $\rho_e$ is the density of electrons, $m_e$ is the electron mass, and $\langle \mathbf{p}(0), \mathbf{p}(t) \mathbf{e} \rangle$ 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:

$$\varepsilon(\omega) = 1 + \frac{4\pi \alpha C}{m_e \omega^2} \left[ 1 + \frac{\chi_e^{(a)}}{m_e \omega^2} \right]$$ \hspace{1cm} (5.42)

$\alpha$ is the fraction of the atoms which are ionized. $\chi_e^{(a)}$ is defined similarly to previous definitions:

$$\chi_e^{(a)} = \int \delta^2 \xi Q_e^{(a)}(\xi) \frac{\partial \mathcal{Q}_e^{(a)}}{\partial \mathcal{Q}_e^{(a)}}$$ \hspace{1cm} (5.43)

where $Q_{e,(a)}(\xi)$ is the interaction between electrons and neutral atoms; $Q_e(\xi)$ is probably well approximated by

$$Q_e(\xi) \approx \frac{e^{-\beta \mathcal{Q}_e^{(a)}}}{\int e^{-\beta \mathcal{Q}_e^{(a)}}}$$ \hspace{1cm} (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 $\leq 4$. 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 $f^{1,1}_{1,0}(x_{1}; t \parallel x_{10})$. $G_s(r,t)$ is defined as the conditional
probability density for finding a specified particle in the neighborhood of configuration phase point \( q_1^+ + r^+ \) at time \( t \), given that at \( t = 0 \) the same particle was at \( q_1^0 \). Since the systems to which this investigation pertain are isotropic, \( G_s \) does not depend on \( q_1^0 \); furthermore, \( G_s(r,t) \) is a function only of the absolute value of \( r^+ \).

Hence,
\[
G_s(r,t) = \int d^3p_1 \int d^3p_0 \frac{-\beta p_0^2/2m}{(2\pi mkT)^{3/2}} f(l_1, l_1^+; q_1^0, q_1^0) \quad \ldots \ldots (6.1)
\]

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

with
\[
G_s[i](r,t) = \int d^3p_1 \int d^3p_0 \frac{-\beta p_0^2/2m}{(2\pi mkT)^{3/2}} f[l_1, r; i, r_0](p_1, r; i, p_0, 0) \quad \ldots \ldots (6.2)
\]

Hence, from 5.8,
\[
G_s^{[0]}(r,t) = \int d^3p_1 \int d^3p_0 \frac{-\beta p_0^2/2m}{(2\pi mkT)^{3/2}} \delta(r-\vec{r}_1 t) \delta(p_1-p_0) \quad \ldots \ldots (6.3)
\]

\[
= \left( \frac{m\beta}{2\pi t^2} \right)^{3/2} e^{-m\beta r^2/2t^2},
\]

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:
\[
G_s^{[1]} = \int d^3p_1 \int d^3p_0 \frac{-\beta p_0^2/2m}{(2\pi mkT)^{3/2}} f(x_1; i, x_0) \quad \ldots \ldots (6.4)
\]

Integrating by parts re. \( p_1 \):
\[
= ct^2 \int d^3p_1 \int d^3p_0 \frac{-\beta p_1^2/2m}{(2\pi mkT)^{3/2}} \left\{ \frac{n_0}{p_1} \delta^2 + \frac{n_1}{m} \delta^2 + \frac{\delta^2}{4m^2g^2} + \frac{\delta^2}{5m} \right\}
\]

\[
= ct^2 \int d^3p_0 \frac{-\beta p_0^2/2m}{(2\pi mkT)^{3/2}} \left\{ \frac{n_0}{p_0} \delta^2 + \frac{\delta^2}{3m} \right\}
\]

\[
\delta(r-\tilde{r}_1 t) \delta(p_1-p_0) \delta(\tilde{q}_1^0-\tilde{q}_0^0 t/m)
\]
Again, integrating by parts:

\[
\frac{ct^2}{\beta} \left( \frac{m}{4m} \left[ \frac{m\beta^2 r^2}{t^2} - 3 \right] - \frac{\chi(2)}{3\beta} \left[ \frac{m\beta^2 r^2}{t^2} - 3 \right] \right) G^{(0)}_s(r, t)
\]

Finally:

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

At high temperatures, \( n(2) = \chi(2) \), so that

\[
\lim_{T \to \infty} G^{(1)}_s(r, t) = -\frac{ct^4}{24m^2} \chi(2) v^2 \left( \frac{n(2)}{4} \right) G^{(0)}_s(r, t)
\]

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

\[
\frac{\partial f^{[i]}_{m_q_1}}{\partial t} + \frac{\partial}{\partial q_1} f^{[i]}_{m_q_1} = \mathcal{S}(q_1, p_1, t) \quad \text{with} \quad f^{[i]}_{m_q_1}(t=0) = 0 \quad \text{having}
\]

\[
f^{[i]}_{m_q_1} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S}
\]

The \( \mathcal{O}_p^{[i]}_{nj} \) are derivative operators on \( p_1 \). Thence:

\[
G^{(i)}_s \int \frac{d^3 p_0}{(2\pi m T)^3/2} e^{-\beta p_0^2/2m} \mathcal{J} \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} \delta(p_1 - p_0)
\]

If one next integrates by parts re. \( p_1 \), he can immediately and easily perform the integration over \( p_0 \), yielding:

\[
G^{(i)}_s \int \frac{d^3 p_1}{(2\pi m T)^3/2} e^{-\beta p_1^2/2m} \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} = \mathcal{J} \mathcal{J}^{[i-1]} \mathcal{J} \mathcal{S} \delta(p_1 - p_0)
\]
As an illustration, let us apply this procedure to a calculation leading to 6.5. It has previously been shown that

\[ \frac{\partial f^{[1]}}{\partial t_{1,1}} + \frac{p_{1}}{m}q_{1} f_{1,1}^{[1]} = \nabla \cdot (n^{[1]} + f^{[0]}(t)) \]

\[ = c \left( \frac{n^{[1]}}{m} \frac{V}{m} + \chi^{[1]} \frac{3 + p_{1}}{p_{1}} \right) f_{1,1}^{[1]}(t) \]

\[ f_{1,1}^{[1]}(p_{1}, q_{1}; 0) = 0 \]

Thus, \[ G_{s}^{[1]} = c \int d^{3} p_{1} e^{-\frac{\beta p_{1}^{2}}{2m} - i \frac{q_{1}}{m} p_{1}} \frac{1}{(2\pi m k T)^{3/2}} \left( \frac{n^{[1]}}{m} \frac{V}{m} + \chi^{[1]} \frac{3 + p_{1}}{p_{1}} \right) \delta(q_{1} - q_{0}) = 0 \]

In this way the complete calculation of \( f_{1,1}^{[2]} \) may be circumvented but the second correction to \( G_{s}^{[2]} \) may still be obtained. We start with the kinetic equation for \( f_{1,1}^{[2]} : \)

\[ \frac{\partial f^{[2]}}{\partial t_{1,1}} + \frac{p_{1}}{m}q_{1} f_{1,1}^{[2]} = \nabla \cdot (n^{[2]} + f^{[0]} + \nabla \cdot f^{[1]} + \nabla \cdot f^{[1]}) \]

where \( \nabla \) are defined by 4.32, 4.37, 4.40-46. Corresponding to each of the \( \nabla \) will be a contribution to \( G_{s}^{[2]} \).

Consider, for example, the contribution due to \( (p_{1} + q_{2}) f_{1,1}^{[1]} \).

From 4.32 and 4.40:

\[ (p_{1} + q_{2}) f_{1,1}^{[1]} = c \int_{0}^{T} dt \left( \frac{n^{[1]}}{m} \frac{V}{m} + \chi^{[1]} \frac{3 + p_{1}}{p_{1}} \right) \delta(t - t') f_{1,1}(t - t') \]
Thus, since $q_2$ is present in the integral only as derivatives, except in $f_{1,1}^1$:

$$\mathcal{J} \varphi^2_{1,1} f_{1,1}^1 = c^2 \int d \tau \left[ (2)_{\mathcal{P}_1} \tau \left( -\frac{ik}{m} \mathcal{P}_1 \right) + (2)_{3+\mathcal{P}_1} \frac{i k P_1}{m} \mathcal{V}_1 \right] = c^2 \int d \tau \left( 2+ \frac{i k}{m} \mathcal{P}_1 \mathcal{V}_1 \right) \mathcal{J} \varphi^2_{1,1} f_{1,1}^1$$

Next, taking the Laplace transform and using the convolution theorem:

$$\mathcal{J} \varphi^2_{1,1} f_{1,1}^1 = c^2 \left[ (2)_{\mathcal{P}_1} \frac{1}{m \mathcal{P}_1[s-ik]} - \frac{i k}{m} \mathcal{P}_1[s-ik] \right]$$

Finally, referring to 5.13:

$$\mathcal{J} \varphi^2_{1,1} f_{1,1}^1 = \left[ \delta \left( \frac{\mathcal{P}_1}{m} - \mathcal{P}_1 \right) \right] \left( (2)_{\mathcal{P}_1} \frac{1}{m \mathcal{P}_1[s-ik]} - \frac{i k}{m} \mathcal{P}_1[s-ik] \right)$$

Now, utilize the procedure described on the bottom of page 6-4. For example, the contribution due to the $\chi^{(2)}$ term is (after integrating by parts twice)

$$\alpha \int \frac{d^3 \mathcal{P}_1}{(2\pi \hbar \mathcal{T})^{3/2}} \mathcal{J} \varphi^2_{1,1} f_{1,1}^1$$
\[
\begin{align*}
&= t^2 \left( \frac{t^4}{180 m^2 \beta^2} \frac{v^2}{r} \right) G^{[0]}_s(r,t) \frac{7}{360 m^2}\left( \frac{v^2}{r} \right) G^{[0]}_s(r,t)
\end{align*}
\]

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 \((\text{(1)} + \text{(2)})_{1,1,1}^f \) is

\[
G_s^{[2] \text{ due to } (\text{1})_{1,1}^f} = \frac{c^2 t^4}{2} \left( \frac{\beta^2}{m^2} \right) G^{[0]}_s(r,t) - \frac{\eta^{(1)}(t)}{m^2} \beta \left( \frac{3 t^4}{280 m^2 \beta^2} \frac{v^2}{r} \right) \frac{v^2}{r} \left( t^2 \frac{v^2}{r} \right) + \frac{\eta^{(2)}}{m^2} \beta \left( \frac{1}{90 m^2 \beta^2} \frac{v^2}{r} \right) 40 \left( \frac{t^4}{280 m^2 \beta^2} \frac{v^2}{r} \right) \frac{v^2}{r} + \frac{7 t^2}{180 m^2} \left( \frac{v^2}{r} \right) G^{[0]}_s(r,t)
\]

(6.8)

As another example, consider the contribution due to \( f_{1,1,1}^{[0]} \). Again remembering that \( \delta_{-t} f_{1,1,1}(t-t) = f_{1,1,1}(t) \), and referring to 4.37, it it quickly seen that

\[
\begin{align*}
\int_{3}^{f_{1,1,1}^{[0]}} & = \frac{c t^3}{6 m^3} \chi^{(4)} \left( \frac{15 m}{\beta} + \frac{5 P^2}{\beta} + \frac{5 mp^2}{\beta} \right) p_{1}^{+} \left( \frac{p_{1}^{+}}{m} \right) \left( \frac{p_{1}^{+}}{m} \right) f_{1,1,1}^{[0]}(t)
\end{align*}
\]

Thus, the contribution to \( G_s^2 \) is

\[
= \frac{c x^{(4)}}{m^3} \int d^3 p_1 e^{-\frac{\beta P^2}{m}} \frac{1}{(2\pi m kT)^{3/2}} \int \frac{1}{s-ik^p_{1}P_{1}} \left( \frac{t^5}{5!} \frac{5 m}{\beta} p_{1}^{+} \left( \frac{p_{1}^{+}}{m} \right) \delta(q_{1}^{+}q_{1}^{+}P_{1}^{t})
\]

so that we finally have
\[ G_s^{[2]}(r,t) = \text{due to } 3 \]

\[ = -c \frac{(4)^4}{m^2} \left( \frac{1}{60} \frac{t^4}{m^2 \beta^2} \right) \frac{v^2}{r} \frac{v^2}{r} + \frac{1}{6} \frac{t^2}{m^2} \frac{v^2}{r} \] \( G_s^{[0]}(r,t) \) (6.9)

One proceeds to calculate the contributions due to \( \mathcal{Q}_4 \) 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 convenient 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 \( \tau \) integration in the collision integrals, one can read off the contributions to \( G_s^{[2]} \). One finds:

\[ G_s^{[2]}(r,t) = \text{due to } 4 \]

\[ = \frac{c n}{m} \frac{t^4}{2} \left( \frac{t^4}{36m^2 \beta^2} \frac{v^2}{r} \frac{v^2}{r} + \frac{1}{3} \frac{t^2}{m^2} \frac{v^2}{r} \right) G_s^{[0]}(r,t) \] (6.10)

\[ G_s^{[2]}(r,t) = \text{due to } 5 \]

\[ = \frac{c n}{m^2} \frac{t}{2} \left( \frac{t^4}{36m^2 \beta^2} \frac{v^2}{r} \frac{v^2}{r} + \frac{1}{6} \frac{t^2}{m^2} \frac{v^2}{r} \right) G_s^{[0]}(r,t) + \]

\[ + c \chi \frac{(2x)^4}{m^2} \frac{t}{2} \left( \frac{t^4}{36m^2 \beta^2} \frac{v^2}{r} \frac{v^2}{r} + \frac{7}{60m^2} \frac{t^2}{m^2} \frac{v^2}{r} \right) G_s^{[0]}(r,t) + \]

\[ + c \chi \frac{(2x)^4}{m^2} \frac{t}{2} \left( \frac{3}{20} \frac{t^2}{m^2} \frac{v^2}{r} \right) G_s^{[0]}(r,t) + \]

\[ + c \chi \frac{(4)^4}{m^2} \chi(3) \frac{t^4}{2} \frac{v^2}{36m^2 \beta^2} \frac{v^2}{r} \frac{v^2}{r} + \frac{13}{180m^2} \frac{t^2}{m^2} \frac{v^2}{r} \] \( G_s^{[0]}(r,t) \) (6.11)
\[ G_{s}^{[2]}(r,t) = \] 

**due to 6**

\[ = -c^4 \psi \frac{t^4}{2m^2} \beta t^4 \left( \frac{1}{2r} \psi \frac{t^2}{r} \psi + \frac{1}{6} \beta^2 \frac{t^2}{m^2} \right) G_{s}^{[0]}(r,t) + \]

\[ + c^4 \psi \frac{t^4}{2m^2} \beta t^4 \left( \frac{1}{60m^2} \psi \frac{t^2}{r} \psi \right) G_{s}^{[0]}(r,t) - \]

\[ - c^2 \psi \frac{t^4}{2m^2} \beta t^4 \left( \frac{1}{210m^2} \psi \frac{t^2}{r} \psi + \frac{1}{180m^2} \right) G_{s}^{[0]}(r,t) \]

**due to 7**

\[ = -c^2 \psi \frac{(2)^4}{2m} \left( \frac{(2)^4}{m} \right) \left[ \frac{t^2}{180m^2} \psi + \frac{1}{90m^2} \right] \psi \frac{t^2}{r} \psi \right) G_{s}^{[0]}(r,t) + \]

\[ + c^2 \psi \frac{(2)^4}{m \beta} \left[ - \frac{t^2}{40m^2} \psi - \frac{t^4}{105m^2} \right] \psi \frac{t^2}{r} \psi \right) G_{s}^{[0]}(r,t) \]

**due to 8**

\[ = \frac{ct}{2m} \beta \left( \frac{u}{192m} - \frac{\psi}{56} \right) \frac{t^4}{m^2} \psi \frac{t^2}{r} \psi \right) G_{s}^{[0]}(r,t) + \]

\[ + c^2 \psi \frac{(4)^4}{2m} \beta \left( \frac{u}{(3)^4} - \frac{\psi}{56} \right) \frac{t^4}{m^2} \psi \frac{t^2}{r} \psi \right) G_{s}^{[0]}(r,t) \]

**due to 9**

\[ = -c^2 \psi \frac{(4)^4}{m} \beta \left[ - \frac{1}{168m^2} \psi \frac{t^2}{r} \psi \right] + \frac{u^4}{m^2} \beta \frac{t^4}{192m^2} \frac{\psi \frac{t^2}{r} \psi \right) x \] 

\[ \times G_{s}^{[0]}(r,t) \]
Upon adding these contributions (6.8 - 6.15) one obtains for the total second order correction to $G_s(r,t)$:

\[
G_s^{[2]}(r,t) = \text{************} \tag{6.16}
\]

\[
= \frac{c t^4}{2m^2} \left[ \frac{n(2)^2}{m^2} \frac{\beta^2}{2r^2} \frac{V^2}{r^2} + \frac{x(2)}{m} \frac{n(2)^2}{m^2} \frac{\beta^2}{2r^2} \frac{V^2}{r^2} \right] G_s^0(r,t)
\]

\[
+ \frac{c t^4}{2m^2} \left[ \frac{[\beta \mu(4) - 19 \beta \psi(4) + \chi(4)]}{64(3)} \frac{V^2}{r^2} + \frac{[\beta \psi(4) + 13 \chi(4)]}{180(3)} \frac{V^2}{r^2} \right] G_s^0(r,t)
\]

\[
+ \frac{c t^4}{2m^2} \left[ \frac{[n - x + \psi + \beta \psi]}{18} \frac{V^2}{r^2} + \frac{[n - x + \psi + \beta \psi]}{192} \frac{V^2}{r^2} \right] \times
\]

\[
\times \frac{t^2 V^2}{m^2} G_s^0(r,t)
\]

At high temperatures, where $\theta = -\beta \phi$, one may make use of the relationships 5.30 - 5.33, also noting that $\beta \psi(4)_{(3)} = \psi(4)_{(3)} = \chi(4) = \frac{\chi(2)^2}{8}$, so that:

\[
G_s^{[2]}(r,t) = \text{************} \tag{6.17}
\]

\[
\lim_{T \to \infty} = \frac{c t^4}{2m^2} \chi^{(2)^2} \left[ \frac{[23 t^4}{630m^2} \frac{\mu}{2} \frac{V^2}{r^2} + \frac{t^2}{15} \frac{V^2}{r^2} \right] G_s^0(r,t) + \]

\[
+ \frac{c t^4}{2m^2} \left[ \frac{n(4)}{90} \frac{\beta^2 \mu}{1728} \frac{V^2}{r^2} + \frac{[13 n - \beta^2 \mu + 3 \chi + \beta \psi]}{20} \frac{V^2}{r^2} \right] \times
\]

\[
\times \frac{t^2 V^2}{m^2} G_s^0(r,t)
\]

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:
\[ G_s(r,t) = \sum_{n=0}^{\infty} t^{2n} D_R^{[n]} G_s^{[0]}(R,t) \]  \hfill (6.18)

where

\[ \tilde{R} \equiv (m\beta)^{1/2} + \frac{r}{t} \quad ; \quad G_s^{[0]}(R,t) = (m\beta/2\pi t^2)^{3/2} e^{-R^2/2} \]  \hfill (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

\[ \varphi(k,t) = e^{-t^2k^2/2m\beta} \sum_{n=0}^{\infty} t^{2n} w[n](\frac{tk}{(m\beta)^{1/2}}) \]  \hfill (6.20)

where the \( w[n](\frac{tk}{(m\beta)^{1/2}}) \) are polynomials in \( tk/(m\beta)^{1/2} \) corresponding to the \( D_R^{[n]} \) and contain terms of even power of \( tk/(m\beta)^{1/2} \) less or equal to than \( 2n \). For example \( w[1] \sim -t^2k^2/m\beta \) corresponds to the differential operator \( D_R^{[1]} \).

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:

\[ S_{inc.}^{cl.}(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \int d^3r e^{-ik\cdot r} G_s^{cl.}(r,t) \]  \hfill (6.21)

\[ = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \varphi_{inc.}^{cl.}(k,t) = \int_{-\infty}^{\infty} dt \frac{e^{-[i\omega t + k^2 t^2]/2m}}{2\pi} \sum_{n=0}^{\infty} t^{2n} w[n](\frac{tk}{(m\beta)^{1/2}}) \]
so that, from 6.3, 6.5, and 6.19:

\begin{equation}
S_{\text{inc}}^{cl}(k,\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{\frac{-i(\omega+kt^2)}{2}} \left[ 1 - \frac{ct^2}{2} \left( \frac{\beta n}{4} - \frac{\chi_{(1)}}{3} \right) + o(\epsilon^4) \right]
\end{equation}

\begin{align*}
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{\frac{-k^2 t^2}{2}} \left[ 1 - \frac{c k^2}{2m} \left( \frac{\beta n}{4} - \frac{\chi_{(1)}}{3} \right) + o(\epsilon^4) \right] \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{\frac{-m \beta \omega^2}{2k^2}} \left[ 1 - \frac{c 8}{24k^2} \left( \frac{3-10m \beta}{k^2} + \frac{m^2 \beta^2 \omega^4}{k^4} \right) \chi_{(2)}(k) + \text{terms in the fourth power of the forces} \right]
\end{align*}

Thus, in the high temperature limit:

\begin{equation}
S_{\text{inc}}^{cl}(k,\omega) = \sqrt{\frac{m \beta}{2\pi k^2}} e^{\frac{-m \beta \omega^2}{2k^2}} \left[ 1 + \frac{c 8}{24k^2} \left( \frac{3-10m \beta}{k^2} + \frac{m^2 \beta^2 \omega^4}{k^4} \right) \chi_{(2)}(k) + \text{terms in the fourth power of the forces} \right]
\end{equation}

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:

\begin{equation}
S_{\text{inc}}(k,\omega) = e^{-\frac{\beta n \omega}{2}} e^{-\frac{\beta n^2 k^2}{8m}} \left[ S_{\text{inc}}^{cl}(k,\omega) + \right.
\end{equation}

\begin{equation}
\left. + \frac{c k^2 \beta^2}{48} \chi_{(2)} \sqrt{\frac{\beta}{2mmk^2}} e^{2k^2} \left( 1 - \frac{\omega^2 m \beta}{k^2} + \frac{2k^2 \beta}{8m} \right) + o(\epsilon^4) \right] \nonumber
\end{equation}

*Rosenbaum, thesis - especially eqn. 5.45;\% Rewritten to our notation.
Thus, using 6.22', one can express the exact scattering function at high temperature as:

\[
S_{\text{inc}}(k,\omega) = \sqrt{\frac{m^2}{2\pi k^2}} e^{-\frac{\beta\hbar\omega}{2} - \frac{\hbar^2 k^2}{8m}} \cdot e^{-\frac{mB\omega^2}{2k^2}} \times \ldots \ldots \ldots \ldots (6.24)
\]

\[
\times \left[ 1 + \frac{c\beta^2}{24k^2} \left( \frac{3-10mB\omega^2}{k^2} + \frac{m^2B^2\omega^4}{k^4} \right) \Delta_2(k,\omega,\beta) + \right.
\]

\[
\left. + \text{terms of } o(\hbar^4, \epsilon^4) \ldots \ldots \ldots \right]
\]

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,

\[
\Delta_2(k,\omega,\beta) = \left[ 1 + \frac{\beta\hbar^2 k^2}{2m} \left( \frac{1-\omega^2 mB}{k^2} + \frac{\hbar^2 k^2 B}{8m} \right) \right] \ldots \ldots \ldots \ldots (6.25)
\]

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.,

\[
S_{\text{inc}}(k,\omega) = e^{-\frac{\beta\hbar\omega}{2} - \frac{\hbar^2 k^2}{8m}} \left[ S_{\text{inc}}^{\text{cl}}(k,\omega) + a_{\text{1}}(k,\hbar,\omega)\chi(2) + \right.
\]

\[
\left. + a_{\text{2}}(k,\hbar,\omega)\chi(4) + \ldots \ldots \text{etc.} \right]
\]

The same system constants which demonstrate the deviation of \( S_{\text{inc}}^{\text{cl}}(k,\omega) \) 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, \( \Delta_2(k,\omega,\beta) \approx 1 \). 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, \( e^{-\beta\hbar^2 k^2/2m} \), remains; however, the quantum interference effects demonstrated by \( \Delta(k,\omega,\beta) \) may be neglected if \( \frac{\beta\hbar^2 k^2}{2m} \ll 1 \). If this requirement is met, the \( A-C-R-Z \) prescription, viz.

\[
S_{\text{inc}}(k,\omega) \approx e^{-\beta\hbar^2 k^2/2m} S_{\text{inc}}^{\text{cl}}(k,\omega)
\]

(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 \( \beta_n \) and \( \chi \). 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.
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 $S^{inc}_{\omega}(k)$ at constant $k$ and $\omega$, as a function of $\omega$.

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,

$$G_s(r,t) = \left[ 1 + \frac{ct^4}{2m^2} \left( \frac{n}{4} - \frac{\eta}{38} \right) \frac{V^2}{r} + o(\epsilon^4), \ldots, \right] G_s^{[0]}(r,t)$$

(6.27)
But,
\[
G_s^{[0]}(r,t) \equiv (m\beta/2\pi t^2)^{3/2} e^{-m\beta r^2/2t^2} \delta^{(+)}(r)
\]
\[
= e^{(t^2/2m\beta) \nabla^2 r} \delta^{(+)}(r)
\]
\[
= [ 1 + \frac{t^2}{2m\beta} \nabla^2 r + \frac{t^4}{4m^2\beta^2} \nabla^2 r \nabla^2 r + \ldots ] \delta^{(+)}(r).
\]

As a consequence, one might wish to represent \(G_s(r,t)\) for short times as:
\[
G_s(r,t) \approx (m\beta/2\pi W^2(t))^{3/2} e^{-m\beta r^2/2W^2(t)}
\]

with
\[
W(t) = t^2 \left[ 1 + \frac{ct^2}{m} \left( \frac{\beta n}{4} - \frac{\chi^{(2)}}{3} \right) \right]
\]
\[
\approx t^2 \left[ 1 - \frac{ct^2}{12m} \chi^{(2)} \right]
\]

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
\[
G_s(r,t) \approx [2\pi \sqrt{W^2(t)}]^{-3/2} e^{-r^2/2W^2(t)}
\]

**One notices that the Fourier transforms of \(\frac{m\beta}{2\pi t} \nabla^2 e^{-m\beta r^2/2t^2} \delta^{(+)}(r)\) and \(e^{(t^2/2m\beta) \nabla^2 r} \delta^{(+)}(r)\) are identical, so that the functions themselves must be equal.

See, e.g., Vineyard, Schofield
where
\[ w^2(t) \equiv \frac{2}{3} \int_0^t \langle \mathbf{v}(0) \cdot \mathbf{v}(t') \rangle \quad \ldots \quad (6.32) \]

Reference to eqn. 5.25 demonstrates
\[ w^2(t) = \frac{t^2}{m \beta} \left[ 1 - \frac{ct^2}{12m} \chi^{(2)} + o(\epsilon^4) + \ldots \right] \quad \ldots \quad (6.33) \]
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. have indicated how the Gaussian approximation may be improved upon, and have suggested
\[ \langle \mathcal{C}_{\text{inc}}^{\mathbf{c}^l}(k, t) \rangle = \exp \sum_{n=1}^{\infty} \gamma_n(t) \quad \ldots \quad (6.34) \]

where
\[ \gamma_1(t) = \int_0^t \int_0^t \langle \mathbf{v}(t_2) \cdot \mathbf{v}(t_1) \rangle \quad \ldots \quad (6.35) \]
\[ \gamma_2(t) = \int_0^t \int_0^t \int_0^t \int_0^t \langle \mathbf{v}(t_4) \cdot \mathbf{v}(t_1) \rangle - \frac{1}{2} [\gamma_1(t)]^2 \]
and so forth. ..

Calculating \( \gamma_1 \) and \( \gamma_2 \) from 5.25 and 5.39, 6.34 provides

**Assuming, of course, that the correct expansion for \( \langle \mathcal{P}_t(\mathbf{v}_0) \cdot \mathcal{P}_t(\mathbf{v}(t)) \rangle \) is used, as per 5.25.
(at high temperature):

\[ A_{inc}^{cl.}(k, t) = e^{-\frac{k^2[t^2(1-ct^2\chi^{(2)}_{..}) +...]}{2m\beta}} e^{\frac{c^4t^2\chi^{(2)}_{..}}{12m\beta^2}} e^{\frac{k^4t^4\chi^{(2)}_{..}}{8m^2\beta^4}} e^{\frac{k^6t^6\chi^{(2)}_{..}}{6m^4\beta^6}} \]

\[ = 1 - \frac{k^2t^2 + c^4t^2\chi^{(2)}_{..}}{2m\beta} \frac{k^4t^4}{24m^2\beta} \frac{k^6t^6\chi^{(2)}_{..}}{8m^2\beta^2} \frac{k^6t^6\chi^{(2)}_{..}}{m^4\beta^4} \frac{1}{48} \frac{1}{298} + \text{terms } o(t^6\epsilon^0), o(t^8\epsilon^2), o(\epsilon^4), \text{etc.} \]

\[ \ldots (6.36) \]

On the other hand, from the exact calculation, 6.20 and 6.5, it is found that

\[ A_{inc}^{cl.}(k, t) = e^{-\frac{k^2t^2/2m\beta}{2}} \left[ 1 + \frac{c^4t^2\chi^{(2)}_{..}}{24m^2\beta} + o(\epsilon^4) \ldots \right] \]

\[ = 1 - \frac{k^2t^2 + c^4t^2\chi^{(2)}_{..}}{2m\beta} \frac{k^4t^4}{24m^2\beta} \frac{k^6t^6\chi^{(2)}_{..}}{8m^2\beta^2} \frac{k^6t^6\chi^{(2)}_{..}}{m^4\beta^4} \frac{1}{48} + \text{terms } o(t^6\epsilon^0), o(t^8\epsilon^2), o(\epsilon^4), \text{etc.} \ldots \]

\[ \ldots (6.37) \]

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 \( f_{1,1}(x_1, t; x_{10}) \) 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, 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:

\[
\frac{3f}{3t^{1,1}}(x_1, t; x_{10}) = \sum_{\eta, \eta_0} c^n A_n(t) \quad \ldots \ldots \quad (7.1)
\]

**The system of interest here is not, because attention is focussed on specific members of the assembly.

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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 suggests choosing \( \varepsilon c \) for this purpose. \( \varepsilon \) 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 double expansion, in \( \varepsilon \) and \( \varepsilon c \).

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, \( f_{s,s}(x_1, \ldots, x_s; t) \), for \( s > 1 \), is assumed to be only implicit: the higher order

** Specifically, \( -P_l \cdot \nabla_{q_1} f_{1,1}(x_1; t) \).
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:
\[
\frac{\partial f_{s_1,1}(x_1;t|\underline{x}_0)}{\partial t} = A(f_{1,1}) = \sum_{m=0}^{\infty} c_n^m (\epsilon C)^n A_m, n-1, f_{1,1}, \ldots (7.2)
\]

and, for \( s \geq 2 \),

\[
f_{s, s}(x_s; t|\underline{x}_0) = \sum_{m=0}^{\infty} c_n^m (\epsilon C)^n f_{s, s}(x_s; f_{1,1}, n-1, f_{1,1}, \ldots (7.3)
\]

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)**:

\[
\frac{\partial f_{s_1, s_1}(x_1; t|\underline{x}_0)}{\partial t} + [H - \epsilon \dot{\phi}_s^a] f_{s_1, s_1} = \ldots (7.4)
\]

\[
= -\epsilon \dot{\phi}_s^a f_{s, s_1, s} + c \int d\underline{x}_{s+1} \left[ \delta_{s, s_1} - \epsilon \dot{\phi}_s^a \right] f_{s_1, s+1, s_1, s+1} (7.4)
\]

The operators appearing in the equation have the following definitions:

**At the end of this chapter, in preparation for studying \( C_\Omega(r, t) \), 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 \( L_0 = -H \) and \( L_1 = \epsilon \dot{\phi}_n - \epsilon \dot{\phi}_n \) (see next page.)
\[ H_s = \sum_{i=1}^{s} \sum_{m} p_i^+ q_i^- \quad ; \quad \Theta_s^r = \sum_{i=1}^{s} \sum_{j} \frac{\partial \phi_{ij}^r}{\partial q_i^-} (p_i^- - p_j^-) \]

\[ \Theta_s^a = \sum_{i=1}^{s} \sum_{j} \frac{\partial \phi_{ij}^a}{\partial q_i^-} (p_i^- - p_j^-) \quad ; \quad \Theta_s^r = \Theta_s^a = 0 \]

\[ \phi_{s,j}^r = \sum_{i=1}^{s} \frac{\partial \phi_{ij}^r}{\partial q_i^-} (p_i^- - p_j^-) \quad ; \quad \phi_{s,j}^a = \sum_{i=1}^{s} \frac{\partial \phi_{ij}^a}{\partial q_i^-} (p_i^- - p_j^-) \]

\[ \phi(\mid q_i^- - q_j^- \mid) \] is the two particle interaction potential energy, and has been broken into two terms, \( \phi_r \) and \( \phi_a \), which represents respectively, the repulsive and attractive terms. \( \epsilon \) is a positive constant; \( \phi_a \) 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". \( \xi \) 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:

\[ a) \quad A_{o,0} = -H \phi_{1,1}^r (x_1it) \quad ; \quad b) \quad A_{m,n} = \Omega \int dx_2 \phi_{2,2}^{m-1,1} \phi_{1,2}^{m-1,1} \]

\[ \quad \text{for } m,n \geq 1 \quad ; \]

\[ c) \quad A_{m,0} = \Omega \int dx_2 \phi_{1,2}^{m-1,0} \phi_{2,2}^{0,0} \quad ; \quad d) \quad A_{0,n} = \Omega \int dx_2 \phi_{2,2}^{0,n} \phi_{1,2}^{0,0} \]
Also, for \( s > 2 \):

\[
\frac{\partial f}{\partial t}, s \delta_{s,1} f_{l,1} \bigg|_{x_{l_{0}}} = \frac{\partial f}{\partial t}, l \bigg|_{l_{0}} = \frac{\partial f}{\partial t}, l \bigg|_{l_{0}} = A_{s,1} f_{l,1} \bigg|_{x_{l_{0}}}
\]

\[
= \sum_{m=0}^{\infty} (m \epsilon c)^{n} A_{m,n} f_{l,1} \bigg|_{x_{l_{0}}} \delta f, s
\]

\[\ldots (7.6)\]

Define \( D_{m,n} \) as the operator which takes the partial derivative with respect to time according to the chain rule, and then replaces \( \frac{\partial f}{\partial t}, l \) by \( A_{m,n} \). In other words,

\[
D_{m,n} \equiv \bigg( \frac{\delta}{\delta f}, l \bigg) + \frac{\partial f}{\partial t}, l + A_{m,n}
\]

\[\ldots (7.7)\]

Hence,

\[
\frac{\partial f}{\partial t}, s = \sum_{m=0}^{\infty} (m \epsilon c)^{n} D_{m,n} f_{s} \bigg|_{x_{l_{0}}}
\]

\[\ldots (7.8)\]

In this way, using Equations (7.8) and (7.3) in the BBGKY hierarchy for \( s > 2 \), and then equating coefficients of powers of the expansion parameters, the following equation is derived.

\[
D_{s,0} f_{s} \bigg|_{x_{l_{0}}} + (H - \Theta^{p}) f_{s} \bigg|_{x_{l_{0}}} = \frac{\partial}{\partial t} f_{s} \bigg|_{x_{l_{0}}}
\]

\[\ldots (7.9)\]
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:

$$\lim_{t \to \infty} \int_{-t}^{t} \mathcal{D} r_{s}^{(i)}(x_{s}; t_{1,1}, x_{1}; t_{0}) - \mathcal{D} f_{1}(x_{1}) \prod_{i=1}^{n} f_{1}(x_{i}) = 0$$

$\mathcal{D} r_{s}^{(i)}$ 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, $\mathcal{D} r_{s}^{(i)}(X_{s_{0}}) = \Lambda(X_{s})$ where $\Lambda(X_{s})$ is the solution of

$$\frac{\partial \Lambda(X_{s})}{\partial t} = [H_{s} - r_{s}^{(i)}] \Lambda(X_{s})$$

$\Lambda(X_{s_{0}})$ being any arbitrary function of the coordinates of the $s$-dimensional phase space, i.e., $\mathcal{D} r_{s}^{(i)} = e^{-(H_{s} - r_{s}^{(i)} t)}$.

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 has indicated

** Uhlenbeck, 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:

\[
\lim_{t \to \infty} \mathbf{A}^{-\mathbf{s}} \mathbf{f}^{R,0}(x; \mathbf{A}^R_{+t} \mathbf{1}_R, \mathbf{1}_R) = \lim_{t \to \infty} \mathbf{A}^{-\mathbf{s}} [\mathbf{A}^R_{+t} \mathbf{f}^{R,0}(x) \mathbf{A}^R_{+t} \mathbf{1}_R(x)]
\]

and

\[
\lim_{t \to \infty} \mathbf{A}^{-\mathbf{s}} \mathbf{f}^m,n(x; \mathbf{A}^R_{+t} \mathbf{1}_R, \mathbf{1}_R)(x_0) = 0,
\]

for \( m \) or \( n \neq 0 \) \hspace{1cm} \( (7.11b) \)

It is now possible to obtain explicit representations for the \( A_{m,n} \) which make up the collision terms in the evolutionary equation for \( \mathbf{1}_R, \mathbf{1}_R \). In Equation (7.9), let \( m = n = 0 \). In this case, the equation reads:

\[
\mathbf{D}_{0,0} \mathbf{f}^{R,0}(i; \mathbf{1}_R, \mathbf{1}_R) + \left[ H_{s} - \mathbf{g}_{s}^R \right] \mathbf{f}^{R,0}(i; \mathbf{1}_R, \mathbf{1}_R) = 0
\]

\hspace{1cm} \( (7.12) \)

However, this equation, which holds for \( \mathbf{1}_R, \mathbf{1}_R \), is equally valid for \( \mathbf{A}^R_{+t} \mathbf{1}_R, \mathbf{1}_R \). Noting that,

\[
\mathbf{D}_{0,0} \mathbf{f}^{R,0}(i; \mathbf{A}^R_{+t} \mathbf{1}_R, \mathbf{1}_R) = \left( \frac{\delta \mathbf{f}^{R,0}}{\delta t} \right) \mathbf{A}^R_{+t} \mathbf{f}^{R,0}(i; \mathbf{1}_R, \mathbf{1}_R)
\]

\hspace{1cm} \( (7.13) \)

so that, because \( \mathbf{A}^R_{+t} \mathbf{1}_R = e^{H_{s} \mathbf{1}_R} \), we can write

\[
\mathbf{D}_{0,0} \mathbf{f}^{R,0}(i; \mathbf{A}^R_{+t} \mathbf{1}_R, \mathbf{1}_R) = e^{H_{s} \mathbf{1}_R} \mathbf{D}_{0,0} \mathbf{f}^{R,0}(i; \mathbf{1}_R, \mathbf{1}_R)
\]

\hspace{1cm} \( (7.13b) \)
Equation (7.12) becomes:

\[
\left( \frac{d}{d\tau} - \left[ H_s - \Theta^r_s \right] \right) f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) = 0 \quad \cdots \cdots \quad (7.14)
\]

This equation has the formal solution,

\[
f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) = \mathcal{G}^r_{-\tau} f^{0,n}_{s,s} \left( ; f_{1,1} \right) \quad \cdots \cdots \quad (7.15)
\]

Multiplying 7.15 by \( \mathcal{G}^r_{-\tau} \), the equation yields:

\[
f^{0,n}_{s,s} \left( ; f_{1,1} \right) = \mathcal{G}^r_{-\tau} f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) \quad \cdots \cdots \quad (7.15a)
\]

Since the left hand side of the above equation does not depend on \( \tau \), the right hand side may be evaluated at any value of \( \tau \) which is convenient. For this purpose, let \( \tau = \tau \) so that in virtue of Equation (7.11a):

\[
f^{0,n}_{s,s} \left( ; f_{1,1} \right) = \mathcal{G}^r_{-\tau} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right] \left( x_{i}; t \left| x_i \right. \right) \mathcal{G}^r_{-\tau} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right] \quad \cdots \cdots \quad (7.16)
\]

How about expressions for \( f^{0,n}_{s,s} \)? From (7.9):

\[
D_{0,s} f^{0,n}_{s,s} + \left[ H_s - \Theta^r_s \right] f^{0,n}_{s,s} = \mathcal{G}^{0,n}_{s,s} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right]
\]

\[
= -\mathcal{G}^{0,n}_{s,s} \mathcal{G}^r_{-\tau} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right] \mathcal{G}^{0,n}_{s,s} \mathcal{G}^r_{-\tau} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right] \quad \cdots \cdots \quad (7.17)
\]

In general, for equations of the form

\[
D_{0,s} f^{0,n}_{s,s} \left( ; f_{1,1} \right) + \left[ H_s - \Theta^r_s \right] f^{0,n}_{s,s} = -\mathcal{G}^r_{-\tau} \left[ \mathcal{G}^1_{+\tau} f_{1,1} \right] \quad \cdots \cdots \quad (7.18)
\]

it is noticed that, upon letting \( f_{1,1} \rightarrow \mathcal{G}^1_{+\tau} f_{1,1} \) and by virtue of

\[
\left( \frac{d}{d\tau} - \left[ H_s - \Theta^r_s \right] \right) f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) \equiv \left( \frac{d}{d\tau} - \left[ H_s - \Theta^r_s \right] \right) f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) \]

\[
= \mathcal{G}^r_{-\tau} f^{0,n}_{s,s} \left( ; \mathcal{G}^1_{+\tau} f_{1,1} \right) \quad \cdots \cdots \quad (7.19)
\]
that (7.18) becomes
\[ \frac{d}{dt} \left[ r_s(s) f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) \right] = -\psi_s(i_{\tau + t}, f_{1,1}) . \]

This has the solution:
\[ r_s(s) f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) = f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) - \int_0^{\tau+t} r_s(s) \psi_s(i_{\tau + t}, f_{1,1}) \, dt . \]

Using (7.11b), we obtain finally:
\[ f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) = \int_0^{\tau+t} r_s(s) \psi_s(i_{\tau + t}, f_{1,1}) \, dt \ldots \ldots \ldots (7.19) \]

In this way, Equation (7.17) has the solution:
\[ f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) = \int_0^{\tau+t} r_s(s) \left( \sum_{q=0}^n f_{s,s}^\circ_q(i_{\tau + t}, f_{1,1}) + \sum_{l=1}^{n-1} a_{s,s} f_{s,s}^{\circ, l,n-1}(i_{\tau + t}, f_{1,1}) + \sum_{l=1}^{n-1} a_{s,s} f_{s,s}^{\circ, l,n-1}(i_{\tau + t}, f_{1,1}) \right) \, dt \ldots \ldots (7.20) \]

In particular, for \( s = 2, n = 1 \):
\[ f_{2,2}^\circ(i_{\tau + t}, f_{1,1}) = \int_0^{\tau+t} r_{2,2} \left( \sum_{q=0}^1 f_{2,2}^\circ_q(i_{\tau + t}, f_{1,1}) + \sum_{l=1}^{n-1} a_{2,2} f_{2,2}^{\circ, l,1}(i_{\tau + t}, f_{1,1}) \right) \, dt \ldots \ldots (7.20a) \]

Similarly,
\[ f_{s,s}^\circ_n(i_{\tau + t}, f_{1,1}) = \int_0^{\tau+t} r_s(s) \left( \sum_{q=0}^n f_{s,s}^\circ_q(i_{\tau + t}, f_{1,1}) + \sum_{l=1}^{n-1} a_{s,s} f_{s,s}^{\circ, l,n-1}(i_{\tau + t}, f_{1,1}) \right) \, dt \ldots \ldots (7.21) \]

and, in particular:
\[ f_{2,2}^\circ(i_{\tau + t}, f_{1,1}) = \int_0^{\tau+t} r_{2,2} \left( \sum_{q=0}^1 f_{2,2}^\circ_q(i_{\tau + t}, f_{1,1}) + \sum_{l=1}^{n-1} a_{2,2} f_{2,2}^{\circ, l,1}(i_{\tau + t}, f_{1,1}) \right) \, dt \ldots \ldots (7.21a) \]

Finally, using Equations (7.2), (7.5), (7.20), and (7.21), the kinetic equation can be written as:
\[
\frac{3\eta^1_{1,1} + \frac{P_{1,1}}{m}}{\nabla q_{1,1}^{f_{1,1}}} = c \frac{I_1(x_1; t) + c^2 I_2(x_1; t) + o(c^3)}{\nabla q_{1,1}^{f_{1,1}}} + \ldots \quad (7.22)
\]

where,

\[
I_1(x_1; t) = \Omega \int \text{d}x_2 \left[ \phi_1(x_2) - \varepsilon \phi_2(x_2) \right] \int_{-\infty}^{\infty} \Delta_{1,1}^{f_{1,1}}(x_1; t|x_1) f_{1,1}(x_2) \quad \ldots \quad (7.23)
\]

\[
I_2(x_1; t) = \Omega \int \text{d}x_2 \left[ \phi_2(x_2) - \varepsilon \phi_1(x_2) \right] \times \ldots \quad (7.24)
\]

\[
\times \int_{-\infty}^{\infty} \mathcal{D}_{1,0}^{f_{1,1}}(\varepsilon \Delta_{0,1}^{f_{1,1}}(x_1; t|x_1) f_{1,1}(x_1) + \varepsilon \phi_1(x_1) f_{1,1}(x_1) + \varepsilon \phi_1(x_1) f_{1,1}(x_1)) \text{d}t
\]

It is clear how one would proceed were he interested in obtaining higher order terms.

Equation (7.22) might now be solved for \( f_{1,1}(x_1; t|x_1) \).

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 focusing 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{\delta f}{\delta t_{1,1}}(x_1;t|x_{10},x_{20}) + H(x_1) f_{1,1}(x_1;t) = \ldots \quad (7.25a)

= \int dx_2 [\phi_{1,2}^{r,-\epsilon\phi_{1,2}^a}] f_{2,2}(x_1,x_2;t|x_{10},x_{20}) + \\
+(n-2) \int dx_3 [\phi_{1,3}^{r,-\epsilon\phi_{1,3}^a}] f_{2,2}(x_1,x_3;t|x_{10}) \ldots \quad (7.25b)

\frac{\delta f}{\delta t_{1,1}}(x_2;t|x_{10},x_{20}) + H(x_2) f_{1,1}(x_2;t) = \ldots \quad (7.25c)

= \int dx_1 [\phi_{1,2}^{r,-\epsilon\phi_{1,2}^a}] f_{2,2}(x_1,x_2;t|x_{10},x_{20}) + \\
+(n-2) \int dx_3 [\phi_{2,3}^{r,-\epsilon\phi_{2,3}^a}] f_{2,2}(x_1,x_3;t|x_{10})

\frac{\delta f}{\delta s_{s,s}} + [H - \phi_s^{a}] f_{s,s} = \ldots \quad (7.25c)

= -\epsilon\phi_s^a f_{s,s} + (n-s) \int dx_{s+1} [\phi_{s+1}^{r,-\epsilon\phi_{s+1}^a}] f_{s+1,s+1} \quad (s \geq 2; (1,2) \epsilon \{s\})

Now, let us make the assumption, analogous to (7.3),

that \( f_{s,s}(x_s; t|x_{10}, x_{20}) \) is not an explicit function of the
time; rather, is functionally dependent on both

\( f_{1,1}(x_1; t|x_{10}, x_{20}) \) and \( f_{1,1}(x_2; t|x_{10}, x_{20}) \) and changes

with time as the latter change. ** Thus, one performs an

expansion:

\( f_{s,s}(x_s; t|x_{1}, x_{2}) = \ldots \quad (7.26) \)

\[ = \sum_{\omega} c^{\omega} f_{s,s}^m(x_s; f_{1,1}(x_1), f_{1,1}(x_2)) \]

\[ = \prod_{n=0} \sum_{m=0} c^{m,n} f_{s,s}^m(x_s; f_{1,1}(x_1), f_{1,1}(x_2)) \]

**...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:

\[
\frac{\partial^2 f}{\partial t_1 \partial t_1} (x_1, t_1 \mid x_2, t_2) = \sum_{\nu=0}^{\infty} c_{\nu} (e \epsilon) \epsilon^n A_{m,n} (x_1; f_1 (x_1)) \ldots \ldots \tag{7.27a}
\]

\[
\frac{\partial^2 f}{\partial t_1 \partial t_1} (x_2, t_1 \mid x_1, t_2) = \sum_{\nu=0}^{\infty} c_{\nu} (e \epsilon) \epsilon^n A_{m,n} (x_2; f_1 (x_2)) \ldots \ldots \tag{7.27b}
\]

Inserting (7.27a) into (7.25a) and equating coefficients of expansion parameters, one obtains exactly the same set of functions for the \(A_{m,n} (x_1; f_1 (x_1))\) as obtained previously (Eq. (7.5), above).** Also, from (7.27b) and (7.25b), a similar set is obtained for \(A(x_2; f_1 (x_2))\).

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:

\[
D_{m,n} = \left[ \frac{\delta}{\delta f_1 (x_1)} \frac{\partial^2 f}{\partial t_1 \partial t_1} (x_1) + \frac{\delta}{\delta f_1 (x_2)} \frac{\partial^2 f}{\partial t_1 \partial t_1} (x_2) \right] \ldots \ldots \tag{7.28}
\]

with:

\[
\frac{\delta}{\delta f_1 (x_1)} \rightarrow A_{m,n} (x_1); \quad \frac{\delta}{\delta f_1 (x_2)} \rightarrow A_{m,n} (x_2)
\]

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 \(f_{2,2}^0\). Immediately, one obtains:

\[
f_{2,2}^0 (x_1, x_2; t \mid x_1^0, x_2^0) = \sum_{k=0}^{\infty} \left( \begin{array}{c}
\delta (x_1^0, x_2^0) \\
\delta (x_1^0, x_2)
\end{array} \right) \left( \begin{array}{c}
f_1 (x_1; t \mid x_1) \\
f_1 (x_2; t \mid x_2)
\end{array} \right) f_{1,1} (x_1; t \mid x_1) f_{1,1} (x_2; t \mid x_2) \ldots \ldots \tag{7.29}
\]

** 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

$$[D_{1,0} + D_{0,1}] f_{2,2}^{0,0} (x_1, x_2; \varphi_{1,1}(x_1), \varphi_{1,1}(x_2)) =$$

$$= \left[ \frac{\delta f^{0,0}_{2,2} (x_1, x_2; \varphi_{1,1}(x_1), \varphi_{1,1}(x_2))}{\delta \varphi_{1,1}(x_1)} \cdot \frac{\partial \varphi_{1,1}(x_1)}{\partial t} \right] + \left[ \frac{\delta f^{0,0}_{2,2} (x_1, x_2; \varphi_{1,1}(x_1), \varphi_{1,1}(x_2))}{\delta \varphi_{1,1}(x_2)} \cdot \frac{\partial \varphi_{1,1}(x_2)}{\partial t} \right] \quad \ldots \quad (7.30)$$

But,

$$f_{2,2}^{0,0} (x_1, x_2; \varphi_{1,1}(x_1), \varphi_{1,1}(x_2)) = f_{1,1} \left( \left[ \int_{-\infty}^{\varphi_{1,1}(x_1, x_2)} \int_{-\infty}^{\varphi_{1,1}(x_2, x_1)} \right] \varphi_{1,1}(x_1, x_2) \right) x_1 \, t \, |x_1, x_2| \, x_2 \, t \, |x_1, x_2| \ldots \quad (7.31)$$

Thus, by (.E.4b) and (.E.4c) of Appendix E:

$$\ldots \ldots \quad (7.32)$$

$$\frac{\delta f^{0,0}_{2,2} (x_1, x_2; \varphi_{1,1}(x_1), \varphi_{1,1}(x_2))}{\delta \varphi_{1,1}(x_1)} = \delta^6 (\hat{z}_1 - x_1) \delta^6 (\hat{z}_2 - x_2) \frac{\partial \varphi_{1,1}(x_1)}{\partial t}$$

where

$$\hat{z}_1 = \left[ \int_{-\infty}^{\varphi_{1,1}(x_1, x_2)} \int_{-\infty}^{\varphi_{1,1}(x_2, x_1)} \right] \varphi_{1,1}(x_1, x_2)$$

$$\hat{z}_2 = \left[ \int_{-\infty}^{\varphi_{1,1}(x_1, x_2)} \int_{-\infty}^{\varphi_{1,1}(x_2, x_1)} \right] \varphi_{1,1}(x_1, x_2) \quad \ldots \ldots \quad (7.33).$$
Thus, (7.30) becomes:

\[
[D_{1,0} + \varepsilon D_{0,1}] f^{0,0}_{2,2} (\cdots) f_{1,1} (\cdots) =
\]

\[
\{ \Omega f_1^a(x_1) \oint_{t} f_{1,1} (\cdots) \times
\]

\[
\{ \int \frac{dx_2}{\Omega} [\delta (z_2 - x_2) f_{1,1} (\cdots)] + \left[ \delta (z_2 - x_2) f_{1,1} (\cdots) \right] \times
\]

\[
\left[ \int \frac{dx_3}{\Omega} [\delta (z_3 - x_3) f_{1,1} (\cdots)] \right] + \left[ \int \frac{dx_4}{\Omega} [\delta (z_4 - x_4) f_{1,1} (\cdots)] \right]
\]

\[
\left[ \int \frac{dx_5}{\Omega} [\delta (z_5 - x_5) f_{1,1} (\cdots)] \right] + \cdots
\]

\[
(7.34)
\]

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:

\[
f^{1,0}_{2,2} (x_2; f_{1,1} (\cdots)) + \varepsilon f^{0,1}_{2,2} (x_2; (\cdots) =
\]

\[
\Omega \int \frac{d\tau}{\Omega} \oint_{t} f_{1,1} (\cdots) \times
\]

\[
\left[ \int \frac{dx_2}{\Omega} [\delta (z_2 - x_2) f_{1,1} (\cdots)] \right] + \left[ \int \frac{dx_3}{\Omega} [\delta (z_3 - x_3) f_{1,1} (\cdots)] \right] + \cdots
\]

\[
(7.35)
\]

..etc. Same as above, only with $\phi^{r+a}_1$ and $\phi^{r+a}_2$ replaced by $\phi^a_1$ and $\phi^a_2$, respectively.
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 \( f_{2,2}(x_1, x_2; t|x_{1o}, x_{2o}) \) is provided by

\[
f_{2,2}(x_2; t|x_{2o}) = f_{2,2}^{[0]} + c f_{2,2}^{[1]} + o(c^2) \quad \ldots \quad (7.36)
\]

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 $\varrho_d (r,t)$

In the preceding chapters, primary interest has been the derivation and solution of equations providing the evolution of the one particle conditional density, $f_{1,1}(x_1; t|\mathbf{x}_{10})$. 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, $f_{2,2}(x_1,x_2;t|\mathbf{x}_{10},\mathbf{x}_{20})$. Properly, one would start with Equation (3.23), with $s = 2$:

$$\frac{\partial f}{\partial t}_{2,2}(x_2; t| x_{20}) + \left( \frac{\rho}{m_1^*} q_1 + \frac{\rho}{m_2^*} q_2 + v_2 \phi_{12} (v_1 - v_2) \right) f_{2,2} = \mathcal{L} \int_0^t L e^{t(1-\mathcal{L})} (1-\mathcal{L}) L f_{2,2}(0)f_{2,2}(t-t) \ldots (8.1)$$

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

$$\left( \frac{\partial}{\partial t} + \sum_{i=1}^3 \frac{\rho_i}{m_i} q_i + v_2 \phi_{12} (v_1 - v_2) \right) f_{2,2}^{[0]}(x_2; t| x_{20}) = 0 \ldots (8.2)$$

with

$$f_{2,2}^{[0]}(x_2; 0| x_{20}) = \delta(x_1 - x_{10}) \delta(x_2 - x_{20}) \ .$$

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:

$$G_d(r,t) = c \int dp_1 dp_2 dq_1 dq_2 \ g_2(q_1, q_2) \ e^{- \frac{g^2 (p_1^2 + p_2^2)}{2m^2 \nu m}} f(x_1, t | x_2, 0) \ f(x_2, t | x_2, 0) \ \\
\tag{8.3}$$

where $g_2$ ($q_1, q_2$) is defined as in Equation (4.19). In this case it is not unreasonable to resort to a form of 'superposition' approximation, viz., assume

$$f_{2,2}(x_1, t | x_2, 0) = f(x_1, t | x_1, 0) f(x_2, t | x_2, 0) \ \\
\tag{8.4}$$

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 not a good approximation, contribute relatively little to the calculation of (8.3) because of the presence of the weighting factor, $g_2(q_1, q_2)$, appearing in the integral.

Hence, by (5.8), (5.13) and (8.4):

$$f_{2,2}(x_1, t | x_2, 0) \equiv \left\{ \begin{align*}
\delta^2 \eta^1(t) \delta^2 \eta^2(t) \delta^2 P_1 \delta^2 P_2 + \\
+ \frac{ct^2}{2} \eta^2(2) \left( \delta^2 \eta^1(\eta^1 + \eta^2) \delta^2 \eta^2 \delta^2 P_1 \delta^2 P_2 + \frac{ct^2}{4m^2} \delta^2 \eta^1(\eta^1 + \eta^2) \delta^2 \eta^2 \delta^2 P_1 \delta^2 P_2 \right) \\
+ \frac{ct^2}{2} \eta^2(2) \left( \delta^2 \eta^1(\eta^1 + \eta^2) \delta^2 \eta^2 + \delta^2 P_1 \delta^2 P_2 \right) \delta^2 \eta^1 \delta^2 \eta^2 \delta^2 P_1 \delta^2 P_2 \\
+ \text{terms } o(\epsilon^n) \end{align*} \right\} \ \\
\tag{8.5}$$

**Cf. Chapter 2, above.**
Consider, e.g., the zero'th term of $G_d$, defined by:

$$G_d(r,t) = \int dp_1 dp_2 dx_1 dp_2 dx_2 g_2(q_1, q_2) e^{-\frac{\delta(p_1^2 + p_2^2)}{2m \hbar^2 \frac{2}{mT}}} e^{-\frac{\delta^4 q_1(t) q_2(t) p_1 p_2}{2m \hbar^2 \frac{2}{mT}}}$$

$$= c \int dq_2 g_2(q_2) \left[ \frac{m^2}{2\pi^2} \right]^{3/2} e^{-\frac{m^2 r^2}{2t^2}} = e^{\frac{t^2 \nu^2}{2m^2 \beta}} \delta(r)$$

But, as before, notice that $\left[ \frac{m^2}{2\pi^2} \right]^{3/2} e^{-\frac{m^2 r^2}{2t^2}} = e^{\frac{t^2 \nu^2}{2m^2 \beta}} \delta(r)$

Thus,

$$G_d(r,t) = c \int dq_2 g_2(q_2) e^{-\frac{t^2 \nu^2}{2m^2 \beta}} \delta(q_2 - q_2)$$

$$= c \int dq_2 g_2(q_2) = \ldots$$

Next, consider

$$G_d(r,t) = \frac{c^2 \hbar^2 \gamma}{2} \int dp_1 dp_2 dx_1 dp_2 dx_2 g_2(q_1, q_2) \times$$

$$\left\{ \delta^4 q_1(t) q_2(t) \left( \nu^2 + \nu^2 \right) \delta P_1 \delta P_2 - \delta^4 q_1(t) q_2(t) \left( \nu^2 + \nu^2 \right) \delta P_1 \delta P_2 \right\}$$

(see eqn. 8.5, above, for detail)

$$\ldots$$

(8.7)
Integrate by parts re. $p_1$ and $p_2$ to obtain:

\[
\begin{align*}
[1] 
\mathcal{G}_d(r,t) &= c^2 \frac{t^2}{2} \int dq_2 dq_1 dp_1 dp_2 \frac{-\beta(p_1^2 + p_2^2)}{2m} g_2(q_1, q_2) \\
&\times \left[ \frac{n}{4} \left( \frac{n}{p_1} + \frac{n}{p_2} \right) - \frac{x(2)}{3m} \right] \delta^{q_1(t)}(t) \delta^{q_2(t)}(t) \\
&= c^2 \frac{t^2}{2} \int dq_2 dq_1 dp_1 dp_2 \frac{-\beta(p_1^2 + p_2^2)}{2m} g_2(q_1, q_2) \\
&\times \left[ \frac{n}{4m} \right] \left[ \frac{x(2)}{3m} \right] \left( \frac{\beta(p_1^2 + p_2^2)}{m} - 6 \right) \delta^{q_1(t)}(t) \delta^{q_2(t)}(t)
\end{align*}
\]

Further reduction yields,

\[
[1] 
\mathcal{G}_d(r,t) = c^2 \frac{t^4}{2m^2} \left[ \frac{n}{4} \right] - \frac{x(2)}{3m} \int dq_2 dq_1 g_s(q_1, q_2) (v^2 + v^2) \\
\left[ \frac{0}{4} \right] \left[ \frac{0}{4} \right] \times G_s(q_1 - q_1, t) G_s(q_2 - q_2, t)
\]

But \( \int dq_1 v^2 G_s(q_1 - q_1) \) yields zero boundary terms; thus,

\[
[1] 
\mathcal{G}_d(r,t) = c^2 \frac{t^4}{2m^2} \left[ \frac{n}{4} \right] - \frac{x(2)}{3m} \int v^2 e^{r \left( t^{2/2m\beta} \right)} g_2(r) \left( \frac{\beta t}{(m\beta)^{1/2}} \right)
\]

Hence, at least for the first two terms,

\[
[1] 
\mathcal{G}_d(r,t) = c^2 \frac{t^{2n}}{n!} \left[ \frac{n}{4} \right] + v^2 e^{R} g_2(\frac{\beta t}{m\beta^{1/2}})
\]

where the \( D_R \) are identical to those defined previously in the study of \( G_s \) (cf., Eq. (6.18)). In fact, because

\[
\int dq_1 \left( \frac{\beta}{q_1} \right)^{m-1} G_s(q_1 - q_1, t) = 0 \quad \text{for all } j \geq 1,
\]

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 $G(r,t)$:

$$G^{cl.}(r,t) = \sum_{n=0}^{\infty} t^{2n} D[n] e^{\frac{\nu^2}{R^2}} G^{cl.}(\frac{Rt}{[mB]^{1/2}}; 0) \quad \cdots \quad (8.9)$$

where

$$G(r,0) = \delta(r) + c g_2(r) \quad \cdots \quad (8.10)$$

The expression given by (8.9) is formally identical to Vineyard's "convolution approximation." 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:

$$S^{cl.}(k,\omega) = \sqrt{\frac{mB}{2\pi k^2}} e^{-\frac{mB\omega^2}{2k^2}} \left[ 1 + c g_2(k,\omega) \right] \times$$

$$\times \left[ 1 + \frac{c\delta}{2k^2} \left( 3 - 10mB\omega^2 + m^2B^2\omega^4 \right) \frac{\delta_{\infty}}{k^4} - \frac{\chi_{\infty}}{3} \right] + o(\omega^4) \quad \cdots \quad (8.11)$$

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:

$$\frac{d^2\sigma}{d\Omega d\omega} \sim \left[ \sigma_{coh} S_{coh}(k,\omega) + \sigma_{inc} S_{inc}(k,\omega) \right] \quad \cdots \quad (8.12)$$
\[ \gamma \left( \frac{m^{2} \beta \omega^2}{2k^2} \right) e^{-m \beta \omega^2/2k^2} \left[ Q_{coh}^2 \left( 1 + c \tilde{g}_2(k, \omega) \right) + Q_{inc}^2 \right] \times \]
\[ \times \left[ 1 + \frac{c \beta}{2k^2} \left( 3 - 10m \beta \omega^2 + \frac{m^2 \beta^2 \omega^4}{k^2} \right) \left( \frac{\beta \hbar^2}{4} \frac{\chi}{3} \right) + \ldots \right] \]

\( \tilde{g}_2(k, \omega) \) 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.,

\[ S(k, \omega) = e^{\frac{\beta \hbar \omega}{2}} e^{-\frac{\beta \hbar^2 k^2}{8m}} \left[ S_{coh}^2(k, \omega) + o(\hbar^2) + \ldots \right] \ldots (8.13) \]

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 \( G_3(r,t) \), i.e., about the 'superposition approximation', (8.4)? Let us, for the moment, refer to the

**Singwi, K.S., and Sjölander, A. \(^{11}\)
zero'th term in the density expansion obtained in the previous chapter:

\[ f_{2,2} (x_2 | x_{20}) = \frac{\partial (x_2 | x_1)}{\partial x_1} \int \frac{f (x_1 | x_{10})}{\partial x_1} \frac{f (x_1 | x_{10})}{\partial x_1} \frac{f (x_3 | x_{30})}{\partial x_3} \frac{f (x_3 | x_{30})}{\partial x_3} \]

The action of the kinetic operators is made clear if one notes that, acting upon any arbitrary function of \( x_s \):

\[ \int_{\tau_1}^{\tau_2} \ldots \int_{\tau_s}^{\tau_s} F(x_s; t) = \]

\[ = F(q_1 + \frac{\partial}{\partial t} \tau_1, p_1; \ldots; q_s + \frac{\partial}{\partial t} \tau_s, p_s; t) \]

Hence,

\[ \int_{-\tau}^{\tau} \frac{\partial (x_s)}{\partial x_s} \ldots \int_{-\tau}^{\tau} \frac{\partial (x_s)}{\partial x_s} F(x_s; t) = \]

\[ = F(q_1 + \frac{\partial}{\partial t} \tau_1, p_1; \ldots; q_s + \frac{\partial}{\partial t} \tau_s, p_s; t) \]

Note that \( \frac{\partial}{\partial t} \) is the momentum which the \( i \)-th particle has before the occurrence of the interaction which results in the configuration \( \{ x_s \} \) at time \( t \). In other words, \( \frac{\partial}{\partial t} \) 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, \( \frac{\partial}{\partial t} \) is the position at which the \( i \)-th particle would have been found at time \( t \) if it had proceeded from infinity with momentum \( \frac{\partial}{\partial t} \).
Referring to the two particle density described by (7.36), for almost all pairs of particles: \( \hat{q}_1(x_2) = \hat{q}_1; \hat{p}_1(x_2) = \hat{p}_1; \hat{q}_2(x_2) = \hat{q}_2; \) and, \( \hat{p}_2(x_2) = \hat{p}_2 \). When this is the case, terms in the density expansion of order higher than the zero'th are zero. Thus, for most pairs,

\[
 f_{2,2}(x_2; t | x_2) = f_{1,1}(x_1; t | x_1) f_{1,1}(x_2; t | x_2). 
\]
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

$$ \frac{\partial f_{11}(\textbf{x}_1,t|\textbf{x}_1\omega)}{\partial t} + \frac{1}{m} \sum_{q} \frac{\partial}{\partial \textbf{p}_q} f_{11} = \sum_{i<j}^{\infty} \int_{\gamma_0}^{\infty} \ldots \ldots \quad (9.1) $$
where the \( \mathcal{M}_{[j]} \) 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:

\[
I = \sum_{k=1}^{\infty} \int_0^t \left( \frac{(2k-2)!}{(2k-2)!} \right) \mathcal{M}_{[k]} \circ \left( p_i \mathbf{v}_{p_i} ; \tau \mathbf{v}_{\mathbf{u}_1} \right) \mathcal{J}_{1,1}(t-\tau) \cdots (9.2)
\]

It is apparent that the collision integral contains a "memory", i.e., it is necessary to integrate over the past history of \( f_{1,1} \). \( \mathcal{J}_{1,1} \) is the streaming operator; \( \mathcal{M}_{[k]} \circ \left( p_i \mathbf{v}_{p_i} ; \tau \mathbf{v}_{\mathbf{u}_1} \right) \) are mixed differential operators in \( p_i \) and \( \mathbf{u}_1 \). The constants \( \mathcal{M}_{[2k]} \) are of the form:

\[
\mathcal{M}_{[2k]} \sim \int d\xi_2 \cdots d\xi_{2k} g_{2k}(\xi_2, \ldots, \xi_{2k}) \left( \frac{\partial^{m_1} \phi(\xi_1)}{\partial \xi_1^{m_1}} \cdots \frac{\partial^{m_{2k}} \phi(\xi_{2k})}{\partial \xi_{2k}^{m_{2k}}} \right) (9.3)
\]

where \( \phi \) 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, with the condition, \( \sum_{i=1}^{2k} \sum_{j=1}^{2k} = 2k \).
although for large values of \( \xi_{2k}, \ldots, \xi_{2k} \), \( g_{2k} \to 1 \),
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:

\[
f_{1,1} = f_{1,1}^{[0]} + f_{1,1}^{[1]} + f_{1,1}^{[2]} + \cdots + o(\epsilon^6)
\]

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 coordinates. Some related correlation functions are also investigated. 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 \( \mathcal{F}_{[j]} \)) will be **For \( \Phi(\rho) \sim 1/\rho \), \( \chi^{(2)} = 0 \).
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 $f_{1,1}$ ($\mathbf{x}_1;t|\mathbf{x}_1;0$). 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:

$$G_s(r,t) = \sum_{n=0}^{\infty} a_n t^{2n} D_{R}[n] G_s^{[0]}(R,t) \quad \cdots \quad (9.5)$$

or, alternatively,

$$G_s(r,t) = \sum_{n=0}^{\infty} a_n t^{2n} D_{R}[n] e^{\frac{v^2}{2}} \partial^2_R \delta(R) \quad \cdots \quad (9.5')$$

where $\vec{R} \equiv (m\beta/t^2)^{1/2} \vec{r}$, $G_s^{[0]}(R,t) = (m\beta/2\pi t^2)^{3/2} e^{-R^2/2}$ and the $D_{R}[n]$
are purely differential operators in $R$ (i.e., they are not
explicitly 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 $f_{1,1}(\mathbf{x}_1;\mathbf{dx}_1)$. 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, 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 scattering 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:

\[ S_{\text{inc}}(k, \omega) = e^{-\frac{\hbar \omega}{2}} e^{-\frac{\hbar^2 k^2}{8m}} \left( S_{\text{inc}}^{\text{cl.}}(k, \omega, \beta) + \hbar^2 A_2(k, \omega, \beta) + \hbar^4 A_4(k, \omega, \beta) + \ldots \right) \]  \hspace{1cm} (9.6)

where the \( \{A_i\} \) are functions of \( k, \omega \) and also the system constants given by (9.3). But, \( S_{\text{inc}}^{\text{coh.}}(k, \omega) \) 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 \( S_{\text{inc}}^{\text{cl.}}(k, \omega, \beta) \) only if \( k \) and \( \omega \) are small; Eq. (9.6) is correct for all \( k \) and \( \omega \), but to apply it in general, one should retain all terms in the expansion in \( \hbar^2 \) consistent with the expansion for \( S_{\text{inc}}^{\text{cl.}}(k, \omega) \).

The approximation,

\[ S_{\text{inc}}(k, \omega) \approx e^{-\frac{\hbar \omega}{2}} e^{-\frac{\hbar^2 k^2}{8m}} S_{\text{inc}}^{\text{cl.}}(k, \omega) \]  \hspace{1cm} (9.7)

is correct only for \( k, \omega \) small or \( \beta^{-1} \) very large. If \( S_{\text{inc}}^{\text{cl.}}(k, \omega, \beta) \) 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 \( G(r,t) \)\textsuperscript{**}.

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 particle moving within a cluster of particles or, a particle trapped in a potential well or, a particle diffusing according to the Langevin equation, and so forth.

\textsuperscript{**} 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 density 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, $f_{2,2}(x_1,x_2;t|x_{10},x_{20})$. 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. Furthermore, 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 and his collaborators.

Also, it might be interesting to investigate the derivation 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 densities 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 correlation functions 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

** For example, for the momentum auto-correlation function,

\[ \langle \xi(t) \rangle = \langle \ddot{\xi}_1(0) \cdot \ddot{\xi}_1(t) \rangle, \]

\[ \frac{\partial \langle \xi(t) \rangle}{\partial t} = \left[ \frac{\partial L}{\partial \xi} \right] \langle \xi(t) \rangle + \frac{\partial}{\partial t} \int_0^t e^{-\lambda (t-t')} \left[ \frac{\partial L}{\partial \xi(t')} \right] \langle \xi(t) \rangle, \]

where \( \xi = \sum_{\nu} \xi_{\nu} \), \( \xi_{\nu} = f_{\nu} (\chi_{\nu}) \xi_{\nu} \cdot \xi_{\nu} \cdot \xi_{\nu} \cdot \xi_{\nu} \); \( \xi = \xi(\xi_{\nu}) \xi \); \( \xi = \xi(\xi_{\nu}) \xi \); and,

\[ A(\xi) = \sum_{\nu} \xi_{\nu} \cdot f_{\nu, m}(\xi_{\nu}) \cdot \xi_{\nu} \cdot \xi_{\nu} \cdot \xi_{\nu} \cdot \xi_{\nu}. \]
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 \( X(\cdot) \), 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 \( s \).

\[ \text{e.g., Consider a set of cows, C, and consider the pertinent property to be the color of the eyes of the individual cows. If, for example, the number 1 is assigned to the property: blue eyes, 2 \rightarrow red eyes, 3 \rightarrow green eyes, etc., then eye-color (E(\cdot)) is a function defined on the space C.} \]

A.2 Definition: A property, \( X(\cdot) \), is said to be a random variable if it is a real valued function defined on a sample space on whose subsets 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.

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A.3 **Definition:** 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 probability function \( \mu_{\text{Pr}}(\cdot) \), defined on the sample space, by summing up the measure of all subsets of \( S \) such that \( X(s) = B \). i.e.,

\[
\text{Pr}_X(B) = \mu_{\text{Pr}}[\{s \in B \mid X(s) \in B\}] = \int_{S \mid \forall s \in B} d\mu_{\text{Pr}}(s)
\]

e.g., If we assign equal measure \( \mu_{\text{Pr}}(\cdot) \), to each cow in our sample space, \( C \), then \( \text{Pr}_E(\cdot) \) is the probability measure for a given eye-color = \( \mu(s; E = \text{given eyecolor}) = N_E/N \), where \( N_E \) = the number of cows having a given eyecolor, \( N \) = the total number of members of the sample space.

However, the choice of the basic probability measure is not unique. It is an a priori assignment, 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 proportional to the weight of the cows having a given eyecolor.

A.4 **Axioms:** For a measure to be a probability measure, it must satisfy the following axioms of probability theory:

**Ax. 1:** \( \mu_{\text{Pr}}(s) \geq 0 \) for every subset \( s \in S \). (As a consequence, \( \text{Pr}_X(\cdot) \geq 0 \) for every event.)

\[
\text{Ax. 2: } \int_{S} d\mu_{\text{Pr}}(s) = 1 \quad \text{( } \implies \int_{S} d\text{Pr}_X(s) = 1 \text{ )}
\]

**Ax. 3:** For subsets \( S_1 \) and \( S_2 \) of \( S \):

\[
\int_{S_1 \cup S_2} d\mu_{\text{Pr}}(s) = \int_{S_1} d\mu_{\text{Pr}}(s) + \int_{S_2} d\mu_{\text{Pr}}(s), \quad \forall S_1 \cap S_2 = 0
\]
A.5 **Definition:** A random variable \(X(\cdot)\) is discrete if \(\Pr_X(\cdot) > 0\) for at most a denumerably infinite number of points, \(x\), and if
\[
\sum_{x: p_X(x) > 0} p_X(x) = 1.
\]
\(p_X(x)\) is the probability that the observed value of the random variable \(X\) will be equal to \(x\).

A.6 **Definition:** The values \(x\) of a discrete r.v. for which \(\Pr_X(x) > 0\) are called probability mass points.

A.7 **Definition:** 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 \(x \in B\), i.e.,
\[
\Pr_X(B) = \int_B f_X(x) \, dx
\]
(Note:\ \(f_X(x) = \int_{S: \mathbb{R}(S) = x} \lambda d\mathbb{P}_n\)).

A.8 **Definition:** \(f_X(x)\), 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 Definition: The distribution function of a random variable, \( X \), denoted by \( F_X(\cdot) \) is defined by

\[
F_X(x) = \Pr[X \leq x] = \int_{-\infty}^{x} f_X(x') \, dx'
\]

(In the case of a discrete r.v., \( \sum_{x_i \leq x} \Pr(X = x_i) = F_X(x) \).

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:

\[
f_X(x) = \sum_i \Pr[X = x_i] \delta(x - x_i), \quad \sum_i \Pr_i = 1.
\]

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

\[
F_X(x) = \begin{cases} 
0 & \text{if } x \leq x_o \\
1 & \text{if } x > x_o
\end{cases}
\]

Also, since \( f_X(x) = \frac{d}{dx} F_X(x) \), thus \( f_X(x) = \sum \delta(x - x_o) \)

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 Definition: Two or more random variables can be defined simultaneously 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
\[
\Pr_{X_1, X_2}(B) = \mu_{\Pr}\{s \in S : [X_1(s), X_2(s)] \in B\}
\]

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

\[
\lim_{x_1 \to -\infty} \lim_{x_2 \to -\infty} F_{X_1, X_2}(x_1, x_2) = 0; \text{ similarly } \lim_{x_1 \to -\infty} \lim_{x_2 \to -\infty} F_{X_1, X_2}(x_1, x_2) = 0.
\]

Also,

\[
\lim_{x_1 \to -\infty} \lim_{x_2 \to -\infty} F_{X_1, X_2}(x_1, x_2) = 1.
\]

A.12 Definition: Similarly, \(\lim_{x_i \to -\infty} \lim_{x_j \to -\infty} F_{X_i, X_j}(x_i, x_j) = F_{X_i}(x_i)\) 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 \(\lim_{x_2 \to -\infty} \lim_{x_1 \to -\infty} F_{X_1, X_2}(x_1, x_2) = F_{X_1}(x_1)\).

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 \(f_{X_1, X_2}(x_1, x_2)\) is "joint probability density".

Note that \(f_{X_1, X_2}(x_1, x_2) > 0\) 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 Definition: 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

$$F_{X_1}(x_1) = \int_{-\infty}^{x_1} f_{X_1}(x_1') \, dx_1' = \int_{-\infty}^{+\infty} \int_{-\infty}^{x_1} f_{X_1, X_2}(x_1', x_2) \, dx_2 \, dx_1'$$

******

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, for independent random variables,

$$F_{X_1, X_2}(x_1, x_2) = F_{X_1}(x_1) \cdot F_{X_2}(x_2), \text{ and, } f_{X_1, X_2}(x_1, x_2) = f_{X_1}(x_1) \cdot f_{X_2}(x_2)$$

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 Definition: For discrete random variables, given two properties, A & B, defined on the same probability space, the conditional probability of property A, given the property B, is defined as:

$$P_r\{A|B\} = \begin{cases} \frac{P_r\{A\cap B\}}{P_r\{B\}}, & P_r\{B\} > 0 \\ \text{undefined}, & P_r\{B\} = 0 \end{cases}$$

For continuous r.v.'s, the above definition is going to lead to difficulty since, if we try to define $P_r\{A|X=x\} = \frac{P_r\{A\cap X=x\}}{P_r\{X=x\}}$, trouble arises because $P_r\{X=x\} = 0$. Instead:

A.17 Definition: The conditional probability distribution, $P_r\{A|X=x\}$, for continuous variables, is defined by:

$$P_r\{A|X=x\} = P_r\{A, X=x\} = \int_{x} P_r\{X=x\} dF_X(x)$$

Note that $P_r\{A\} = \int_{-\infty}^{+\infty} P_r\{A|X=x\} dF_X(x)$. Furthermore, if A and X are independent, $P_r\{A|X=x\} = P_r\{A\}$ and the above equation is trivially satisfied.

A.18 Definition: The conditional distribution function of Y, given X, is defined by: $F_{Y|X}(y|x) = P_r\{Y \leq y | X = x\}$. Consequently,

$$P_r\{X \leq x, Y \leq y\} = F_{Y|X}(y|x) = \int_{-\infty}^{x} F_{Y|X}(y|x') dF_X(x')$$
A.19 Definition: The conditional probability-density function of the random variable $Y$, given the random variable $X$, is defined by:

$$f_{Y|X}(y|x) = \frac{\partial}{\partial y} F_{Y|X}(x|y).$$

We are thus led to the important relation:

$$f_{Y|X}(y|x) = \frac{f_{X,Y}(x,y)}{f_{X}(x)}$$

Proof:

In light of A.19:

$$\frac{\partial}{\partial x} F_{X,Y} = f_{X,Y}(x|y) \cdot f_{X}(x).$$

Next, differentiating re $y$:

$$\frac{\partial}{\partial y} F_{X,Y} = f_{X,Y}(x|y) \cdot f_{X}(x).$$

Also consider:

$$f_{X,Y}(x|y) = \int_{\mathbf{R}} f_{X,Y,z}(x,y,z) \, f_{z|Y}(y,z) \, dz$$

Proof:

The "conditional probability" of realizing an event $A$, given that $Y = y'$, $Z = z'$, is defined by the following relationship.

$$\mathbb{P}(A \text{ such that } (Y,Z) \in B) = \int_{B} \mathbb{P}(A | (Y,y',Z,z')) \, dF_{Y,Z}(y',z') = \int_{B} \mathbb{P}(A | (Y,y',Z,z')) \, f_{Y,Z}(y',z') \, dz'$$

But, if $B$ is such that $\Lambda(-\infty \leq z \leq \infty)$, then

$$\mathbb{P}(A \text{ s.t. } (Y,Z) \in B') = \mathbb{P}(A \text{ s.t. } Y \in B') \text{ where } B' = \text{ range of } Y.$$

Thus,

$$\mathbb{P}(A \text{ s.t. } Y \in B') = \int_{B'} 1_{B} \, dP_{A | Y} = \int_{B'} dP_{A | Y} = \int_{B'} \mathbb{P}(A | (Y,y',Z,z')) \, dF_{Y,Z}(y',z')$$

Now, suppose that $B'$ is the range $\{\gamma_{1}, \gamma_{2}\}$ and $A$ is the event that $X$ falls within the range $A = \{\gamma_{1}, \gamma_{2}\}$. We thus find the following relationship for probability distribution functions:

$$F_{X,Y}(x,y) = \int_{\gamma_{1}}^{\gamma_{2}} \int_{x \in \mathbf{R}} \int_{y \in \mathbf{R}} f_{X,Y}(x,y,z) \, dx \, dy \, dz,$$

where $f_{X,Y}(x,y,z) = f_{X}(x) \cdot f_{Y|X}(y|x) \cdot f_{Z|Y,X}(z|y,x)$. We thus find the following relationship for probability distribution functions:
If we next take derivatives re x, y we obtain:

\[
\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \frac{\partial^2}{\partial x \partial y} f_{x,y}(x,y) \, dx \, dy = f_{x,y}(x,y) \frac{\partial}{\partial x} f_{x,y}(x,y)
\]

where \( f_{x,y}(x,y) = \frac{\partial}{\partial x} f(x,y) \) = conditional probability density.

Hence, since \( f_{x,y}(x,y) = f_x(x) \cdot f_y(y) \), then

\[
f_{x,y}(x|y) = \int_{-\infty}^{+\infty} f_{x|y}(x|y) f_z|y(z|y) \, dz, \qquad q.e.d.
\]

5. **EXPECTATIONS**

Given a function of the random variable x: \( g(x) \).

A.20 **Definition**: The expected value of \( g(x) \), with regard to the distribution \( F_X(x) \) is defined as:

\[
\mathbb{E}[g(x)] = \langle g \rangle = \int_{-\infty}^{+\infty} g(x) f_X(x) \, dx = \int_{-\infty}^{+\infty} g(x) f_x(x) \, dx
\]

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:

\[
\langle h \rangle = \mathbb{E}[h(x,y)] = \iint_{-\infty}^{+\infty} h(x,y) f_{x,y}(x,y) \, dx \, dy = \iint_{-\infty}^{+\infty} h(x,y) f(x,y) \, dx \, dy
\]

\[
= \iint_{-\infty}^{+\infty} h(x,y) f_{x|y}(x|y) \, dx \, dF_y(y)
\]

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:

\[
I^{[2a]} = I^{[2a]} + I^{[2b]} \quad \text{with} \quad I^{[2a]} = \sum_{\kappa=1}^{\Lambda} I_{\kappa}^{[2a]} 
\]  

(B.1)

according to the definitions:

\[
I_{1}^{[2a]} = \bar{\theta} \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1} e^{\Delta \tau_{2} L_{0} \cdot L_{1} + \tau_{1} L_{0}^{+}} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots \quad (B.2a)
\]

\[
I_{2}^{[2a]} = \bar{\theta} \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1} e^{\Delta \tau_{2} L_{0} \cdot L_{1} + \tau_{1} L_{0}^{+}} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots \quad (B.2b)
\]

\[
I_{3}^{[2a]} = \bar{\theta} \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1} e^{\Delta \tau_{2} L_{0} \cdot L_{1} + \tau_{1} L_{0}^{+}} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots \quad (B.2c)
\]

\[
I_{4}^{[2a]} = \bar{\theta} \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1} e^{\Delta \tau_{2} L_{0} \cdot L_{1} + \tau_{1} L_{0}^{+}} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots \quad (B.2d)
\]

\[
I_{5}^{[2a]} = -\bar{\theta} \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1} e^{\Delta \tau_{2} L_{0} \cdot L_{1} + \tau_{1} L_{0}^{+}} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots \quad (B.2e)
\]

In addition, expand

\[
I_{1}^{[2a]} = I_{1}^{[2a]} + I_{1}^{[2a]} + I_{1}^{[2a]} + \ldots
\]  

(B.3)

with

\[
I_{1}^{[2a]} = \bar{\theta}(\tau_{1}) \int_{0}^{t} dt_{1} \int_{0}^{\tau_{1}} dt_{2} L_{1}(\tau_{1}) e^{\Delta \tau_{2} L_{0}(\tau_{1}) + \tau_{1} L_{0}^{+}(\tau_{1})} f_{m_{1} L_{1}} f_{1,1}(t-t_{1}) \quad \ldots
\]  

(B.4a)
\[
\begin{align*}
I_2^{[2a]} & = 0 \int_0^t d\tau \int_0^\tau \delta \tau \cdot \delta \tau \cdot L_1^0 \cdot L_0^L \cdot f_{n1} \cdot f_{n1}(t - \tau) \\
I_2^{[2a]} & = 0 \int_0^t d\tau \int_0^\tau \delta \tau \cdot \delta \tau \cdot \delta \tau \cdot L_1^0 \cdot L_0^L \cdot f_{n1} \cdot f_{n1}(t - \tau)
\end{align*}
\] (B.4b) (B.4c)

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
\[
I_2^{[2a]} = I_2^{[2a]} + I_2^{[2a]} + \ldots
\] (B.5)

with
\[
I_2^{[2a]} = 0 \int_0^t d\tau \int_0^\tau \delta \tau \cdot \delta \tau \cdot L_1^0 \cdot L_0^L \cdot f_{n1} \cdot f_{n1}(t - \tau)
\] (B.6a)

\[
I_2^{[2a]} = 0 \int_0^t d\tau \int_0^\tau \delta \tau \cdot \delta \tau \cdot \delta \tau \cdot L_1^0 \cdot L_0^L \cdot f_{n1} \cdot f_{n1}(t - \tau)
\] (B.6b)

\[
I_2^{[2a]} = 0 \int_0^t d\tau \int_0^\tau \delta \tau \cdot \delta \tau \cdot \delta \tau \cdot L_1^0 \cdot L_0^L \cdot f_{n1} \cdot f_{n1}(t - \tau)
\] (B.6c)

etc.

It is then found that (cf., Eq. (4.40), (4.41))
\[
Q_2 = I_2^{[1]} + I_2^{[2a]}
\] (B.7)
Similarly, expand

\[ I^{[3\lambda]} = I_{1}^{[3\lambda]} + I_{2}^{[3\lambda]} + I_{3}^{[3\lambda]} + \ldots \]  

(B. 9)

where

\[ I_{1}^{[3\lambda]} = \mathbf{\Theta} \int_{0}^{t} \int_{0}^{\tau_{1}} \int_{0}^{\tau_{2}} \int_{0}^{\tau_{3}} (\tau, \tau_{3}) L_{0}^{+} \tau_{1} L_{1} \mathbf{L}_{2}^{+} f_{1}(t, \tau_{3}) f_{1}(t, \tau_{1}) \]  

(B. 10a)

\[ I_{2}^{[3\lambda]} = \mathbf{\Theta} \int_{0}^{t} \int_{0}^{\tau_{1}} \int_{0}^{\tau_{2}} \int_{0}^{\tau_{3}} \tau_{2} L_{1} \mathbf{L}_{2}^{+} f_{1}(t, \tau_{3}) f_{1}(t, \tau_{2}) \]  

(B. 10b)

\[ I_{3}^{[3\lambda]} = \mathbf{\Theta} \int_{0}^{t} \int_{0}^{\tau_{1}} \int_{0}^{\tau_{2}} \int_{0}^{\tau_{3}} \tau_{3} L_{1} \mathbf{L}_{2}^{+} f_{1}(t, \tau_{3}) f_{1}(t, \tau_{3}) \]  

(B. 10c)

Then, (cf., (4.42))

\[ I_{5}^{[3\lambda]} = \mathbf{I}_{3}^{[3\lambda]} + \theta_{1} \mathbf{I}_{4}^{[3\lambda]} + \mathbf{I}_{2}^{[3\lambda]} \]  

(B. 11)

where \( \mathbf{I}_{3}^{[3\lambda]} \) is obtained from (B. 2c) by an obvious definition, \( \mathbf{I}_{4}^{[3\lambda]} \) and \( \mathbf{I}_{2}^{[3\lambda]} \) are obtained from the expansion for \( I_{2}^{[3\lambda]} \), viz.,

\[ I_{2}^{[3\lambda]} = \mathbf{I}_{1}^{[3\lambda]} + I_{2}^{[3\lambda]} + \ldots \]  

(B. 12)

where

\[ \mathbf{I}_{1}^{[3\lambda]} = \Theta(\mathbf{L}) \int_{0}^{t} \int_{0}^{\tau_{1}} \int_{0}^{\tau_{2}} \int_{0}^{\tau_{3}} (\tau, \tau_{3}) L_{0}^{+} \tau_{1} L_{1} \mathbf{L}_{2}^{+} f_{1}(t, \tau_{3}) f_{1}(t, \tau_{1}) \]  

(B. 13a)
\[ I^{[3a]}_1 \equiv - \Theta \int_0^t \int_0^\tau_1 \int_0^{\tau_2} \int_0^{\tau_3} \mathcal{L}_1 \mathcal{L}_2 \mathcal{L}_3 \mathcal{L}_4 \mathcal{L}_5 \mathcal{L}_6 \mathcal{L}_7 \mathcal{L}_8 \ \text{(B.13b)} \]

\[\mathcal{L}_1 \mathcal{L}_2 \mathcal{L}_3 \mathcal{L}_4 \mathcal{L}_5 \mathcal{L}_6 \mathcal{L}_7 \mathcal{L}_8 \ \text{etc.} \]

For \( I^{[4]}_{6, 43} \) we have:

\[ I^{[4]}_{6} \equiv I^{[2a]}_4 + I^{[3a]}_2 + I^{[3a]}_2 \ \text{(B.14)} \]

where \( I^{[3a]}_4 \) is obtained from an expansion of \( I^{[2a]}_2 \). \( I^{[3a]}_2 \) and \( I^{[3a]}_2 \) follow from an expansion of \( I^{[3a]}_2 \), defined by:

\[ I^{[3a]}_2 \equiv - \Theta \int_0^t \int_0^{\tau_1} \int_0^{\tau_2} (\tau_2, \tau_3) L_0^+ L_4 L_5 L_6 L_7 L_8 L_9 L_{10} \ \text{(B.15)} \]

Similarly, defining (cf. B.10b):

\[ I^{[3a]}_3 \equiv - \Theta \int_0^t \int_0^{\tau_2} \int_0^{\tau_3} (\tau_2, \tau_3) L_0^+ L_4 L_5 L_6 L_7 L_8 L_{10} \ \text{(B.16)} \]

we have

\[ I^{[3a]}_3 \equiv I^{[3a]}_2 + I^{[3a]}_2 \ \text{(B.17)} \]

Finally,

\[ I^{[3a]}_4 \equiv I^{[3a]}_3 + I^{[3a]}_3 \ \text{(B.18)} \]

\[ I^{[3a]}_5 \equiv I^{[3a]}_5 + I^{[3a]}_5 \ \text{(B.19)} \]
All terms to $\Theta(\varepsilon^q)$ are included in $\mathcal{L} \to \mathcal{L}$.

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,

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 L_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.20)$$

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 L_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.21)$$

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 L_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.22)$$

which is to be compared with

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 \mathcal{L}_1 \mathcal{L}_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.23)$$

Notice that $\mathcal{L}_\gamma L_1 = \mathcal{L}(T) \mathcal{L}_\gamma$, where $\mathcal{L}(T) \equiv L_1 + \varepsilon - \mathcal{F}_{\text{int}} \cdot \frac{T}{m} \mathcal{L}_\gamma$, so that

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} L_1 \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 \mathcal{L}_1 \mathcal{L}_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.24)$$

Integrate by parts over $\tau_4$ and then $\tau_3$:

$$I_{\gamma} = \mathcal{O}(\mathcal{Y})\int_{t_0}^{t_3} \int_{t_0}^{t_2} \int_{t_0}^{t_1} \mathcal{L}_\gamma L_1 \mathcal{L}_3 L_1 \mathcal{L}_1 \mathcal{L}_1 \mathcal{L}_1 \int_{t_0}^{t_1} f_{\text{int}}(t, \tau_1) \ldots \ldots \ldots (B.25)$$
Next, integrate by parts over $\tau_2$.

\[ \int_0^{\tau_2} \mathcal{L}_\tau \frac{\partial}{\partial \tau} \left( \frac{\partial}{\partial \tau} \mathcal{L}_\tau \right) \frac{\partial}{\partial \tau} \mathcal{L}_\tau \left[ L_1 + \frac{1}{3} \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \right] L_1 + L_1 \frac{2}{3} \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} + \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \left( \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \right) \right] \mathcal{L}_\tau \left( t - \tau_1 \right) \]

But, as can be easily verified, the last terms is just the negative of $\int_0^{\tau_2} \mathcal{L}_\tau \frac{\partial}{\partial \tau} \mathcal{L}_\tau \left( t - \tau_1 \right)$. Thus, we define one of the 'basic' collision integrals (B.18).

\[ \mathbb{G} = \int_3^{[3a]} + \int_4^{[3a]} + \int_{[4a]} = \]

\[ = \int_0^t \frac{\partial}{\partial \tau} \mathcal{L}_\tau \left[ L_1 + \frac{1}{3} \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \right] L_1 + L_1 \frac{2}{3} \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} + \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \left( \xi - \mathcal{F}_{ik} \cdot \nabla_{\mathbf{k}} \right) \left( t - \tau_1 \right) \]
APPENDIX C

RELATIONSHIPS BETWEEN SYSTEM CONSTANTS

We shall prove that \( \chi^{(i)} = 3 \chi^{(i,2)} \); it is expeditious to evaluate these coefficients in spherical coordinates. Thus,

\[
\chi^{(i)} = \int d^3\vec{q} \, g_3(\vec{q}) \frac{\partial^4 \phi(\vec{q})}{\partial q_x^4} = \\
\int_0^\infty d\rho \int_0^{2\pi} d\theta \int_0^\pi d\phi \, \rho^2 \sin \phi \, g_3(\rho) \times \\
\left\{ \frac{\partial^4 \phi(\rho)}{\partial x_4^4} + \frac{3}{\rho} \frac{\partial^3 \phi(\rho)}{\partial x_3^3} + \frac{3}{\rho^2} \frac{\partial^2 \phi(\rho)}{\partial x_4^2} + \frac{\partial \phi(\rho)}{\partial x_3} + \frac{\partial \phi(\rho)}{\partial x_4} \right\} .
\]

\( \cdots \) (C.1)

Hence, since \( \chi = \rho \sin \phi \cos \theta \); \( \eta = \rho \sin \phi \sin \theta \); \( z = \rho \cos \phi \):

\[
\chi^{(i)} = \int_0^\infty d\rho \int_0^{2\pi} d\phi \, \rho^2 \sin \phi \, g_3(\rho) \times \left\{ \frac{3}{\rho^2} \frac{\partial^3 \phi(\rho)}{\partial x_3^3} \right\} + \\
\frac{3}{\rho} \frac{\partial^3 \phi(\rho)}{\partial x_3^3} \right\} + \\
\frac{12}{\rho^2} \frac{\partial^2 \phi(\rho)}{\partial x_3^2} \left[ \sin^2 \phi \cos^2 \theta - 1 \right] + \\
\frac{1}{\rho^3} \frac{\partial \phi(\rho)}{\partial x_3} \left[ 1 - 6 \sin^2 \phi \cos^2 \theta + 5 \sin^3 \phi \cos^4 \theta \right] .
\]

Next, performing the integration over \( \theta \) and \( \phi \), one obtains

\[
\chi^{(1)} = \frac{\pi}{15} \int_0^\infty d\rho \, \rho^2 \phi(\rho) \left\{ \frac{12}{\rho^4} \frac{\partial^4 \phi(\rho)}{\partial x_4^4} + \frac{48}{\rho^3} \frac{\partial^3 \phi(\rho)}{\partial x_3^3} \right\} .
\]

\( \cdots \) (C.1')
In the same way, one shows:

\[
\chi^{(4,2)} = \frac{\pi}{15} \int_{0}^{\infty} \rho^2 \frac{\partial^2 \phi}{\partial \rho^2} \left\{ \frac{4^{\frac{3}{2}}}{\rho^4} \phi + \frac{16}{\rho} \frac{\partial^2 \phi}{\partial \rho^2} \right\} \ldots \quad (C.2)
\]

It is quite straightforward to show the validity of the other relationships 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**

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^4}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

**Proof:**

\[
\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t) = -\int^{2} d^3p \frac{e^{-\frac{p^2}{2m^2}}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
= \int^{2} d^3p \frac{3 - \frac{p^2}{m^2}}{(2\pi)^{3/2}} \frac{t^3}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
= \int^{2} d^3p \frac{3 \nabla^2 \nabla^2 G_{S}^{101}(r,t)}{e^{-\frac{p^2}{2m^2}} (2\pi)^{3/2}}
\]

\[
= -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

\[
= -\frac{\beta_m}{m^2} \frac{t^4}{m^2} \frac{p^2}{m^2} \nabla^2 \nabla^2 G_{S}^{101}(r,t)
\]

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Table D-2: Contributions to $G_s^{(2)}(r,t)$

<table>
<thead>
<tr>
<th>Term in Colllsn Integral</th>
<th>Corresponding Contribution to $G_s^{(2)}(r,t)$</th>
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<tbody>
<tr>
<td>$t^3 \frac{m_p}{\beta} \nabla^2 \rho_{\text{p}}, t_{11}(t)$</td>
<td>$\frac{t^4}{60} \left( \frac{t^2}{m_p} \nabla^2 r \right) G_s^{(01)}(r,t)$</td>
</tr>
<tr>
<td>$\frac{t^4}{m_p} \nabla^2 \rho_{\text{b}}$</td>
<td>$\frac{t^4}{30} \left( \frac{t^2}{m_p} \nabla^2 r \right) G_b^{(01)}$</td>
</tr>
<tr>
<td>$\frac{t^4}{m_p} \nabla^2 \rho_{\text{s}}$</td>
<td>$\frac{t^4}{5} \left( \frac{t^2}{m_p} \nabla^2 r \right) G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 \frac{\nabla^2 \rho_{\text{p}}}{\nabla^2 \rho_{\text{b}}}$</td>
<td>$- \frac{t^4}{20} \left[ \frac{t^2}{m_p} \nabla^2 r + 15 \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 \frac{\nabla^2 \rho_{\text{p}}}{\nabla^2 \rho_{\text{s}}}$</td>
<td>$- \frac{t^4}{5} \left( \frac{t^2}{m_p} \nabla^2 r \right) G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla^2 \rho_{\text{p}})$</td>
<td>$\frac{t^4}{4} \left[ \frac{23}{15} \frac{t^2}{m_p} \nabla^2 r + \frac{1}{15} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla_{\text{p}} \nabla_{\text{p}})$</td>
<td>$t^4 \left[ \frac{2}{3} \frac{t^2}{m_p} \nabla^2 r + \frac{1}{30} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla_{\text{p}} \nabla_{\text{p}} \nabla_{\text{b}})$</td>
<td>$t^4 \left[ \frac{13}{35} \frac{t^2}{m_p} \nabla^2 r + \frac{1}{30} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla_{\text{p}} \nabla_{\text{s}})$</td>
<td>$t^4 \left[ \frac{3}{2} + \frac{1}{4} \frac{t^2}{m_p} \nabla^2 r + \frac{1}{60} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla_{\text{p}} \nabla_{\text{p}} \nabla_{\text{s}})$</td>
<td>$t^4 \left[ \frac{1}{2} \frac{t^2}{m_p} \nabla^2 r + \frac{1}{30} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>$t^3 (\rho_{\text{p}} \nabla_{\text{p}} \nabla_{\text{p}} \nabla_{\text{b}})$</td>
<td>$- \frac{t^4}{5} \left[ \frac{1}{12} \frac{t^2}{m_p} \nabla^2 r + \frac{t^4}{140} \frac{t^4}{m_p^2} \nabla^2 \nabla^2 r \right] G_s^{(01)}$</td>
</tr>
<tr>
<td>Term in Collsn Integral</td>
<td>Corresponding Contribution to $G_s^{127}(r, t)$</td>
</tr>
<tr>
<td>-------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>$\frac{t^4}{m^2} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$-\frac{\beta}{m} t^4 \left[ \frac{2}{15} t^4 \nabla^2 + \frac{t^4}{105m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^5}{m^3} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$-\frac{\beta}{m} t^4 \left[ \frac{1}{6} t^4 \nabla^2 + \frac{t^4}{42m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^3}{m^2} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$\left(\frac{\beta}{m^2}\right)^2 t^4 \left[ \frac{1}{280} \frac{t^4}{m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^4}{m^3} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$\frac{\beta}{m} t^4 \left[ \frac{1}{160} \frac{t^4}{m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^5}{m^4} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$\frac{\beta}{m} t^4 \left[ \frac{1}{120} \frac{t^4}{m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^6}{m^5} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$\frac{\beta}{m} t^4 \left[ \frac{1}{56} \frac{t^4}{m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^7}{m^6} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$-\frac{\beta}{m} t^4 \left[ \frac{t^2}{20m^2} \nabla^2 + \frac{t^4}{140m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^4}{m^2} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$-\frac{\beta}{m} t^4 \left[ \frac{t^4}{105m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
<tr>
<td>$\frac{t^5}{m^3} \nabla^2 p_0 \nabla^2 p_0$</td>
<td>$-\frac{\beta}{m} t^4 \left[ \frac{t^4}{42m^2} \nabla^2 \nabla^2 \right] G_s^{(10)}$</td>
</tr>
</tbody>
</table>
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 $\alpha, \beta, \ldots$ in the following form: $Z(\alpha, \beta, \ldots)$. Changing the notation, $Z$ can also be written as: $Z(u_\alpha, u_\beta, \ldots)$. Now, suppose the set $\{ u_\alpha, u_\beta, \ldots \}$ is a continuous set of infinitely many points in the interval (a, b). The set of variables $\{ u_\alpha, u_\beta, \ldots \}$ 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 $Z(\int_a^b u(t) dt)$. 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 $y_1, y_2, \ldots$. Such a functional might be written in the following form:

$$F(y_1, y_2, \ldots | u(t), v(t)),$$

**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 \( \frac{df}{du_i} \) is related to the total differential through

\[
df = \sum_i \frac{df}{du_i} \, du_i.
\]

In the theory of functionals, the summation becomes the integral,

\[
\int \frac{dF}{d\nu(x)} \, \nu(x) \, dx = \epsilon \int \frac{dF}{d\nu(x)} \, \nu(x) \, dx
\]

and leads to the following definition: \( F'[u(t); \nu] \), defined as the first derivative of the functional \( F \) with respect to the function \( u(t) \) at the point \( \nu \), is determined by the following relationship:

\[
\int_{a}^{b} F'[u(t); \nu] \, \nu(x) \, dx = \lim_{\epsilon \to 0} \left\{ \frac{F[u(t)+\epsilon \nu(t)] - F[u(t)]}{\epsilon} \right\}
\]

\[
= \int_{a}^{b} \frac{dF}{d\nu(x)} \, \nu(x) \, dx
\]

Another definition, involving somewhat more rigor, is stated as follows. In the neighborhood of a value \( x_o \), let \( y(x) \) be given a continuous increment \( \Theta(x) \) which does not change sign, and such that \( |\Theta(x)| < \epsilon \) for \( x_o - h \leq x \leq x_o + h \) and \( \Theta(x) = 0 \) for \( x \) otherwise. Form the limit \( \frac{\Delta F}{\Theta} \)

where \( \Delta F = F[y(x) + \Theta(x)] - F[y(x)] \) and \( \Theta = \int_{x_o}^{b} \Theta(x) \, dx \). If \( \frac{\Delta F}{\Theta} \) approaches (uniformly) a limit as \( \epsilon \) and \( h \) approach zero in an arbitrary manner, then the limit is defined as the functional derivative of \( F[y(x)] \) at the point \( x_o \): \( F'[y(x); x_o] \). Hence, the definition is analogous to the definition of the ordinary partial derivative:

\( {**} \) ibid., chapt. I, sec. II.
\[ \frac{\partial f}{\partial y_i} = \lim_{h \to 0} \frac{\Delta f}{h} = \lim_{h \to 0} \frac{f(y_1, \ldots, y_i+h, \ldots, y_n) - f(y_1, \ldots, y_n)}{h} \]

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 \( \frac{\delta G}{\delta u(y)} \) to the functionals \( G = \frac{\delta F}{\delta u(y)} + \frac{\delta^2 F}{\delta u(y) \delta u(y)} + \cdots \), etc., one can show, as a logical consequence, that the appropriate defining relationship for the \( n \)th functional derivative of \( F \) is:

\[
\frac{d^n}{d\varepsilon^n} \left[ F \left[ u(t) + \varepsilon \eta(t) \right] \right]_{\varepsilon = 0} = \\
= \int_a^b \ldots \int_a^b F^{(n)} \left[ u(t), \xi_1, \ldots, \xi_n \right] \eta(\xi_1) \ldots \eta(\xi_n) \, dx_1 \ldots dx_n
\]

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 \( \eta \Delta F = F [ u(x) + \varepsilon \eta(x) ] - F[u(x)] = \varepsilon \int a(x) \eta(x) \, dx + \Theta(\varepsilon^2) \) so that the definition,

\[
\lim_{\varepsilon \to 0} \frac{\Delta F}{\varepsilon} = \int \frac{\delta F}{\delta u(x)} \eta(x) \, dx \quad \text{implies:} \quad \frac{\delta F}{\delta u(x)} = a(x).
\]

b) Suppose \( F [ u ] = u(y) \). Therefore, \( \frac{F[u + \varepsilon \eta] - F[u]}{\varepsilon} = \eta(y) = \int \frac{\delta F}{\delta u(x)} \eta(x) \, dx \).

Hence, \( \frac{\delta F}{\delta u(x)} = \frac{\delta u(y)}{\delta u(x)} = \delta \text{divac} \left( x - y \right) \).
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., \( A[u(x)] = \int a(x) \cdot u(x) \, dx \) and \( B[u(x)] = \int b(y) \cdot u(y) \, dy \). In this case,

\[
\Delta F = F[u + \varepsilon \eta] - F[u] = \int [a(x) b(y) (u(x) + \varepsilon \eta(x)) (u(y) + \varepsilon \eta(y)) - a(x) b(y) u(x) u(y)] \, dx \, dy
\]

\[
= \varepsilon \int [a(x) b(y) \eta(x) u(y) + \eta(x) \eta(y) u(x)] \, dx \, dy + O(\varepsilon^2) = \varepsilon \int [a(x) b(y) + a(y) b(x)] \eta(x) u(y) \, dx \, dy + O(\varepsilon^2).
\]

\[
\therefore \frac{\delta F}{\delta u} = \frac{SA[u] \cdot B[u]}{\delta u} = \int [a(x) b(y) + a(y) b(x)] u(y) \, dy = \frac{SA[u]}{\delta u} \cdot B[u] + A[u] \frac{\delta B[u]}{\delta u}.
\]

q.e.d.

---

d) Suppose \( F_n[u(x)] \) is a regular homogeneous functional of degree \( n \), i.e., \( F_n[u(x)] = \int \cdots \int a(x_1, \ldots, x_n) \cdot u(x_1) \cdots u(x_n) \, dx_1 \cdots dx_n \)

and, in addition, the kernel \( a(x_1, \ldots, x_n) \) is symmetric with respect to permutation of its \( n \) variables.

Then, \( \Delta F_n = F_n[u + \varepsilon \eta] - F_n[u] = \varepsilon \int \cdots \int [a(x_1, \ldots, x_n) + \sum_{j=1}^{n} \varepsilon \eta(x_j)] \eta(x_1) u(x_1) \cdots u(x_n) \, dx_1 \cdots dx_n \)

\[
= \varepsilon \int \cdots \int \left[ \sum_{j=1}^{n} \varepsilon \eta(x_j) \frac{\partial}{\partial x_j} a(x_1, \ldots, x_n) \right] \eta(x_1) u(x_1) \cdots u(x_n) \, dx_1 \cdots dx_n + O(\varepsilon^2)
\]

** A functional of the form:

\[
F_n[y(t)] = \int_a^b \cdots \int_a^b k(t, x_1, \ldots, x_n) y(t_1) \cdots y(t_n) \, dt_1 \cdots dt_n
\]

is called a regular homogeneous functional of degree \( n \).
Hence, due to the symmetric property of the kernel, $a$, the first functional derivative is

$$\frac{\delta F_n}{\delta u(x)} = \eta \int \ldots \int a(x_1, \ldots, x_n) u(x_1) \ldots u(x_n) \, dx_1 \ldots dx_n.$$  

Repeated differentiation yields, for the $s$\textsuperscript{th} functional derivative:

$$\frac{\delta^s F_n}{\delta u(x_1) \ldots \delta u(x_s)} = \frac{n!}{(n-s)!} \int \ldots \int a(x_1, \ldots, x_n) \, u(x_{s+1}) \ldots u(x_n) \, dx_{s+1} \ldots dx_n$$

\text{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 provides the temporal evolution of the $s$ particle probability density in terms of the $s + 1$st 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:

$$\frac{\partial f_{n,m}}{\partial t} = \left[ H_n^0 + \sum_{i<j}^{n} \xi_{i,j} Q_{i,j} \right] f_{n,m} \quad \ldots \ldots \quad (F. 1)$$

where $H_n^0 = \sum_{i=1}^{n} \hat{\mathcal{H}}_i$ is the Hamiltonian of motion and $\xi_{i,j} Q_{i,j}$ is the internal potential energy of the assembly. Let the $n$-particle density be designated as $f_{n,m}(x_n; t \mid x_{1:0})$, as a reminder that the system is symmetric under interchange of designation of any pair of particles, except a pair in which one of the members is particle number 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 $f_{n,m}(x_n; 0 \mid x_{1:0})$ is not symmetric under interchange of the variable $x_1$ with any other $x_j$. On the other hand, $f_{n,m}(x_n; t \mid x_{1:0})$ is invariant under interchange of the designation of all other particles; $f_{n,m}(x_n; t \mid x_{1:0})$ will therefore have a similar symmetry.**

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\[
\frac{\partial f_{s,s}}{\partial t}(x, t | x_{10}) = \left[ H_0 + \sum_{\xi \neq 0}^{\infty} \Phi^\xi_{i,j} ; f_{s,s} \right] + \\
+ \left\{ \partial_{x_{i+1}} \partial_{x_{j}} \left[ \sum_{i=-1}^{n-1} \Phi^x_{i,j} ; f_{n,m} (x, t | x_{10}) \right] \right\} \\
\]  (F. 2)

where \( f_{s,s} (x, t | x_{10}) \) is defined by Eq. (3.2) of the text. To derive Eq. (F.2) we have noted that \( \int \int \partial_{\xi} \partial_{\eta} \left[ \Phi^\xi_{i,j} ; f_{n,m} \right] = 0 \)
and that, also, \( \int \partial_{\xi} \partial_{\eta} \left[ \Phi^\xi_{i,j} ; f_{n,m} \right] = 0 \).

Now, because of the symmetry properties of \( f_{n,m} (x, t | x_{10}) \), the previous equation yields the hierarchy:

\[
\frac{\partial f_{s,s}}{\partial t}(x, t | x_{10}) = \left[ H_0 + \sum_{\xi \neq 0}^{\infty} \Phi^\xi_{i,j} ; f_{s,s} \right] = \\
= (n-1) \left\{ \partial_{x_{i+1}} \partial_{x_{j}} \left[ \sum_{i=-1}^{n-1} \Phi^x_{i,j} ; f_{s+1,s+1} \right] \right\} \\
\]  (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:

\[
\frac{\partial f_{1,1}}{\partial t}(x_1, t | x_{10}, x_{20}) + \frac{\partial f_{2,2}}{\partial t}(x_2, t | x_{10}, x_{20}) = \\
= \left\{ \partial_{x_1} \partial_{x_2} \left[ \Phi^x_{1,1} ; f_{2,2} (x_1, x_2, t | x_{10}, x_{20}) \right] + \right\} \\
= (n-2) \left\{ \partial_{x_1} \partial_{x_2} \left[ \Phi^x_{1,1} ; f_{2,2} (x_1, x_2, t | x_{10}, x_{20}) \right] \right\} \\
\]  (F. 4a)
\[
\frac{\partial f_{s,11}}{\partial t}(\mathbf{x}_2, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) + \frac{\partial}{\partial x_1} \mathbf{J}_{b,c} f_{s,1}(\mathbf{x}_2, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) = \\
= \int d\mathbf{x}_i \mathbb{E}_{l,i} f_{s,1}(\mathbf{x}_2, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) + \ldots, \quad (F.4b)
\]

\[
+ (M-2) \int d\mathbf{x}_3 \left[ \mathbb{E}_{l,i} f_{s,2}(\mathbf{x}_2, \mathbf{x}_3, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) \right]
\]

\[
\frac{\partial f_{s,5}}{\partial t}(\mathbf{x}_5, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) - \left[ \mathbb{H}_{s} + \sum_{l,j} \mathbb{E}_{l,i} f_{6,5}(\mathbf{x}_5, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) \right] = \\
= (\eta-5) \int d\mathbf{x}_{s+1} \sum_{l,(1,2)} \mathbb{E}_{l,1} f_{s+1,5}(\mathbf{x}_{s+1}, t | \mathbf{x}_{i0}, \mathbf{x}_{i0}) \quad (F.4c)
\]

\[
S \geq 2, \quad (1,2) \in \xi_s, \xi
\]

Both sets, (F.3) and (F.4) are pertinent to the main text of this analysis.
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