KINETIC EQUATION FOR A CLASSICAL GAS
WITH A LONG RANGE ATTRACTION

by

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A classical gas whose particles interact through a weak long range attraction and a strong short range repulsion is studied. The Liouville equation is solved as an infinite order perturbation expansion. The terms in this series are classified by Prigogine type diagrams according to their order in the ratio of the range of the interaction to the average interparticle distance. It is shown that, provided the range of the short range force is much less than the average interparticle distance which in turn is much less than the range of the long range force, the terms can be grouped into two classes. The one class, represented by chain diagrams, constitutes the significant contributions of the short range interaction; the other, represented by ring diagrams, makes up, apart from a self-consistent field term, the significant contributions from the long range force. These contributions are summed to yield a kinetic equation. The orders of magnitude of the terms in this equation are compared for various ranges of the parameters of the system. Retaining only the dominant terms then produces a set of eight kinetic equations each of which is valid for a definite range of the parameters of the system.

The short-time stability of the system is examined and a criterion for stability obtained. The equilibrium two-particle correlation function and an equation of state are determined, the latter being compared to the Van de Waals equation of state.
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CHAPTER I

INTRODUCTION

A model of a gas which took account of the long range attractive forces between molecules as well as their repulsive cores was first studied by Van der Waals\(^1\). The semi-quantitative success enjoyed by the model which he proposed stimulated an intensive study, especially in connection with the problem of condensation. Recent progress has been made in the understanding of the equilibrium properties of the Van der Waals gas, notably by: Kac, Uhlenbeck and Hemmer\(^2\); Van Kampen\(^3\); and Lebowitz and Penrose\(^4\).

The non-equilibrium problem, which is of importance in understanding the dynamics of condensation has been considered by Sobrino\(^5\). He began with a kinetic equation that takes account of the long range forces only through a self-consistent field approximation and assumes that particles before making a strong collision are correlated only because of the reduction in the available amount of phase space due to the non-zero size of the particles.

In the light of these recent developments it was considered desirable to examine the problem of the non-equilibrium behaviour of gases with strong short range repulsive and weak long range attractive forces, the aim being to derive, in as rigorous a manner as possible, kinetic equations describing the development of such systems and to determine the range of validity of these equations. In this way it was hoped that the conditions under which Sobrino's assumptions were justified could be determined
and at the same time to see if the correlations due to the long range forces could in some measure explain the behaviour of gases near the critical point.

The study of non-uniform gases initiated by Maxwell\textsuperscript{6} culminated in the famous Boltzmann equation\textsuperscript{7} which describes the evolution of the one-particle distribution function of a gas as due to a flow and a collision term. The collision term has usually been approximated by considering only interactions of a few particles at a time. If the particles interact through a long range force and the gas is not extremely dilute this is clearly an unjustified assumption. The addition of a self-consistent field approximation is a decided improvement but a complete treatment of the long range part of the force is desirable. The Prigogine theory of non-equilibrium statistical mechanics\textsuperscript{8} has been applied by Balescu\textsuperscript{9,10} to a problem involving long range forces, namely a plasma, but a kinetic treatment of systems involving both long and short range forces apparently does not exist. The emphasis of Balescu's work was on spatially homogeneous plasmas although he also considered non-uniform systems. Severne\textsuperscript{11} has developed the Prigogine theory for non-uniform systems in a consistent and elegant manner. This paper is the starting point of this investigation.

We begin in Chapter II by obtaining a formal solution of the Liouville equation as a perturbation expansion in the interaction. Reduced distribution functions and correlation functions are defined and their equations of evolution determined from this
formal solution. The time rate of change of the one particle distribution function is given by an equation consisting of a flow term, a self-consistent field term, a destruction term and a collision term. The latter two of these are infinite order perturbation series with the destruction term arising solely from the initial state correlations. The correlation functions obey equations involving a destruction term and a creation term, the latter being due to correlations created through the interaction of the particles. The derivation of these equations is facilitated by the use of Prigogine type diagrams. Aside from a slight modification of the diagram technique the derivation is that of Severne.

In Chapter III the development of Chapter II is applied to the special case of a gas whose particles interact through a strong short range repulsion and a weak long range attraction, the length scale being the average interparticle distance. In section 2 the terms in the expansion of the collision term are classified by means of diagrams according to their order in the ratio of the range of the interaction to the average interparticle distance. This allows the selection of two types of contributions, one represented by ring diagrams for the long range part of the interaction and the other represented by chain diagrams for the short range interaction. This procedure is also applied to the creation terms. In section 3 the behaviour of the collision, creation and destruction terms for asymptotically long times is examined. It is shown that the destruction terms can be ignored
in the long-time development and the terms in the expansion of the creation and collision terms can be simplified. This simplification allows the contributions to the collision term represented by rings and chains to be summed exactly by techniques developed by Balescu and Taylor\textsuperscript{12} and Prigogine and Henin\textsuperscript{13} respectively. These summations are performed in sections 4 and 5. In section 6 the results of the preceding sections of Chapter III are collected and a set of kinetic equations produced together with conditions under which they are applicable. An H-Theorem is proved for these equations. Section 7 deals with the question of the initial stability of the system. In section 8 a calculation of the equilibrium two body correlations is performed and this is used in section 9 to obtain the equation of state of the system. The results are discussed in Chapter IV.
CHAPTER II

GENERAL EQUATIONS OF EVOLUTION

1. The Liouville Equation and Its Formal Solution

The statistical mechanical state of a system of a large number of particles is specified by the density of its representative statistical ensemble in phase space. This phase density is a function of \( N \) positions, \( N \) velocities and time, \( N \) being the number of particles in the system. Accordingly this function is called the \( N \)-particle distribution function and is written 

\[
F_N(z_1, \ldots, z_n; \mathbf{u}_1, \ldots, \mathbf{u}_n; t)
\]

It is to be interpreted as the probability density that the system will be in a microstate such that particle 1 have position \( z_1 \), and velocity \( \mathbf{u}_1 \), particle 2, position \( z_2 \), and velocity \( \mathbf{u}_2 \) and so on for all particles in the system. The values of macroscopically observable quantities are calculated by taking the ensemble average of the quantity. That is, if \( G(z, \mathbf{u}) \) is a function of the position and velocity co-ordinates the observable value of \( G \) is found by integrating \( G(z, \mathbf{u}) \) weighted with \( F_N \) over all positions and velocities:

\[
\langle G(t) \rangle = \int (dz)_N (d\mathbf{u})_N G(z_1, \ldots, z_n; \mathbf{u}_1, \ldots, \mathbf{u}_n) F_N(z_1, \ldots, z_n; \mathbf{u}_1, \ldots, \mathbf{u}_n; t)
\]

Quantities calculated in this way are accurate for very large \( N \) and the method is thus applicable only to very large systems. This is no hardship as any systems of interest to us consist of the order of \( 10^{23} \) particles and one can take the so called thermodynamic limit

\[
N \to \infty, \quad \Omega \to \infty, \quad N/\Omega = c = \text{finite}
\]
where \( \Omega \) is the volume of the system and \( c \) is then the average concentration.

We consider a system of \( N \) identical interacting particles whose Hamiltonian is

\[
H = H_0 + \lambda \nabla
\]

\[
= \sum_{i=1}^{N} \frac{1}{2} m \dot{\mathbf{r}}_i^2 + \lambda \sum_{i<j}^{N} \nabla(|\mathbf{r}_i - \mathbf{r}_j|)
\]

This presupposes that the interactions between particles are central two-body forces. Also it is assumed that the range of the interactions is much less than the size of the container. The well-known Liouville theorem of classical mechanics\(^{15}\) states that the phase density develops in time according to the equation

\[
\frac{\partial F_N}{\partial t} = -\sum_{i=1}^{N} \mathbf{u}_i \cdot \frac{\partial F_N}{\partial \mathbf{r}_i} + \lambda \sum_{i<j}^{N} \frac{\partial V(|\mathbf{r}_i - \mathbf{r}_j|)}{\partial \mathbf{r}_i} \cdot \left[ \frac{\partial F_N}{\partial \mathbf{r}_j} - \frac{\partial F_N}{\partial \mathbf{r}_i} \right]
\]

Or defining the Liouville operator as

\[
(2.6a) \quad \mathcal{L} = \mathcal{L}_0 + \lambda \delta \mathcal{L}
\]

\[
= -i \sum_{i=1}^{N} \mathbf{u}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + i \frac{\lambda}{m} \sum_{i<j}^{N} \frac{\partial V}{\partial \mathbf{r}_j} \cdot \left( \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial}{\partial \mathbf{r}_j} \right)
\]

we have

\[
(2.7) \quad i \frac{\partial F_N}{\partial t} = \mathcal{L} F_N
\]

The formal solution of the Liouville equation is accomplished by Laplace transforming (2.7) to get
It is easily shown\(^8\) that the Liouville operator \(L\) is Hermitean and thus has only real eigenvalues. The resolvent operator \((L - z)^{-1}\) is therefore bounded for all non-real \(z\) and has singularities only on the real \(z\)-axis\(^1\). Application of the inverse Laplace transform to (2.9) gives

\[
\begin{align*}
\mathcal{F}_N(t) &= \frac{-i}{2\pi} \int_{-\infty + i\delta}^{\infty + i\delta} d\zeta \ e^{-\zeta t} (L - \zeta)^{-1} F_N(0) \quad ; \quad \delta > 0
\end{align*}
\]

The exponential factor \(e^{\zeta t}\), with \(t \geq 0\), allows us to close the path of integration, indicated in (2.10), along a semicircle of infinite radius in the lower half-plane.* Designating this closed contour as \(\Gamma\) and integrating around it in a counter clockwise manner produces the following expression for \(\mathcal{F}_N(t)\)

\[
\begin{align*}
\mathcal{F}_N(t) &= \frac{-1}{2\pi i} \oint_{\Gamma} d\zeta \ e^{-\zeta t} (L - \zeta)^{-1} F_N(0)
\end{align*}
\]

The operator identity

\[
\begin{align*}
A^{-1} - B^{-1} &\equiv A^{-1}(B-A)B^{-1}
\end{align*}
\]

permits us to write, using the definition of \(L\) given in (2.6a),

\[
\begin{align*}
(L - \zeta)^{-1} - (L - \zeta)^{-1} = (L - \zeta)^{-1} \lambda \delta \lambda (L - \zeta)^{-1}
\end{align*}
\]

* If \((L - \zeta)^{-1} F_N(0)\) has a discontinuity across the real axis its analytic continuation into the lower half-plane is to be used in the calculation of the contour integral.
By iteration one obtains

\[(2.14) \quad (L - \varepsilon)^{-1} = \sum_{n=0}^{\infty} (-\lambda)^n (L_0 - \varepsilon)^{-1} \left[ \delta L (L_0 - \varepsilon)^{-1} \right]^n\]

Putting this into (2.11) yields a formal perturbation solution of the Liouville equation:

\[(2.15) \quad F_N(t) = -\frac{i}{2\pi i} \int d\xi e^{-i\varepsilon t} \sum_{n=0}^{\infty} (L_0 - \varepsilon)^{-1} \left[ -\lambda \delta L (L_0 - \varepsilon)^{-1} \right]^n F_N(0)\]

We shall now proceed to expand \(F_N\) in eigenfunctions of the unperturbed Liouville operator \(L_0\). As only asymptotically large systems are of interest (see (2.2)) it can be argued that the effect on any local quantity by particles near the surface of the container is negligible. This allows freedom of choice for the boundary conditions which we take to be periodic. The container is assumed cubic for simplicity.

The eigenfunctions of the operator \(L_0 = -i \sum_{j} \frac{\partial}{\partial z_j}\) are clearly of the form

\[(2.16) \quad \phi_{\{\xi\}} = \prod_{j=1}^{N} \epsilon^{i\xi_j \cdot \vec{z}_j}\]

and have the eigenvalues

\[(2.17) \quad \lambda_{\{\xi\}} = \sum_{j=1}^{N} \xi_j \cdot \vec{z}_j\]

Imposing the periodic boundary conditions

\[(2.18) \quad \phi_{\{\xi\}}(\{z\}) = \phi_{\{\xi\}}(\{z + \lambda_j \xi_j \vec{z}_j\}) = \phi_{\{\xi\}}(\{z \pm \lambda_j \xi_j \vec{z}_j\}) = \phi_{\{\xi\}}(\{z \mp \lambda_j \xi_j \vec{z}_j\})\]

requires that
(2.19) \[ \delta_j^i = \frac{2\pi}{\Delta z} (n_x \delta_j^x + n_y \delta_j^y + n_z \delta_j^z) \]

\( n_x, n_y, n_z \) being integers. The eigenvalue spectrum is therefore discrete. Expanding \( F_N(z_1, \cdots; z_N; t) \) in the eigenfunctions of \( L_0 \), which form a complete set in configuration space, one obtains the Fourier series

(2.20) \[ F_N(z_1, \cdots; z_N; t) = \sum_{\xi_1, \cdots, \xi_N} \rho_{\xi_1, \cdots, \xi_N}(z_1, \cdots; z_N; t) e^{i(\xi_1 z_1 + \cdots + \xi_N z_N)} \]

with the Fourier coefficients \( \rho_{\xi_1, \cdots, \xi_N} \) being given by

(2.21) \[ \rho_{\xi_1, \cdots, \xi_N}(z_1, \cdots; z_N; t) = \int (dz)^N F_N(z_1, \cdots; z_N; z; t) e^{-i(z_1 \xi_1 + \cdots + z_N \xi_N)} \]

The formal solution of the Liouville equation (2.15) now can be written

(2.22) \[ \rho_{\xi_1, \cdots, \xi_N}(z_1, \cdots; z_N; t) = \frac{-i}{2\pi i} \int (dz)^N e^{i\xi_i} \sum_{\{\xi^R\} \in \{\{z^R\}\}} \sum_{n=0}^{\infty} \langle \{\xi^R\} | (L_0 - z)^n | \{\xi^R\} \rangle \langle \{z^R\} | (L_0 - z)^n | \{\xi^R\} \rangle \]

with the definition of the matrix element being

(2.23) \[ \langle \{z^R\} | A | \{\xi^R\} \rangle = \mathcal{J} \int (dz)^N e^{-i(z_1 \xi_1 + \cdots + z_N \xi_N)} e^{i\xi_i} \]

The matrix elements of the operator \((L_0 - z)^{-1}\) follow immediately from (2.17) and (2.23). They are

(2.24) \[ \langle \{z^R\} | (L_0 - z)^{-1} | \{\xi^R\} \rangle = \left( \sum_{j=1}^{N} \delta_{\xi_j}^z - z \right)^{-1} \prod_{\xi_j \neq z_j}^N \delta_{\xi_j - z_j}^R \]
with \( \delta_{kr} \) being the Kronecker delta. Obviously this matrix is diagonal.

The interaction matrix elements are also easily calculated. One defines the Fourier transform of the interaction potential to be

\[
\sqrt{\| \mathbf{v} \|} = \sum_{\mathbf{k}} \mathcal{V}_k \, e^{i \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_n)}
\]

so that

\[
\frac{\partial \sqrt{\| \mathbf{v} \|}}{\partial \mathbf{r}_j} = \sum_{\mathbf{k}} \mathcal{V}_k \, i \mathbf{k} \, e^{i \mathbf{k} \cdot (\mathbf{r}_j - \mathbf{r}_n)}
\]

also

\[
\lambda \delta_{L} = i \sum_{\mathbf{k} \neq \mathbf{n}} \frac{\lambda}{m} \frac{\partial \sqrt{\| \mathbf{v} \|}}{\partial \mathbf{r}_j} \left( \frac{\partial}{\partial \mathbf{r}_j} - \frac{\partial}{\partial \mathbf{r}_n} \right)
\]

Substituting this into (2.23) one obtains:

\[
\langle \mathbf{v} \rangle - \lambda \delta_{L} \left\langle \mathbf{v} \right\rangle = \frac{\lambda}{m} \sum_{\mathbf{k} \neq \mathbf{n}} \frac{\partial \sqrt{\| \mathbf{v} \|}}{\partial \mathbf{r}_j} \left( \frac{\partial}{\partial \mathbf{r}_j} - \frac{\partial}{\partial \mathbf{r}_n} \right)
\]

where

\[
\Theta^{Kn}(\mathbf{k}) = \frac{\lambda}{m} \mathcal{V}_k \, i \mathbf{k} \left( \frac{\partial}{\partial \mathbf{r}_j} - \frac{\partial}{\partial \mathbf{r}_n} \right)
\]

It is clear that \( \lambda \delta_{L} \) has no diagonal matrix elements but determines transitions where only two wave vectors are modified. This is a consequence of the interactions being two body. The sum of the wave vectors remains invariant, \( \sum_{j=1}^{N} \mathbf{k}_j = \sum_{j=1}^{N} \mathbf{k}_j^{\prime} + \mathbf{k}_j^{\prime\prime} \).

This is due to the fact that \( \sqrt{\| \mathbf{v} \|} \) depends only on the distance between particles \( j \) and \( n \) and is thus invariant with respect to translation. In fact the conservation of wave vectors is equivalent to the conservation of momentum.
2. Reduced Distribution Functions

A prescription for calculating macroscopic observables was given in equation (2.1). However these quantities depend not on all $N$ velocities and positions but on only a few of them\(^{17}\). This means that some of the information contained in $F_N$ is redundant and what is needed is a weighting function involving only those positions and velocities on which the quantity to be averaged depends. We accordingly define reduced distribution functions as follows:

\[(2.29) \quad f_{s \ldots s} (x, \ldots, x_s; \nu, \ldots, \nu_s, t) \]

\[\equiv \frac{N!}{(N-s)!} \int (d\nu)^{N-s} (d\nu\ldots d\nu) (x, \ldots, x_s; \nu, \ldots, \nu_s; t) \]

In the limit of a large system, (2.2), this can be written

\[(2.30) \quad f_{s \ldots s} (x, \ldots, x_s; \nu, \ldots, \nu_s, t) = N^s \int (d\nu)^{N-s} (d\nu\ldots d\nu) (x, \ldots, x_s, \nu, \ldots, \nu_s; t) \]

and as $F_N$ is normalized to unity it follows that $f_{s \ldots s}$ is normalized to $N^s$. The following abbreviated notations will frequently be used.

\[(2.31) \quad f_s (1, \ldots, s) \equiv f_{s \ldots s} (x, \ldots, x_s; \nu, \ldots, \nu_s) \]

and

\[\phi (\nu) \equiv f_{s \ldots s} (\nu) \]

These reduced distribution functions allow us to calculate values for any macroscopic quantity in which we may be interested. For example the local number density at $x$ is given by

\[(2.32) \quad n(x, t) = \int d\xi, d\nu, \delta(x - \xi) f_s (\xi, \nu; t) \]
and the pressure tensor by

\[
P(\mathbf{z}, t) = \int d\mathbf{z}_s d\mathbf{v}_s \delta(\mathbf{z}-\mathbf{z}_s) m \mathbf{v}_s \mathbf{v}_s \cdot f_t(\mathbf{z}_s, \mathbf{v}_s; t)
\]

\[
- \frac{1}{2} \int d\mathbf{z}_s d\mathbf{v}_s d\mathbf{z}_t d\mathbf{v}_t \delta(\mathbf{z}-\mathbf{z}_s) \lambda \frac{\partial V(\mathbf{z}_s, \mathbf{z}_t)}{\partial \mathbf{z}_s} (\mathbf{z}_s, \mathbf{z}_t) f_t(\mathbf{z}_s, \mathbf{z}_t; \mathbf{v}_s, \mathbf{v}_t; t)
\]

Two conditions are imposed on the reduced distribution functions at the initial time.

A) There exists no velocity correlations independent of the relative position of the particles. This implies the following factorization property for the reduced distribution functions \( f_{s, s'} \), \( s > s' \),

\[
f_{s, s'}(\mathbf{z}, \mathbf{z}_s; \mathbf{v}, \mathbf{v}_s, 0) = f_s(\mathbf{z}; \mathbf{v}, 0) \prod_{s' \neq s} \phi(\mathbf{v}_s)
\]

and is generally called the 'weak' molecular chaos assumption.

B) At the initial time the reduced distribution functions remain finite in passing to the limit of an infinite system (2.2), thus ensuring that all intensive properties of the system are initially finite.

Substituting the Fourier expansion of the N-particle distribution function (2.20) into the definition of the reduced distribution functions we have

\[
f_{s, s'}(\mathbf{z}, \mathbf{z}_s; \mathbf{v}, \mathbf{v}_s, 0) = c^s \int (d\mathbf{v})^{N-s'} \sum_{\mathbf{v}_s} \rho_{s_1, \ldots, s_N}(\mathbf{v}, \ldots, \mathbf{v}_N)
\]

\[
\delta_{s, s_1} \cdots \delta_{s, s_N} e^{i(\mathbf{v}_1 \cdot \mathbf{z}_1 + \cdots + \mathbf{v}_N \cdot \mathbf{z}_N)}
\]

consistent with this we define reduced Fourier coefficients
\[ (2.36) \quad \rho_{\xi_3}^{(s)}(\omega, \ldots, \omega_s) = \rho_{\xi_3}^{(0)}(\omega, \ldots, \omega_s) \] such that

\[ (2.37) \quad \xi_{s+5}(\omega, \ldots, \omega_{s+5}) = \xi_{s+5}(\omega, \ldots, \omega_s) \]

The weak molecular chaos hypothesis (A) imposes a factorization condition on the initial reduced Fourier coefficients

\[ (2.38) \quad \rho_{\xi_3}^{(s)}(\omega, \ldots, \omega_s; 0) = \rho_{\xi_3}^{(0)}(\omega, \ldots, \omega_s; 0) \prod_{i=s+1}^{s+5} \rho_{\xi_3}^{(0)}(\omega_i; 0) \]

The passage to the limit of an infinite system implies that the wave vector spectrum becomes continuous. A summation over a wave vector then goes over to an integral

\[ (2.39) \quad \sum_{\xi} \longrightarrow \frac{\Omega}{8\pi^3} \int d\xi \]

This introduces divergent volume factors into (2.37) so that in order for the reduced distribution functions to satisfy condition (B) the \( \rho_{\xi_3}^{(0)} \) must be related to coefficients \( \tilde{\rho}_{\xi_3}^{(s)} \) defined by

\[ (2.40) \quad \tilde{\rho}_{\xi_3}^{(s)}(\omega, \ldots, \omega_s) = \left( \frac{\Omega}{8\pi^3} \right)^{s} \rho_{\xi_3}^{(s)}(\omega, \ldots, \omega_s) \]

the coefficients \( \tilde{\rho}_{\xi_3}^{(s)} \), which we call regular, remaining finite in passing to the limit (2.2) of an infinite system.

The spatial correlations between particles can be expressed by the correlation functions \( g_s(\ldots, s) \) defined by the cluster decomposition.\(^{18}\)
\[ f_1(1) = q_1(1) \]

\[ f_2(1, 2) = q_1(1) q_1(2) + q_2(1, 2) \]

\[ f_3(1, 2, 3) = q_1(1) q_1(2) q_1(3) + q_1(1) q_2(2, 3) + q_2(2) q_3(1, 3) \]

\[ + q_1(3) q_2(1, 2) + q_3(1, 2, 3) \]

\[ \vdots \]

\[ f_s(l, \ldots, s) = \sum \prod_{s'} q_{s'}(l, \ldots, s') \]

where the summation is over all distinct partitions of the set \( s \) into subsets \( s' \) to each of which is associated a function \( q_{s'}(l, \ldots, s') \) in the product \( \prod_{s'} \).

The definitions (2.41) along with (2.37) define a cluster decomposition of the reduced Fourier coefficients.

\[ \rho_{s_1}(\nu_1) = y_{s_1}(\nu_1) \]

\[ \rho_{s_1, s_2}(\nu_1, \nu_2) = y_{s_1}(\nu_1) y_{s_2}(\nu_2) + y_{s_1, s_2}(\nu_1, \nu_2) \]

\[ \rho_{s_1, \ldots, s_s}(\nu_1, \ldots, \nu_s) = \sum \prod_{s'} y_{s_1, \ldots, s_s}(\nu_1, \ldots, \nu_s') \]

The \( \gamma_{s_1 s_2}^{(5)} \) thus defined are the Fourier coefficients of the correlation functions

\[ q_s(l, \ldots, s) = c_s \sum_{s_1 s_2} \gamma_{s_1 s_2}^{(5)}(\nu_1, \ldots, \nu_s) e^{i(l_1 \nu_1 + \ldots + l_s \nu_s)} \]
and associated with the $\gamma_{k^2}^{(s)}$ are regular coefficients $\gamma_{k^2}^{(s)}$ (see (2.40))

\[(2.44) \quad \gamma_{k^2}^{(s)}(\psi_1, \ldots, \psi_s) = \left(\frac{1}{\sqrt{\pi}}\right)^s \gamma_{k^2}^{(s)}(\psi_1, \ldots, \psi_s)\]

that remain finite as $\sigma \to \infty$.

If the particles of the system are uncorrelated then

\[f_s(i_1, \ldots, i_s) = \prod_{i=1}^{s} f_i(i)\]

and also

\[\rho_{k^2}^{(s)} = \prod_{i=1}^{s} \rho_{k_i}(\psi_i)\]

This we term the correlation vacuum and rewrite (2.42) separating out the vacuum term explicitly,

\[(2.45) \quad \rho_{k^2}^{(s)}(\psi_1, \ldots, \psi_s) = \rho_{k^2}^{(s)}(\psi_1, \ldots, \psi_s) + \Gamma_{k^2}^{(s)}(\psi_1, \ldots, \psi_s)\]

with

\[(2.46) \quad \rho_{k^2}^{(s)}(\psi_1, \ldots, \psi_s) \equiv \prod_{i=1}^{s} \rho_{k_i}(\psi_i)\]

and

\[(2.47) \quad \Gamma_{k^2}^{(s)}(\psi_1, \ldots, \psi_s) \equiv \sum' \prod_{s'} \gamma_{k^2}^{(s')}(\psi_1, \ldots, \psi_{s'})\]

where $\sum'$ means the sum over all distinct partitions of the set $s$ into subsets $s'$ except the completely factorized vacuum term $\rho_{k^2}^{(s)}$, (all $s' = 1$).
3. Diagram Representation

The N-particle distribution function, as stated earlier, contains more information than can be used. Thus the formal solution for \( F_N(t) \) or equivalently the time development of the N-body Fourier coefficients is not actually required. What is needed is an expression for the evolution of the reduced Fourier coefficients, \( \rho_{(s)}^{(s)} \). The definition of the reduced coefficients (2.36) together with the perturbation expansion for \( \rho_{(s)}^{(s)}(t) \) as given in (2.22) yields the following expression for \( \rho_{(s)}^{(s)}(z)\):

\[
(2.48) \quad \rho_{(s)}^{(s)}(z, \ldots, z', t) = \frac{-1}{2\pi i} \int \frac{d\varepsilon}{\varepsilon} e^{-i\varepsilon t} \int (d\omega)^{N-S} \cdot \sum_{\ell=0}^{\infty} \sum_{n=0}^{\infty} \langle \ell \mid (L_{-\varepsilon} - L_{\varepsilon})^n \rangle \langle \ell \mid (L_{-\varepsilon})^n \rangle \rho_{(s)}^{(s)}(z, \ldots, z', 0)
\]

Subsequently we shall consider only those reduced coefficients which have \( s = s' \). This merely serves to simplify the notation since one can obtain \( \rho_{(s)}^{(s)}(z, \ldots, z', t) \), \( s < s' \) from \( \rho_{(s)}^{(s)}(z, \ldots, z', t) \) simply by setting the wave vectors labelled \( s+1, \ldots, z' \) equal to zero. Also \( \rho_{(s)}^{(s)}(z, \ldots, z', t) \), \( s > s' \) is obtained by integrating \( \rho_{(s)}^{(s)}(z, \ldots, z', 0) \) over the velocities \( z_{s+1}, \ldots, z_s \). The notation

\[
(2.49) \quad \rho_{\ell, s}^{(s)}(\varepsilon, \ldots, \varepsilon_s, t) \equiv \rho_{\ell}^{(s)}(\varepsilon, \ldots, \varepsilon_s, t)
\]

will be used. We rewrite equation (2.48) to read

\[
(2.50) \quad \rho_{\ell, s}^{(s)}(\varepsilon, \ldots, \varepsilon_s, t) = \frac{-1}{2\pi i} \int \frac{d\varepsilon}{\varepsilon} e^{-i\varepsilon t} \int (d\omega)^{N-S} \cdot \sum_{\ell=0}^{\infty} \sum_{n=0}^{\infty} \langle \ell \mid (L_{-\varepsilon} - L_{\varepsilon})^n \rangle \langle \ell \mid (L_{-\varepsilon})^n \rangle \rho_{\ell}^{(s)}(\varepsilon, \ldots, \varepsilon_s, 0)
\]
We now proceed to represent the terms in this expansion by Prigogine type diagrams\(^8,9\). These diagrams are constructed in the following manner:

I) With each matrix element of the propagator \((L_0-z)^{-1}\), 

\[ \langle \xi' | (L_0-z)^{-1} | \xi \rangle \]

is associated a set of lines running from right to left - one line for each non-zero wave vector which is labelled with the index of that wave vector.

II) With each matrix element of the interaction \(\delta L^{\gamma_1} \delta L^{\gamma_2} \delta L^{\gamma_3} \), 

\[ \langle \xi | \delta L^{\gamma_1} | \xi' \rangle \langle \xi' | \delta L^{\gamma_2} | \xi'' \rangle \langle \xi'' | \delta L^{\gamma_3} | \xi''' \rangle \]

is associated a vertex consisting of the confluence of lines labelled by \(j\) and \(n\) in the set \(\{ \xi \} \) and the similarly labelled lines in the set \(\{ \xi' \} \).

As an example consider a particular first order contribution to a particular reduced coefficient, say the contribution from an interaction between particles 1 and 2 to \(\rho_{\{\xi\};\{\xi',\xi''\}}^{(3)}(\xi')\) which we write \(\rho_{\{\xi\};\{\xi',\xi''\}}^{(3)}(\xi')\)\(\big|_{l_1,\lambda}^{(0)}\) the superscript indicating the first order and the subscripts the particles involved.

\[
(2.51) \quad \rho_{\xi, \xi', \xi''}^{(3)}(\xi', \xi''; \xi; t) \big|_{l_1,\lambda}^{(0)} = \frac{1}{2\pi i} \int_{\mathbb{R}} dx e^{-ixt} \int_0^{N-3} \sum_{\{\xi''\}} \langle \xi, \xi', \xi'' | (L_0-z)^{-1} \lambda \delta L^{\xi_1} (L_0-z)^\dagger | \xi'' \rangle \rho_{\{\xi''\}; \{\xi\}}^{(3)}(\xi'')
\]

Using the definitions of the matrix elements (2.24) and (2.27) this becomes

\[
\rho_{\xi, \xi', \xi''}^{(3)}(\xi', \xi''; \xi; t) \big|_{l_1,\lambda}^{(0)} = \frac{1}{2\pi i} \int_{\mathbb{R}} dx e^{-ixt} \int_0^{N-3} \sum_{\{\xi''\}} \frac{1}{\delta_{\xi_1, \xi_1 + \xi_2 - \xi_3 - \xi} \delta_{\xi_2, \xi_2 + \xi_3 - \xi} \delta_{\xi_3, \xi_3 + \xi_1 - \xi}} \frac{1}{\sum_{\xi''} \delta_{\xi_1, \xi''} \delta_{\xi_2, \xi''} \delta_{\xi_3, \xi''}} \rho_{\{\xi''\}; \{\xi\}}^{(3)}(\xi''; 0)
\]
Because of the factorization condition (2.38) and the fact that \( \rho_2(u_1, 0) \) is normalized to unity we have

\[
(2.52) \quad \rho_{\delta_1, \delta_2, \delta_3} (u_1, u_2, u_3, \epsilon) = \frac{1}{\pi i} \oint d\epsilon e^{-i\epsilon} \frac{1}{\delta_1, \delta_2, \delta_3 - \epsilon} \sum_{\delta_1', \delta_2'} \frac{\delta^n}{\pi^2} \Theta^{ij}(\delta_1', \delta_2') \delta^{i, j}_{\delta_1' + \delta_2' - \delta_1 - \delta_2}
\]

The diagram representing this contribution is shown in Fig. 2.1.

![Diagram](image)

**Fig. 2.1**

Our diagrams differ from those used by the Prigogine school in that we do not separate out and represent by a separate diagram the value \( k = 0 \) in the summations over the wave vectors. That is, using the above example we do not draw a separate diagram to represent the contribution when \( \frac{\delta_1}{\delta_2} \) or \( \frac{\delta_2}{\delta_1} \) are zero. However, since we are looking for contributions to specified reduced coefficients the values of all the wave vectors at the left of a diagram are fixed and therefore the distinction between diagrams which have one and two lines on the left is maintained. We then have two basic types of diagrams, type A and type B.
These are displayed as Fig. 2.2a and Fig. 2.2b.

The diagram of Fig. 2.2c would also appear to be important. However, it can be shown that because of the integration over N-s velocities this type of diagram does not contribute to \( \rho_{\xi}^{(s)}(\xi, \ldots \xi, 0) \) unless one of its indices j or n is one of the set of indices \( (i, \ldots, s') \). And since we are concerned only with reduced coefficients with \( s = s' \) and all wave vectors labelled from 1 to s are non zero, this type of diagram does not contribute.

Each term in the perturbation expansion ultimately connects on the right to an initial reduced Fourier coefficient \( \rho_{\xi}^{(s)}(\xi, 0) \) (c.f. (2.52)). If the cluster decomposition of this coefficient as given by (2.45) with \( \rho_{\xi}^{(s)} \) written in the fully expanded form (2.47) is inserted for \( \rho_{\xi}^{(s)}(\xi, 0) \) a set of contributions each of which arises from a distinct correlation pattern (i.e. a term in the series (2.47)) at the time \( t = 0 \) results. Each of this set of contributions is represented by a distinct diagram in which the solid lines representing wave vectors of correlated particles are connected by vertical dotted lines.
Fig. 2.3 represents a fifth order contribution to \( \rho_{2,2}^{(u,i,t)} \) arising from the initial correlation pattern \( \rho_{2}^{(u,i;0)} \rho_{3}^{(u,i;0)} \rho_{3}^{(u,i;0)} \rho_{3}^{(u,i;0)} \rho_{2}^{(u,i;0)} \).

The same diagram without the dotted line between the solid lines labelled 2 and 3 would represent a fifth order contribution to \( \rho_{2,2}^{(u,i,t)} \) arising from the completely factorized correlation vacuum

\[
\rho_{2}^{(u,i;0)} \rho_{3}^{(u,i;0)} \rho_{3}^{(u,i;0)} \rho_{2}^{(u,i;0)} \rho_{2}^{(u,i;0)} .
\]

The vertices of the diagrams are considered to be ordered from right to left. Breaking the diagram of Fig. 2.3 at the arrows \( t' \) results in two fragments with the one on the right representing a contribution to the "intermediate state"

\[
\rho_{2,2,2,2}^{(u,i,u,i; t')} \quad \text{where} \quad t > t' > 0.
\]

Diagrams are termed non-connex provided they are made up of two or more component structures which are unconnected to each other. Dotted lines representing the initial correlations are to be included in determining the connexity of the diagram. The
permutation class of a non-connex diagram is formed by changing the relative ordering of the component structures. The permutation class being all such possible permutations. Fig. 2.4a displays a simple non-connex diagram. This together with the diagram of Fig. 2.4b forms the permutation class of this diagram.

![Diagram](a) ![Diagram](b)

**Fig. 2.4**

The following factorization theorem is due to Balescu but a more general proof has been given by Resibois.¹⁹

A non-connex diagram completed by its permutation class represents a sum of contributions which is equal to the product of the contributions represented by each of the component structures.

A simple example of this theorem is worked out in Appendix A.

The consequence of this theorem is that contributions to the Fourier coefficient \( \rho_{\Delta z}^{(s)}(\tau) \) can be written as a product of factors, the number of factors being determined by the number of unconnected component structures of the representative diagram.
Moreover, each component structure of the diagram represents a term in the development of some Fourier coefficient, \( f_{L_3}^{(s')} (t) \).

Since these component structures are connex they represent non-factorizable contributions to the \( f_{L_3}^{(s')} (t) \) and when these are compared to the factorization properties of the terms in the cluster decomposition (2.45) it is clear that they must be contributions to the \( f_{L_3}^{(s')} (t) \). This means that the time development of each term in the cluster decomposition of \( f_{L_3}^{(s')} \) is represented by a class of diagrams whose factorization property as determined from the connexity of the class is the same as the factorization property of that term in the cluster decomposition. Equivalently: if a set of particles is uncorrelated at \( t = 0 \) (no vertical dotted lines between the solid lines labelled by this set) and there are no interaction matrix elements involving the members of this set (no vertices labelled by the set) then the set of particles is uncorrelated at time \( t \); but, if the members of the set are initially correlated (vertical dotted lines connecting the solid lines labelled by the set) or if there are interaction matrix elements involving the particles of the set (vertices labelled by the set) then the set is correlated at time \( t \). For example, contributions to the two particle coefficient \( \rho_{\xi_1 \xi_2} (\xi_1, \xi_2, t) \) can be separated into two classes. One, which is represented entirely by connex diagrams, is non-factorizable and contributes only to \( \gamma_{\xi_1 \xi_2} (\xi_1, \xi_2, t) \). The other, which is represented by non-connex diagrams containing two component structures (each component representing a contribution to either \( \rho_{\xi_1} (\xi_1, t) \) or \( \rho_{\xi_2} (\xi_2, t) \)) is factorizable and contributes only to
A typical non-connex diagram representing a contribution to $\hat{\gamma}_{s, b_2}(\sigma_1,\sigma_2; t)$ and a connex diagram representing a contribution to $\gamma_{s, b_2}$ are displayed in Fig. 2.5a and Fig. 2.5b respectively.

A contribution to the reduced $s$-particle coefficient $\rho_{(s)}^{(s)}(\ell^{(s)}; t)$ is said to be reducible if its representative diagram can be divided into two fragments, with at least one vertex in each, by a vertical cut such that the fragment on the right represents a contribution to the completely factorized correlation vacuum of the intermediate state $\hat{\rho}_{(s)}^{(s)}(\ell^{(s)}; t')$. That is, if the fragment on the right is non-connex and has as many unconnected component structures as it has lines at the left, the complete diagram is termed reducible. Otherwise it is said to be irreducible and if besides being irreducible it also represents a contribution to the $s$-particle correlation coefficient.
\( \gamma^{(5)}_{\{K, \bar{K}\}}(u_3; t) \) is said to be strictly irreducible. It should be noted that all zero and first order contributions are inherently strictly irreducible since one cannot divide the representative diagrams into two fragments with one vertex in each. Examples of diagrams representing the three types of contributions to \( \gamma^{(5)}_{\{K, \bar{K}\}}(u_3; t) \) are given in Fig. 2.6. The diagram Fig. 2.6a represents a reducible contribution and Fig. 2.6b a strictly irreducible contribution to \( \gamma^{(5)}_{\{K, \bar{K}\}} \) while Fig. 2.6c represents an irreducible contribution to \( \gamma^{(5)}_{\{K, \bar{K}\}} \).

Fig. 2.6
This completes the exposition of the general properties of the diagrams. The only restriction that has been made is that the interactions be central two-body forces whose range is much less than the dimensions of the system as a whole. In the next section it will be shown how the concept of irreducibility can be used to derive equations of evolution for the reduced Fourier coefficients. This will be applied to the particular case of a classical gas with a long range attraction in Chapter III.
4. Equations of Evolution of the Reduced Fourier Coefficients

First let us consider the reduced one-particle Fourier coefficient. According to equation (2.50) it evolves in time as

\[ \rho_{\phi_1}(\varphi_1; t) = \frac{-i}{2\pi} \oint d\zeta e^{-i\zeta t} \int (dy)^{N-1} \]

\[ \cdot \sum \sum_{n=0}^{\infty} \langle \xi_r | (L_{-z})^{-1} [-\lambda \delta_L (L_{-z})^{-1}]^n | \xi_{k_f} \rangle \rho_{\xi_{k_f}}(\varphi_1, \ldots, \varphi_N; 0) \]

This is equivalent to the two equations

\[ \rho_{\phi_1}(\varphi_1; t) = \frac{-i}{2\pi} \oint d\zeta e^{-i\zeta t} \rho_{\phi_1}(\varphi_1; z) \]

and

\[ \rho_{\phi_1}(\varphi_1; z) = \]

\[ -i \int (dy)^{N-1} \sum \sum_{n=0}^{\infty} \langle \xi_r | (L_{-z})^{-1} [-\lambda \delta_L (L_{-z})^{-1}]^n | \xi_{k_f} \rangle \rho_{\xi_{k_f}}(\varphi_1, \ldots, \varphi_N; t=0) \]

Following Severne\textsuperscript{11} we separate out the contributions up to arbitrary order m in \( \lambda \) and rewrite (2.55) as

\[ \rho_{\phi_1}(\varphi_1; z) = -i \int (dy)^{N-1} \left\{ \sum \sum_{n=0}^{m+1} \langle \xi_r | (L_{-z})^{-1} [-\lambda \delta_L (L_{-z})^{-1}]^n | \xi_{k_f} \rangle \rho_{\xi_{k_f}}(\varphi_1, \ldots, \varphi_N; t=0) \right. \]

\[ \left. + \sum \langle \xi_r | [(L_{-z})^{-1} (-\lambda \delta_L)]^{m+1} \xi_{k_f} \rangle \rho_{\xi_{k_f}}(\varphi_1, \ldots, \varphi_N; z) \right\} \]

with \( \rho_{\xi_{k_f}}(\varphi_1; z) \) satisfying an equation analogous to (2.55).

The cluster decomposition (2.45) can of course be applied to these Laplace transformed coefficients. We use this and rewrite (2.56) as the sum of contributions from initial state correlations.
and from intermediate correlation vacuum (completely factorized) states. This is accomplished in the following way. We write (2.56) for \( m = 0 \) and retain in the second term only the contribution from the correlation vacuum:

\[
-i \langle \xi_i | (L_{-z})^{-1} | \xi_i \rangle \rho_{\xi_i}^{(\xi_i)}(\xi_i; t = 0)
\]

\[
+ \sum_{\xi'_{\ell \gamma}} \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) | \xi'_{\ell \gamma} \rangle \hat{\rho}_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; z)
\]

For \( m \geq 1 \) we write in the first term the irreducible contributions of order \( m \) from the initial state correlations and in the second term the irreducible contributions of order \( m + 1 \) from the intermediate state correlation vacuum. Thus

\( m = 1: \)

\[
-i \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) (L_{-z})^{-1} | \xi_{\ell \gamma} \rangle \Gamma_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; t = 0)
\]

\[
+ \sum_{\xi'_{\ell \gamma}} \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) | \xi'_{\ell \gamma} \rangle \hat{\rho}_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; z)
\]

\( m = 2: \)

\[
-i \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) (L_{-z})^{-1} | \xi_{\ell \gamma} \rangle \Gamma_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; t = 0)
\]

\[
+ \sum_{\xi'_{\ell \gamma}} \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) | \xi'_{\ell \gamma} \rangle \hat{\rho}_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; z)
\]

\( \vdots \)

\( m = m': \)

\[
-i \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) (L_{-z})^{-1} | \xi_{\ell \gamma} \rangle \Gamma_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; t = 0)
\]

\[
+ \sum_{\xi'_{\ell \gamma}} \int (d\xi) \langle \xi | (L_{-z})^{-1} (-\lambda \delta L) | \xi'_{\ell \gamma} \rangle \hat{\rho}_{\xi_{\ell \gamma}}^{(\ell \gamma)}(\xi_{\ell \gamma}; z)
\]

Where \( \sum^{(ir)} \) means that only irreducible contributions are included.
This condition of irreducibility ensures that no contribution written above for a given \( m = m_1 \) has already been included in a correlation vacuum contribution of order \( m < m_1 \). That the expressions written above, when summed over all \( m \), also constitute an exhaustive reclassification of the terms in the expansion (2.55) is fairly obvious. For, (i) all irreducible contributions from initial state correlations are written as such and (ii) all irreducible contributions from the initial state correlation vacuum as well as all reducible contributions are included in the contributions from the intermediate state. As an example to illustrate the second statement consider the contributions to \( f_3(x; \vec{z}) \) represented by the diagrams displayed in Fig. 2.7a, that is, an irreducible contribution from the initial correlation vacuum, and Fig. 2.7b, that is, a reducible contribution from the initial state.

![Diagrams](a) and (b)

**Fig. 2.7**

The term in equation (2.55) corresponding to Fig. 2.7a is
This can be rewritten as

\[-i \int (d\psi) \sum_{\xi_{1}' \xi_{2}'} \langle \xi_{1}' | (L_{0} - z)^{-1} (-\lambda \delta L) (L_{0} - z)^{-1} \xi_{2} ; \xi_{1}' \xi_{2}' \rangle \left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] \]

with

\[\left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] = -i \int (d\psi) \sum_{\xi_{1}' \xi_{2}'} \langle \xi_{1}' | (L_{0} - z)^{-1} (-\lambda \delta L) (L_{0} - z)^{-1} \xi_{2} \rangle \left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] \]

which is the zero order contribution to \( \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \). Similarly the term in equation (2.55) represented by Fig. 2.7b is

\[-i \int (d\psi) \sum_{\xi_{1}' \xi_{2}'} \langle \xi_{1}' | (L_{0} - z)^{-1} (-\lambda \delta L) \xi_{2} \rangle \left[ (L_{0} - z)^{-1} (-\lambda \delta L) (L_{0} - z)^{-1} \xi_{2} \right] \left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] \]

This can be rewritten as

\[\int (d\psi) \sum_{\xi_{1}' \xi_{2}'} \langle \xi_{1}' | (L_{0} - z)^{-1} (-\lambda \delta L) \xi_{2} \rangle \left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] \]

with

\[\left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] = -i \int (d\psi) \sum_{\xi_{1}' \xi_{2}'} \langle \xi_{1}' | (L_{0} - z)^{-1} (-\lambda \delta L) (L_{0} - z)^{-1} \xi_{2} \rangle \left[ \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \right] \]

\[\cdot \hat{\rho}_{\xi_{1}', \xi_{2}'}^{(0)} (\psi_{1}; \lambda_{1}, \lambda_{2} ; z) \]

This can be rewritten as
which is a first order contribution to \( \hat{P}^{(2)}(z^\prime ; z) \).

Summing over all \( m \) we now have:

(2.57)

\[
\rho^m_z(x_i; z) = -i \left\langle b_i \right| (L_x - \bar{z})^{-1} \left| b_i \right\rangle \rho^m_z(x_i; t = 0)
\]

\[
+ \int (d\omega)^{M_{x_i}} \sum_{\{l, v\}} \left\langle b_i \right| (L_x - \bar{z})^{-1} \left| -\lambda v L \right\rangle \left\{ b_{l, v} \right\} \hat{P}^{(5)}(\xi_{l, v}; z)
\]

\[
- i \int (d\omega)^{N-1} \sum_{\{l, v\}} \sum_{\eta = 1}^{\infty} \left\langle b_i \right| (L_x - \bar{z})^{-1} \left[ -\lambda v L (L_x - \bar{z}) \right]^{-\eta} \left\{ b_{l, v} \right\} \Gamma^{(\xi_{l, v})}_{\eta, 0} (\eta^\prime_{\xi_{l, v}}; t = 0)
\]

\[
+ \int (d\omega)^{S_{x_i}} \sum_{\{l, v\}} \sum_{\eta = 2}^{\infty} \left\langle b_i \right| \left[ (L_x - \bar{z})^{-1} (\lambda v L) \right]^{-\eta} \left\{ b_{l, v} \right\} \hat{P}^{(5)}(\xi_{l, v}; z)
\]

Writing the matrix element of the final state propagator explicitly yields

(2.58)

\[
\rho^m_z(x_i; z) = \frac{1}{\omega_{x_i} - \omega - \bar{z}} \left\{ \rho^m_z(x_i; t = 0)
\]

\[
+ i \int (d\omega)^{M_{x_i}} \sum_{\{l, v\}} \left\langle b_i \right| (-\lambda v L) \left\{ b_{l, v} \right\} \hat{P}^{(5)}(\xi_{l, v}; z)
\]

\[
+ \int (d\omega)^{N-1} \sum_{\{l, v\}} \sum_{\eta = 1}^{\infty} \left\langle b_i \right| \left[ -\lambda v L (L_x - \bar{z}) \right]^{-\eta} \left\{ b_{l, v} \right\} \Gamma^{(\xi_{l, v})}_{\eta, 0} (\eta^\prime_{\xi_{l, v}}; t = 0)
\]

\[
+ i \int (d\omega)^{S_{x_i}} \sum_{\{l, v\}} \sum_{\eta = 2}^{\infty} \left\langle b_i \right| \left[ (L_x - \bar{z})^{-1} (\lambda v L) \right]^{-\eta} \left\{ b_{l, v} \right\} \hat{P}^{(5)}(\xi_{l, v}; z)
\]

under application of the inverse Laplace transform

\[
- \frac{1}{2\pi} \oint_{\gamma} dz e^{-i z t} \]

equation (2.58) becomes
where we have used the definitions

\begin{align}
(2.60) \quad \hat{\Phi}(z,|\ell;3) & \equiv i \langle \ell | (-\lambda \hat{S}_l) | \ell;3 \rangle \\
(2.61) \quad \hat{\varphi}(z;\ell;1;\ell') & \equiv -\frac{1}{2\pi} \int d\zeta e^{-i\zeta z} \sum_{\ell \neq 1} \sum_{n=1}^{\infty} \langle \ell | \Gamma_{\ell} \left[ -\lambda \hat{S}_l (L_{\ell} \cdot \zeta)^{-1} \right]^{n} (-\lambda \hat{S}_l) | \ell;3 \rangle \langle \ell;3 | (\ell;1;\ell') | \ell;3 \rangle ; \zeta = 0
\end{align}

and

\begin{align}
(2.62) \quad \hat{\psi}(z,|\ell;3;\ell') & \equiv -\frac{i}{2\pi} \int d\zeta e^{i\zeta z} \\
& \cdot \sum_{n=1}^{\infty} i \langle \ell | \Gamma_{\ell} \left[ -\lambda \hat{S}_l (L_{\ell} \cdot \zeta)^{-1} \right]^{n} (-\lambda \hat{S}_l) | \ell;3 \rangle \langle \ell;3 | (\ell;1;\ell') | \ell;3 \rangle ; \zeta = 0
\end{align}

Since there are no correlations in the intermediate state the irreducibility property is a characteristic of the transitions represented by the matrix elements of (2.62), Hence the notation \( \langle \ell;1;\ell' \rangle \).

When we write out the matrix element of (2.60) explicitly, using (2.27) and (2.28) we have

\begin{align}
(2.63) \quad \left[ d\nu \right]^{\nu;1} \sum_{\ell;3} \hat{\Phi}(z,|\ell;3) \hat{\rho}_{\ell;3}^{(\nu;1)}(\ell;3;\ell) & = i \frac{\gamma \alpha^3}{m} \frac{N}{\alpha} |d\nu| \\
& \cdot \sum_{\ell} \langle \ell;1;\ell' \rangle \cdot (z_1 - z_2) \cdot \left( \frac{3}{2} \frac{\partial}{\partial z_1} - \frac{3}{2} \frac{\partial}{\partial z_2} \right) \hat{\rho}_{\ell;1}^{(\nu;1)}(\ell;1;\ell) \hat{\rho}_{\ell;2}^{(\nu;1)}(\ell;2;\ell')
\end{align}
The quantities we are actually interested in are not the Fourier coefficients but the reduced distribution functions. Applying the inverse Fourier transform to (2.63) yields the contribution from that term to the time development of the one-particle distribution function. The result is:

\[(2.64) \quad -\frac{3}{m} \int dz \int d\epsilon_a \frac{\partial}{\partial z_i} \nabla G(z_i, z) \cdot \frac{\partial}{\partial \epsilon_a} f(z_i, \epsilon; \tau) f(z_i, \epsilon; \tau)\]

which is a self-consistent field or Vlassov term.

The quantity \( \sigma_{\epsilon_a}(\epsilon; \tau) \), the "destruction term", describes the propagation of the initial correlations through the system. It will be seen later that its effect is generally transient and may be neglected for long times.

The operator \( \chi_{\epsilon_a}(\epsilon; \tau) \) is to be interpreted as a general collision operator. Its form is intimately related to that of the interactions and its properties will be discussed in detail later.

An entirely similar method may be used to obtain the time development of the s-particle Fourier coefficients, \( \chi_{\{S\}}^{(s)} \). According to the discussion in Section 3, the contributions to the correlation coefficient \( \chi_{\{S\}}^{(s)} \) must not factorize. The diagrams representing these contributions are then connex. Separating out the irreducible contributions from the initial state correlations and the intermediate state correlation vacuum we can write
The superscript (irs) means that strict irreducibility is to be applied to ensure that the contributions determine \( \chi_{(s)} \) and not some other term of the cluster expansion of \( \chi_{(s)}^{(s)} \). Diagrams contributing to \( \chi_{(s)}^{(s)} \) have s lines on the left and since each vertex involves at most two lines no connex diagram connecting to the intermediate correlation vacuum can be constructed with fewer than s-1 vertices. We define the creation operators as

\[
(2.66a) \quad C(\ell_1, \ldots, \ell_s | \ell'_{s+1}, \ldots, \ell'_N; z) \equiv \sum_{n=s}^{\infty} \langle \ell_1, \ldots, \ell_s | (L_{(s-2)} \cdot (-\lambda b L))^n | \ell'_s, \ldots, \ell'_N, \ell'_{s+1}, \ldots, \ell'_N \rangle_{(s)}
\]

which under inverse Laplace transformation becomes

\[
(2.66b) \quad C(\ell_1, \ldots, \ell_s | \ell'_{s+1}, \ldots, \ell'_N; z) = \sum_{n=s}^{\infty} \int d\xi \int d\zeta \ e^{i \xi \zeta} \langle \ell_1, \ldots, \ell_s | (L_{(s-2)} \cdot (-\lambda b L))^n | \ell'_s, \ldots, \ell'_N, \ell'_{s+1}, \ldots, \ell'_N \rangle_{(s)}
\]

The first term of (2.65) when the inverse Laplace transform has been applied we write as

\[
(2.67) \quad \theta_{(s)}^{(s)}(\ell_{s+1}; t) = -\frac{i}{2\pi} \int d\xi \int d\zeta \ e^{-i \xi \zeta} \sum_{n=s}^{\infty} \sum_{(s)} \langle \ell_1, \ldots, \ell_s | (L_{(s-2)} \cdot (-\lambda b L))^n | \ell'_s, \ldots, \ell'_N, \ell'_{s+1}, \ldots, \ell'_N \rangle_{(s)}
\]

This enables us to write the following equation for the s-particle correlation coefficient:
Here again the \( \mathcal{D} \) term represents the effect of the initial state correlations and the creation operator \( \mathcal{C} \) is closely related to the collision operator \( \mathcal{I} \).

Equations (2.59) and (2.68) are exact within the limits imposed by the N-body formalism. Summation of the infinite series of (2.61), (2.62), (2.66a) and (2.67) would be equivalent to solving the N-body problem exactly. An attempt at an exact summation is therefore quite useless. In the next chapter we shall develop criteria for retaining those diagrams which yield significant contributions to the development of a classical gas with a weak long range attraction. These restricted classes of terms are then summed to yield the equations of evolution.
CHAPTER III

EVOLUTION OF A CLASSICAL GAS WITH A LONG RANGE ATTRACTION

1. The System and Interactions

In this chapter we shall apply the methods outlined in Chapter II to the particular case of a gas of identical particles whose interactions are derived from a potential which is the sum of a strong short range repulsion and a weak long range attraction. The scale to which the ranges of the two potentials are compared is the average interparticle distance while the strength of the interaction is compared to the average kinetic energy of a particle. To be more precise, we write the interaction between two particles separated by a distance $r$, $\lambda V(r)$, as

$$\lambda V(r) = \mu U(r) - \nu W(r)$$

(3.1)

The functions $U(r)$ and $W(r)$ having the properties

$$U(r) \sim 1, \quad r < \kappa^{-1}$$

$$\equiv 0, \quad r > \kappa^{-1}$$

(3.2)

and

$$W(r) \sim 1, \quad \kappa^{-1} < r < \alpha^{-1}$$

$$\equiv 0, \quad \kappa^{-1} > r ; \quad \alpha > \alpha^{-1}$$

(3.3)

with the inverse ranges, $\kappa$ and $\alpha$, satisfying the inequalities
Here \( \alpha \) is the concentration of the gas, \( \alpha^{-1/3} \) then being the average interparticle distance. Since the range of the interactions is assumed to be much less than the size of the container we have also that

\[ \Omega \gg \alpha^{-3} \]

If the average kinetic energy per particle is \( 1/\beta \) then the strength parameters of the interactions, \( \mu \) and \( \nu \), satisfy the inequalities

\[ \mu \gg \frac{1}{\beta} \gg \nu \]

At the same time we assume that the volume integrals of the interactions are such that

\[ \nu \int_{V} W(y) \equiv \nu c \tilde{W} \approx \nu c \alpha^{-3} \sim \frac{1}{\beta} \]

and

\[ \mu \int_{V} U(r) \equiv \mu \tilde{U} \approx \mu \alpha^{-3} \ll \nu \tilde{W} \]

No further restrictions are placed on the interactions. However we distinguish between the following two cases which relate the range of the long range interaction to the length scale of the inhomogeneities of the system. That is, if \( L \) is the shortest wavelength of the spatial Fourier transform of the one particle distribution function, then we consider the two cases.
In what follows we shall first work under the assumption that (3.8a) is valid. After criteria have been established for obtaining all significant contributions to the collision term of equation (2.59) and these contributions summed we shall consider what happens when the restriction is relaxed to that of (3.8b).

The nature of the Fourier transform is such that if the original function extends over a range $R$ in coordinate space then the spectral breadth of the image function in $k$ space is $K \approx R^{-1}$. This means, since the one particle distribution function $f_1$ varies over a distance $L_h$, with $L_h$ very large, that the one body reduced Fourier coefficient, $f_A$, is sharply peaked about $k_1 = 0$ with a width $\approx L_h^{-1}$. Writing $U_k$ and $W_k$ as the Fourier transforms of the potentials $U(r)$ and $W(r)$, we have that the range of $U_k$ in $k$ space is $\approx \lambda$ and that the spectral breadth of $W_k$ is $\approx \alpha$. Since $\alpha \gg \lambda \gg L_h^{-1}$, by (3.4) and (3.8a), $U_k$ is a very broad function of $k$ in comparison with the sharply peaked behaviour of $W_k$ and the even more sharply peaked $f_A$.

According to equations (2.59) and (2.60) the contributions to the time development of the Fourier coefficients are of two types: one which arises from the completely factorized correlation vacuum of an intermediate state and one from the initial
state correlations. The specification of these initial correlations is necessary before one can select the dominant contributions to the evolution of the system. It is desirable not to be too restrictive but rather to specify a general class of initial conditions in order that the equations derived be more widely applicable. We shall assume that the initial time does not play a privileged role, the correlations at time $t = 0$ being of the same nature as those at later times. This amounts to assuming that the initial correlations are of the same nature as arise from the interactions. Under this assumption it is obvious that these correlations between particles become vanishingly small when the particles are separated by some distance $L_c$ and moreover

$$L_c \ll \alpha^{-1}$$

For example, consider the two particle correlation $\mathcal{g}_2(z_1, z_2)$. This can be rewritten in terms of the coordinates of the centre of mass of the two particles and their relative separation,

$$R = \frac{z_1 + z_2}{2}, \quad r = \frac{z_1 - z_2}{2}$$

(3.10)

to give $\mathcal{g}_2(R, r)$. Since we insist on long wavelength inhomogeneities the function $\mathcal{g}_2(R, r)$ will be a slowly varying function of $R$ and the fact that the particles are uncorrelated when widely separated means that $\mathcal{g}_2(R, r)$ must become zero when $r \geq L_c$. The regular Fourier coefficient $\tilde{g}_{k, l}$ is given by
or writing \( A_i = k_i + \xi_k \), \( A_{-i} = -k_i \)

\[
(3.12) \quad \tilde{g}_{k + \xi_k, -\frac{\lambda}{2}} = \frac{1}{q} \left( \frac{1}{(\pi T)^{\frac{n}{2}}} \right) \int d\xi \int d\eta \quad e^{-i(\xi + \eta) \cdot \xi} \quad e^{-i(\xi + \eta) \cdot \eta} \quad q_0(\xi, \eta)
\]

Clearly \( \tilde{g}_{k + \xi_k, -\frac{\lambda}{2}} \) is a sharply peaked function of \( q \) about \( q = 0 \) with a width \( \sim L_n^{-1} \) and at the same time due to the finite range of the correlations it is peaked about \( k = 0 \) with a width \( \sim L_n^{-1} \geq \alpha \).

It is not necessary, as will be seen later, to make any assumption about the size of the initial correlations, other than that they be finite, in order to derive an equation of evolution valid for long times. However, not too surprisingly, the size of the correlations at time zero is crucially important for the short-time equations. If it is assumed that the correlations at \( t = 0 \) are of the same order of magnitude as at equilibrium then the size of the correlations can be estimated in a manner similar to the following for the two body correlation.

The equilibrium \( N \)-body distribution function is given by

\[
F_N^0 = \frac{1}{Z_N^{-1}} e^{-\frac{H}{\hbar^2 T}}
\]

\[
= \frac{1}{Z_N^{-1}} e^{-\frac{1}{\hbar^2 T} \left[ \sum_{i \leq \lambda} m \frac{\nu^2}{2} + \lambda \sum_{i < \lambda} V(12_i - 12_{\lambda}) \right]}
\]

where the partition function

\[
Z_N = \int (d\psi)^N (d\bar{\psi})^N e^{-\frac{H}{\hbar^2 T}}
\]
and \( k_B \) is Boltzmann's constant, \( T \) being the temperature. The indicated velocity integrations can be immediately performed to give

\[
Z_N = \left( \frac{2\pi k_B T}{m} \right)^{\frac{3N}{2}} Q_N
\]

with the configuration integral

\[
Q_N = \int (d\mathbf{x})^N e^{-\frac{1}{T} \beta \sum_{i<j} \mathbf{v}_i \cdot \mathbf{v}_j}
\]

From the definition of the reduced distribution functions (2.29) we have

\[
\bar{f}_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{x}, \mathbf{x}_2) = N(N-1) \int (d\mathbf{u})^{N-1} (d\mathbf{v})^{N-2} F_N
\]

Again the velocity integrals are straightforward, each giving a factor \( \left( \frac{2\pi k_B T}{m} \right)^{\frac{3}{2}} \) which cancels with one of the factors in \( Z_N \) to give

\[
\bar{f}_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{x}_1, \mathbf{x}_2) = \frac{N(N-1)}{2!} \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} e^{-\frac{m}{2k_B T} (x_1^2 + x_2^2)} \int Q_N \int (d\mathbf{z})^{N-2} e^{-\frac{2}{k_B T} \sum_{i<j} \mathbf{v}_i \cdot \mathbf{v}_j}
\]

The function \( F(\mathbf{x}_1, \mathbf{x}_2) \) can be expanded in terms of the cluster integrals. To first order this gives

\[
F(\mathbf{x}_1, \mathbf{x}_2) \approx e^{-\frac{2}{k_B T} V^{12}}
\]

and we write

\[
f_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{x}_1, \mathbf{x}_2) \approx c^2 \phi'(\mathbf{u}_1) \phi''(\mathbf{u}_2) e^{-\frac{2}{k_B T} U(1|\mathbf{x}, \mathbf{x}_2)} e^{-\frac{2}{k_B T} W(|\mathbf{x}, \mathbf{x}_2|)}
\]

(3.13)

\[
\approx c^2 \phi'(\mathbf{u}_1) \phi''(\mathbf{u}_2) e^{-\frac{2}{k_B T} U^{12}} \left\{ 1 + \frac{v}{k_B T} W^{12} + \cdots \right\}
\]
By (2.41)

\[ f_1^0(\mathbf{x}, \mathbf{x}_1; \mathbf{y}, \mathbf{y}_1) = c^2 \phi(\mathbf{x}_1) \phi(\mathbf{y}_1) + g_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{y}, \mathbf{y}_1) \]

For \(|\mathbf{x} - \mathbf{x}_1| < \kappa^{-1}\), (3.13) states that \( f_2 \approx 0 \) and therefore

\[ g_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{y}, \mathbf{y}_1) \approx -c^2 \phi(\mathbf{x}_1) \phi(\mathbf{y}_1) \quad ; \quad |\mathbf{x} - \mathbf{x}_1| < \kappa^{-1} \]

For \(|\mathbf{x} - \mathbf{x}_1| > \kappa^{-1}\)

\[ f_2^0 \approx c^2 \phi(\mathbf{x}_1) \phi(\mathbf{y}_1) \left\{ 1 + \frac{\kappa}{\mathcal{H}_0 T} \mathcal{V}(1\mathbf{x} - \mathbf{x}_1) \right\} \]

and

\[ g_2^0(\mathbf{x}, \mathbf{x}_1; \mathbf{y}, \mathbf{y}_1) \approx \frac{\kappa}{\mathcal{H}_0 T} \mathcal{V}(1\mathbf{x} - \mathbf{x}_1) c^2 \phi(\mathbf{x}_1) \phi(\mathbf{y}_1) \quad ; \quad |\mathbf{x} - \mathbf{x}_1| > \kappa^{-1} \]

Treating (3.14) and (3.15) as exact and using (3.12) yields

\[ \gamma_{\xi, \eta}^0(\mathbf{y}_1; \mathbf{x}_1) \approx \frac{1}{4} \left\{ \frac{i}{2\pi^3 \mu^2} \frac{\hat{\mathcal{V}}(\kappa \mu)}{\kappa / \mu} + \frac{\kappa}{\mathcal{H}_0 T} \mathcal{V}_\kappa \right\} \phi(\mathbf{y}_1) \phi(\mathbf{y}_1) \]

In obtaining the second term of (3.16) the integration over \( r \) has been extended into the region \( r < \kappa^{-1} \) it being negligibly small. Since the spherical Bessel function \( \hat{\mathcal{V}}(r) \) behaves asymptotically as \( 1/r \) and also \( \hat{\mathcal{V}}(r) \to r \) as \( r \to 0 \) the first term of (3.16) is \( \sim 1/\kappa^3 \). The second term is very small because \( \kappa / \mathcal{H}_0 T \ll 1 \). The one particle coefficient is of order unity and therefore we maintain that the equilibrium correlation coefficients satisfy the inequality

\[ \gamma_{\xi, \eta}^{(s)} \ll \rho_{\xi, \eta}^{(s)} = \frac{\rho}{i = 1} \rho_{\xi, \eta}, \]

A calculation of the equilibrium two particle correlation function will be performed in section 8 of this chapter. It will be seen then that (3.14) and (3.15) are consistent with the approximations used throughout this work.
2. Ring and Chain Diagrams

In this section the classes of diagrams representing significant contributions to the time development of the system will be determined. First let us consider the evolution of the one-particle Fourier coefficient \( n_2(\bar{s}, \bar{t}) \) which is controlled by equation (2.59). The contributions arising from the intermediate state correlation vacuum are given by the collision term

\[
J_{\bar{s}}(\bar{s}, \bar{t}) = \int (d\omega) \sum_{\bar{t}'} \psi_{\bar{t}}(\bar{s}, \bar{t}'; \bar{t} - \bar{t}') \sum_{\bar{t}'} \hat{\rho}_{\bar{s}}(\bar{s}, \bar{t}')
\]

With the collision operator \( \psi_{\bar{t}}(\bar{s}, \bar{t}'; \bar{t} - \bar{t}') \) being defined by (2.62). The Laplace transform of this operator as determined by transforming equation (2.62) is

\[
\psi(\bar{s}, \bar{t}'; \bar{t} - \bar{t}') = \sum_{n=1}^{\infty} i <k_{\bar{s}}|(-\alpha \delta L(\bar{z} - \bar{z}'))^{n}(-\alpha \delta L)|\{k_{\bar{t}'}\}_{(ir)}>
\]

The diagram technique can be more conveniently applied when we define a new operator

\[
\bar{\psi}(\bar{s}, \{k_{\bar{t}'}\}; \bar{z}) = (\bar{L} - \bar{z})^{-1} \psi(\bar{s}, \{k_{\bar{t}'}\}; \bar{z}) (\bar{L} - \bar{z})^{-1}
\]

Each term in the expansion of (3.20b) is represented by a diagram. Referring back to Chapter II.3 and noting that the final state involves only one non-zero wave-vector, \( k_{\bar{l}} \), it is clear that each diagram begins on the left with a type B vertex (see Fig. 2.2b). The requirement that the contributions be irreducible is equivalent to requiring that it be impossible to divide the diagram, by a vertical cut, such that the
fragment on the right be non-connex and have as many component
structures as it has lines on the left. This means, since
there are no correlations among the particles of the set \( \{ \nu' \} \)
and thus no dotted lines connecting the solid lines labelled
by the \( \{ \nu' \} \), that the first vertex on the right of a diagram
must be a type A vertex (see Fig. 2.2a). Each diagram representing
a term in \((3.20b)\) therefore consists of a type B vertex on
the left connected through combinations of vertices of types A
and B to a type A vertex on the right. The diagrams with
fewest vertices which can be constructed in this manner are
displayed in Fig. 3.1. The simplest possible diagram which
represents a term in the expansion of the collision operator
is Fig. 3.1a. The diagram Fig. 3.1b is typical of diagrams
which are called 'chains'. They are made up of a single B
type vertex and a number of type A vertices. Fig. 3.1c and
Fig. 3.1f are examples of diagrams called 'rings'. These
diagrams are constructed from a single A type vertex together
with a number of type B vertices.

The explicit form of the term in the expansion \((3.20)\)
corresponding to the diagram Fig. 3.1a, as determined from
\((2.24), (2.27)\) and \((2.28)\) is

\[
(3.21) \quad i \left( \frac{\gamma^2 \hbar^2}{m \Omega \hbar} \right)^2 \sum_{j=2} \sum_{(j') \neq (j)} \frac{1}{(j')_j \cdot \nu_j - \Xi_j} \left( \nu_j - \nu_{j'} \right) \cdot \left( \frac{\partial}{\partial \nu_j} - \frac{\partial}{\partial \nu_{j'}} \right)
\]

\[
\cdot \frac{1}{(j', \nu_{j'} + \nu_j, \nu_{j'} + \nu_j - \Xi_j)} \left( \nu_{j'} - \nu_{j''} \right) \cdot \left( \frac{\partial}{\partial \nu_{j'}} - \frac{\partial}{\partial \nu_{j''}} \right) \frac{1}{(j'_{j''}, \nu_{j''} + \nu_j, \nu_{j''} + \nu_j - \Xi_{j''})}
\]

The effect of the Kronecker deltas has been implicitly included
at each vertex and the wave vectors labelled according to the
Fig. 3.1
convention illustrated in Fig. 3.2.

Fig. 3.2

Also, the labelling of the lines in Fig. 3.1 obeys the convention that numbered lines correspond to a single particle and are not summed over while lettered lines imply a summation over all particles of the system except those already fixed. For example, the indices labelling the lines of Fig. 3.1e are $l$, $j$, $m$, and $n$. This implies the summations: \( \sum_{\ell} \) over all particles of the system except that labelled $l$: \( \sum_{m} \) over all particles except those labelled $l$ or $j$: and \( \sum_{m} \) over all particles except those labelled by $l$, $j$ or $m$. The distribution functions and hence the reduced Fourier coefficients are symmetric with respect to the permutation of the particles. This means that each term in the summations over the indices labelling the lines is equivalent to every other term. Therefore the $j$ summation can be replaced by $(N-1)$ times one of the terms, the $m$ summation by $N-2$ times one of the terms and the $n$ summation by $N-3$ times one of the terms.
In the thermodynamic limit \((2.2)\) these factors \(N-s\) can be replaced by \(N\). Also, the \(\ell\) summation of \((3.21)\) goes over to an integral (see \((2.39)\)) and \((3.21)\) becomes

\[
(3.22) \quad i \, g \, n_c^2 \left( \frac{\Lambda^2}{m} \right)^3 \frac{l}{(\ell_1 + \ell_2) \cdot \ell_3 - \ell} \int \frac{d \ell}{2 \pi} \, V_{\ell_1 \ell_2 \ell_3} (\ell_1 - \ell_2) \cdot \ell_{12} \frac{1}{\ell_1 \cdot \ell_3 + \ell_2 \cdot \ell_3 + \ell_{12} \cdot \ell_3 - \ell}
\]

where

\[
(3.23a) \quad \ell_{12} \equiv \ell_1 - \ell_2
\]

and

\[
(3.23b) \quad \ell_{12} \equiv \frac{\partial \ell_1}{\partial \ell_3} - \frac{\partial \ell_2}{\partial \ell_3}
\]

The terms in the expansion \((3.19)\) of the collision operator corresponding to those in the expansion \((3.20)\) are immediately obtainable by dropping the propagators from either end of the latter expressions. Thus \((3.22)\) corresponds to the following term in the expansion of the collision operator

\[
(3.24a) \quad i \, g \, n_c^2 \left( \frac{\Lambda^2}{m} \right)^3 \int \frac{d \ell}{2 \pi} \, V_{\ell_1 \ell_2 \ell_3} (\ell_1 - \ell_2) \cdot \ell_{12} \frac{1}{\ell_1 \cdot \ell_3 + \ell_2 \cdot \ell_3 + \ell_{12} \cdot \ell_3 - \ell}
\]

where the Kronecker delta has been replaced to make explicit the conservation of wave vectors. Similar calculations yield the following expressions for the terms of \((3.19)\) corresponding to the diagrams Fig. 3.1b - \(\mathfrak{R}\)
\[ (3.24b) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}}^{*} \cdot (\psi_{j_{2}}^{*}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}}^{*} \cdot (\psi_{j_{2}}^{*}) \cdot \mathbf{r}_{2} \]

\[ (3.24c) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} - \mathbf{z}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} - \mathbf{z}) \cdot \mathbf{r}_{2} \]

\[ (3.24d) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} - \mathbf{z}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} - \mathbf{z}) \cdot \mathbf{r}_{2} \]

\[ (3.24e) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \psi_{j_{3}} - \mathbf{z}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \psi_{j_{3}} - \mathbf{z}) \cdot \mathbf{r}_{2} \]

\[ (3.24f) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \mathbf{z} - \mathbf{z}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \mathbf{z} - \mathbf{z}) \cdot \mathbf{r}_{2} \]

\[ (3.24g) \quad i \, \sigma_{i,i} \left( \frac{3}{m} \right)^{2} \iint_{x} \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \mathbf{z}) \cdot \frac{1}{\delta \cdot \mathbf{r} + \delta_{i,i} + \delta_{j_{1},j_{2}} - \mathbf{z}} \quad \nabla \psi_{j_{1}} \cdot (\psi_{j_{2}}^{*} + \mathbf{z}) \cdot \mathbf{r}_{2} \]
The inequalities given in (3.8a) and the subsequent discussion enables us to place certain restrictions on the magnitude of the wave-vectors appearing in these expressions. Because of the long wavelength nature of the inhomogeneities all the primed wave vectors are very small, \( A_i' \sim L^{-1}_n \). The wave vectors, \( \ell \), which are integration variables are not so restricted. The average value of these wave vectors is of the order of the inverse of the range of the interaction. That is, \( \langle \ell \rangle \approx \alpha \gg L^{-1}_n \). To a good approximation we can neglect the \( \ell \) in comparison with the \( J \)'s and write the following approximate expressions for those of (3.24):

(3.25a) \[-i \sigma n^2 c \left( \frac{\lambda}{m} \right)^2 \int d^L \nabla \cdot \ell \cdot \partial_{12} \frac{1}{\ell \cdot \partial_{12} - z} \nabla J \cdot \partial_{12} \delta_{s_i, -s_i} \]

(3.25b) \[-i \sigma n^2 c \left( \frac{\lambda}{m} \right)^2 \int d^L \int d^L' \nabla \cdot \ell \cdot \partial_{12} \frac{1}{\ell \cdot \partial_{12} - z} \nabla J \cdot \ell' \delta_{s_i, -s_i} \delta_{s_i, -s_i} \]

(3.25c) \[i (\sigma n^2 c)^3 \left( \frac{\lambda}{m} \right)^3 \int d^L \nabla \cdot \ell \cdot \partial_{12} \frac{1}{\ell \cdot \partial_{12} - z} \nabla J \cdot \partial_{23} \frac{1}{J \cdot \partial_{23} - z} \nabla J \cdot \partial_{13} \delta_{s_i, -s_i} \delta_{s_i, -s_i} \]

(3.25d) \[-i (\sigma n^2 c)^3 \left( \frac{\lambda}{m} \right)^3 \int d^L \nabla \cdot \ell \cdot \partial_{12} \frac{1}{\ell \cdot \partial_{12} - z} \nabla J \cdot \partial_{3} \frac{1}{J \cdot \partial_{3} - z} \nabla J \cdot \partial_{12} \delta_{s_i, -s_i} \delta_{s_i, -s_i} \]
Comparing (3.25c) and (3.25d) with particular reference to the factors underlined with a wavy line we see that the ratio of (3.25d) to (3.25c) is \( \sim n / \langle \phi \rangle \). We therefore consider all terms in the expansion of the collision operator (3.20) which are associated with diagrams of the type Fig. 3.1d to be negligible in comparison to those associated with diagrams of the type Fig. 3.1c. A similar argument can be used to show that (3.25e) is negligible \( \sim n \langle \phi \rangle / \langle \phi \rangle \) in comparison with (3.25f). The only difference between these diagrams is in the labelling of the lines. In future the labels may be dropped with the understanding that the diagram is actually of the type Fig. 3.1c and Fig. 3.1f. Diagrams of the type Fig. 3.1d and Fig. 3.1e are excluded from the class of diagrams termed 'rings'.

\[
(3.25e) \quad i(\gamma n c^2) \left( \frac{d}{m} \right)^{\frac{1}{2}} \int d\beta \quad \gamma_n \cdot \partial_{22} \quad \frac{1}{\beta_{33} - \beta} \quad \gamma_{\beta} \cdot \partial_{23} \quad \frac{1}{\beta_{44} - \beta} \quad \gamma_{\beta^\prime} \cdot \partial_{34}
\]

\[
(3.25f) \quad -i(\gamma n c^2) \left( \frac{d}{m} \right)^{\frac{1}{2}} \int d\beta \quad \gamma_n \cdot \partial_{22} \quad \frac{1}{\beta_{33} - \beta} \quad \gamma_{\beta} \cdot \partial_{23} \quad \frac{1}{\beta_{44} - \beta} \quad \gamma_{\beta^\prime} \cdot \partial_{34}
\]

\[
(3.25g) \quad i(\gamma n c^2) \left( \frac{d}{m} \right)^{\frac{1}{2}} \int d\beta d\beta^\prime \quad \gamma_n \cdot \partial_{22} \quad \frac{1}{\beta_{33} - \beta} \quad \gamma_{\beta^\prime} \cdot \partial_{23} \quad \frac{1}{\beta_{44} + \beta_{33} - \beta}
\]
A cursory examination of the expressions (3.25) and the diagrams of Fig. 3.1 reveals a remarkable property of these diagrams. Namely, the addition of each vertex of type $A$ (−→) entails an additional integration over wave vectors while the addition of each $B$ type vertex (−⊂) gives a new particle index and a factor $c$ but no integration over wave vectors. For example both (3.25b) and (3.25c) are of order $\lambda^3$ but the former is of first order in $c$ and has integrations over $\lambda$ and $\lambda'$ whereas the latter has only an $\lambda$ integration and is of order $c^2$. It is easy to see that this is true in general.

It will be shown later that the only value of $\varepsilon$ that is important in the expressions of (3.25) is $\varepsilon = 0$. If we now assume for purposes of illustration that

\begin{equation}
(3.26)
V_\lambda \approx \mathcal{U} , \quad \lambda < \pi
\end{equation}

\begin{equation}
= 0 , \quad \lambda > \pi
\end{equation}

insert this in the expressions of (3.25) and estimate the order of magnitude of these quantities there results, respectively,

\begin{equation}
(3.27a)
\sim (\lambda \mathcal{U})^2 c \lambda^\gamma
\end{equation}

\begin{equation}
(3.27b)
\sim (\lambda \mathcal{U})^3 c \lambda^\gamma
\end{equation}

\begin{equation}
(3.27c)
\sim (\lambda \mathcal{U})^3 c^2 \lambda^\gamma
\end{equation}

\begin{equation}
(3.27f)
\sim (\lambda \mathcal{U})^4 c^3 \lambda^\gamma
\end{equation}
In general it can be asserted that a diagram containing \( m \) type A vertices and \( n \) type B vertices is of the order of

\[
(\lambda U)^{m+n} c^m H^{3m+1}
\]

Clearly, if \( H^3 < c \), the dominant contribution of order \( p \) in the interaction, \( p = m+n \), since \( m \geq 1 \) and \( n \geq 1 \), is of the order of

\[
(\lambda U)^p c^{p-1} H^p
\]

It is equally obvious that if \( H^3 \gg c \) the dominant contribution of order \( p \) in the interaction is of the order of

\[
(\lambda U)^p c H^{3p-2}
\]

The class of diagrams for which \( n = 1 \) are those with a single type B vertex. These we have called chains. The class with \( m = 1 \) are those which have a single type A vertex and are called rings. Of course, diagrams of the type Fig. 3.1d and Fig. 3.1e are excluded from the class of rings as they are deemed to be negligible.

It is now evident that so far as the short range interaction is concerned the only significant terms in the expansion of the collision operator are those corresponding to the chain diagrams. Also, the only significant contributions due to the long range interaction are those represented by rings. These statements follow directly from the inequality

\[
\kappa^3 \gg c \gg \alpha^3
\]
and the fact that the Fourier transforms of the short and long range interactions have spectral widths of the order of $\kappa$ and $\alpha$ respectively.

This is not to say that either the strong short range or weak long range part of the interaction may not be completely overshadowed by the other. This would depend on the magnitude of the parameters of the interactions. Since, as we shall show later, the collision operator causes the system to approach equilibrium, one would expect that both parts of the interaction would be equally effective if the relaxation times for either part separately were of the same order of magnitude. The relaxation time of a gas of hard spheres of diameter $\kappa ^{-1} \ll \frac{c}{\sqrt{3}}$ is*

\begin{equation}
(3.31) \quad T_r^{(s)} \sim \frac{\kappa^2}{c} (m \beta)^{1/2}
\end{equation}

while that of a gas whose interactions are described by the long range potential $\frac{\kappa}{\alpha r} \ll \frac{\alpha}{c}$, is

\begin{equation}
(3.32) \quad T_r^{(l)} \sim \frac{\alpha^2}{\nu^2 c} \left( \frac{m}{\beta^4} \right)^{1/2}
\end{equation}

Equating (3.31) and (3.32) yields

\begin{equation}
(3.33) \quad \nu \beta \frac{\kappa}{\alpha} \sim 1
\end{equation}

as the condition that the two parts of the interaction play roughly equal roles in driving the system to equilibrium. If

$\nu \beta \frac{\kappa}{\alpha} \gg 1$ the long range interaction should dominate whereas if

$\nu \beta \frac{\kappa}{\alpha} \ll 1$ the short range part should. Retaining both the

* See reference 9, section 9
chains and rings ensures that no significant contributions are
discarded although one class or the other may be negligible.

When the Fourier transform of the potential $\lambda \varphi$ is replaced
by $\mu \lambda - \nu \lambda$, the products involved in the expressions (3.25)
necessarily introduce cross terms of the form $(\mu \lambda)^a (\nu \lambda)^b$.
It might be expected in the light of the preceding discussion
that terms of this type with $a = m, (the number of type A vertices)$
and $b = n, (the number of type B vertices)$ would give significant
contributions. This possibility can be ruled out on the basis of
the following argument.

The average values of $\lambda \lambda$ and $\lambda \lambda$ in the integrations of (3.25)
are $\lambda \lambda$ and $\lambda \lambda$, respectively, where these are defined by (3.6)
and (3.7). The contribution of a cross term of the above type is,
since the presence of $\lambda \lambda$ effectively cuts off the integration at
$\lambda = \alpha$
is

$$ (3.34) \sim (\mu \lambda)^m (\nu \lambda)^n \alpha^{2m+1} $$

This is to be compared with an $(m + n)$th order ring which is

$$ (3.35) \sim (\nu \lambda)^{m+n} \alpha^{m+n-1} \lambda $$

and an $(m + n)$th order chain which is

$$ (3.36) \sim (\mu \lambda)^{m+n} \lambda \alpha^{3(m+n)-2} $$

The ratio of (3.34) to (3.36) is

$$ (3.37) \sim \left( \frac{\nu \lambda}{\mu \lambda} \right)^n \left( \frac{\alpha}{\lambda} \right)^{3m+1} \left( \frac{\alpha}{\mu^3} \right)^{n-1} $$
Noting that $K^{-3}$ and $\omega \sim \kappa^{-3}$ and using (3.6) this becomes

\[(3.38) \quad \sim \left(\frac{1}{c\kappa^2}\right)^n \frac{\alpha^3}{\kappa} \left(\frac{\alpha}{\kappa}\right)^{3m-2}\]

which by (3.4) and (3.5) is clearly $\ll 1$ and thus (3.34) is negligible in comparison with (3.36) for all $n \geq 1$ and all $m \geq 1$. The ratio of (3.34) to (3.35) is

\[(3.39) \quad \sim \left(\frac{\mu\kappa}{\nu\omega}\right)^n \left(\frac{\alpha^3}{c}\right)^{n-1}\]

which by (3.4) and (3.7) is $\ll 1$ for all $m$. This shows that these cross terms may be neglected.

Extending this development to the Fourier coefficients of the correlation functions presents no new difficulties. The requirement of strict irreducibility for the contributions to the creation operator (2.66a) means that the diagrams have no structures which are not connected together and that the first vertex on the right of the diagram is of type A. The long range interaction again contributes significantly only through terms represented by diagrams which contain the minimum possible number of type A vertices while the short range interaction contributes only when the representative diagrams contain the minimum possible number of type B vertices. Applying these rules to the diagrams contributing to the two body correlation coefficient $\gamma_{4,4z}$ we see that they are identical to the rings and chains with the leftmost vertex split off. Typical of these diagrams are Fig. 3.3a and Fig. 3.3b respectively. Diagrams representing contributions to higher correlation coefficients are slightly more complex. However as we shall only be interested in the two
body correlation we shall not discuss these further.

(a)

(b)

Fig. 3.3
3. Asymptotic Forms of the Collision, Creation and Destruction Terms

In this section the forms taken by the collision, creation and destruction terms of equations (2.59) and (2.68) for long times will be determined. It is shown in Appendix B that the collision operator (2.62) tends to zero for times much greater than the collision time,

\[ \psi(t) \rightarrow 0 \quad \text{for} \quad t >> t_c \]  \hspace{1cm} (3.40)

with the collision time defined as the time required for a particle of average velocity, \((m_\beta)^{1/2}\), to traverse the range of the interaction, \(K^{-1}\):

\[ t_c \sim h^{-1}(m_\beta)^{1/2} \]  \hspace{1cm} (3.41)

Provided then, that we are interested in times much greater than the collision time the statement (3.40) allows us to extend the upper limit of integration in (3.18) to infinity and write the collision term as

\[ \int_{0}^{\infty} \psi(t; \{x', t\}; t') \rho_{\{x'; y, t\}}^{(\psi)}(\{y'; \tau - t\}) \]  \hspace{1cm} (3.42)

This is clearly non-Markoffian but \(\rho_{\{x'; y, t\}}^{(\psi)}(\{y'; t - t\})\) can be expanded in a Taylor series, assumed convergent, about \(t\). The collision term is then written

\[ \int_{0}^{\infty} \psi(t; \{x', t\}; t') \sum_{\{y'\}} \rho_{\{y, \tau - t\}}^{(\psi)}(\{y'; t - t\}) \]  \hspace{1cm} (3.43)

which, since the collision operator \(\psi(t) \rightarrow 0\) for \(\tau >> t_c\) and

\[ \frac{\partial^n}{\partial \tau^n} \rho_{\{y, t\}}^{(\psi)} \sim \tau^{-n}, \quad \tau \text{ being the relaxation time, is essentially} \]
an expansion in $t_c/t_r$. The relaxation time of the system is the shorter of $t_r^{(s)}$ or $t_r^{(l)}$ which are given by (3.31) and (3.32) as

$$t_r^{(s)} \sim \frac{\tau^1}{c} (m/\beta)^{1/2}$$
$$t_r^{(l)} \sim \frac{\alpha^2}{\nu^{1/2} c} \left( \frac{m}{\beta^2} \right)^{1/2}$$

The collision times appropriate to the short and long range parts of the interaction are from (3.41)

(3.44)  
$$t_c^{(s)} \sim \tau^1 (m/\beta)^{1/2}$$

and

(3.45)  
$$t_c^{(l)} \sim \alpha^2 (m/\beta)^{1/2}$$

Since

(3.46)  
$$\frac{t_c^{(s)}}{t_r^{(s)}} \sim \frac{\tau^1}{\alpha^2} \ll 1$$

and

(3.47)  
$$\frac{t_c^{(l)}}{t_r^{(l)}} \sim \left( \frac{\nu^1 \beta^2 c}{\alpha^3} \right) \sim \nu \ll 1$$

and only terms in the expansion of the collision operator represented by rings need be considered if $t_r^{(l)} \ll t_r^{(s)}$, while only chains need be considered if $t_r^{(s)} \ll t_r^{(l)}$, we have that

(3.48)  
$$t_c/t_r \ll 1$$

Therefore only the $n = 0$ term of (3.43) is retained and the collision term takes the Markoffian form*

* Severne, reference 11, gives an iterative expression for the collision term which includes higher order in $t_c/t_r$, but (3.49) is consistent with our retaining only the rings and chains.
The time integral of the collision operator is

\[ \int_0^\infty \psi(b, b'; \tau) \frac{-i}{2\pi} \oint db e^{-i\tau \cdot b} \psi(b, b'; \tau) \]

(3.50)

where \( z = -it + io \) means that the limiting value \( z = 0 \) is approached from above the real axis (\( \text{Im} \ z > 0 \)). Using this (3.49) becomes

\[ \mathcal{J}_b(n, z; t) = \int (dz)^{z} \sum_{b-b'} \psi(b, b'; z) \frac{-i}{2\pi} \oint db e^{-i\tau \cdot b} \psi(b, b'; z) \]

(3.51)

The discussion in Chapter III.2 showed that only ring and chain type diagrams need be retained. The further restriction of the collision operator to \( z = +i\alpha \) will enable us to sum these two infinite series exactly. This will be done in sections 4 and 5 of this chapter.

The lowest order contribution to the destruction term (2.61) is

\[ \mathcal{D}_b(n, z; t) = \frac{-i}{2\pi} \oint db e^{-i\tau \cdot b} \sum_{b-b'} \left( \frac{\langle b, b'|(-\alpha \delta b/L_\alpha)(L_{\alpha} - z)^{-1} | b', b' \rangle}{\gamma_{b', b'}(n, z; t \rightarrow 0)} \right) \]

This becomes, on passing to the limit of an infinite system (2.2) and calculating the matrix elements by using (2.24), (2.27) and (2.28)

\[ \mathcal{D}_b(n, z; t) = \frac{1}{2\pi} \oint db e^{-i\tau \cdot b} \sum_{b-b'} \frac{8n^2 \lambda}{m} \int d\omega \omega \cdot \frac{1}{d \cdot z + \frac{\omega_1^2}{2m}} \gamma_{b', b'}(n, z; \omega, \tau \rightarrow 0) \]

(3.53)
The discussion of Chapter III.2 assures us that $k_1 \sim L_n^{-1}$ and that $l \ll \alpha$. The inequality of (3.8a) then indicates that we can ignore the wave vector $k_1$ in comparison with $l$. Thus

\begin{equation}
\begin{split}
\mathcal{D}^t_{k_1}(\mathbf{x}_1,t) &\sim \frac{1}{2\pi} \int d^2 \mathbf{z} e^{-i\mathbf{z} \cdot \mathbf{x}} \frac{2\pi^2 \hbar^3}{m} \int d^2 q \mathbf{V}_q \cdot \mathbf{k}_1
\end{split}
\end{equation}

This is closely related to terms in the collision operator (see (3.25a)) and an argument like that of Appendix B can be used to show that, provided the range of the correlations is of the order of or less than the range of the interactions, the destruction term decays to zero for times much greater than the collision time:

\begin{equation}
\mathcal{D}^t_{k_1}(\mathbf{x}_1,t) \rightarrow 0 \quad \text{for } t \gg t_c
\end{equation}

The creation operator defined by (2.66b) and the destruction term of (2.67) are closely related to the collision operator (2.62) and the destruction term (2.61) respectively and we assume that they have the same time dependence. That is

\begin{equation}
\mathcal{C}(\mathbf{k}_1,\mathbf{k}_2,\mathbf{k}_2';t) \rightarrow 0 \quad \text{for } t \gg t_c
\end{equation}

and

\begin{equation}
\mathcal{D}^{(s)}(\mathbf{k}_2;\mathbf{t}) \rightarrow 0 \quad \text{for } t \gg t_c
\end{equation}

The statement (3.56) allows us to extend the $t'$ integration of (2.68) to infinity and perform a Taylor series expansion similar to that of (3.43). The result is that the creation
term of (2.68) is given by

\begin{equation}
\mathcal{C}^{(i)}_{\xi_{ij}^3}(\nu_{ij}; \tau) = \int d\nu \sum_{i \xi_{ij}^3} \mathcal{C}(\frac{1}{2}, \ldots, \frac{1}{2}; \nu_{ij}^3, \pm = \pm \nu_{ij}) \rho^{(i)}_{\nu_{ij}}(\xi_{ij}; \tau)
\end{equation}

The decay of the destruction terms (3.55) and (3.56) for times much greater than the collision time means that the long time behaviour of the system is essentially independent of the initial correlations provided the range of these initial correlations is of the order of the range of the interactions. In this case the destruction terms of (2.59) and (2.68) can be ignored for times much greater than the collision time.
4. Summation of the Rings

We now proceed to obtain an explicit form for the contribution to the collision term of (2.59), \( J_{\mathbf{k}_1}(\mathbf{z}_1;\mathbf{t}) \), by the long range interaction. This is achieved by summing over all possible ring diagrams. The complete class of rings can be systematically generated by adding basic vertices of type B to the diagram Fig. 3.1a in the manner illustrated in Fig. 3.4.

The term of the collision operator represented by the lower left diagram of Fig. 3.4 is given by (3.25f). According to (3.51) the contribution from the diagram to the collision term for long times is obtained by operating on \( \hat{P}_{\mathbf{E}^3}(\mathbf{E}^3;\mathbf{t}) \) with the operator of (3.25f), letting \( z \to +\text{i}0 \), integrating over \( s' \)-l velocities and summing over \( \mathbf{E}^3 \). Taking the limit \( z \to +\text{i}0 \) means that the factors \( (q \cdot z - z)^{-1} \) must be written as \( \pi \text{i} \delta_-(q \cdot z) \) where

\[
\delta_-(q) = \lim_{\mathbf{z} \to \text{i}0} \frac{1}{\mathbf{x} - \mathbf{z} \mathbf{\epsilon}} = i \int_{0}^{\infty} d\kappa e^{-\kappa x} = \pi \text{i} \delta_-(q \cdot z)
\]

The contribution to the collision term from this diagram is then

\[
-i \sum_{\mathbf{k}_1} \sum_{\mathbf{E}_1} \sum_{\mathbf{E}_2} \int d\mathbf{y}_1 d\mathbf{y}_2 d\mathbf{y}_3 (\mathbf{g} \cdot \mathbf{E}_1)^3 (\mathbf{g} \cdot \mathbf{E}_2)^3 \int d\mathbf{W}_3 \mathbf{g} \cdot \mathbf{\hat{e}}_3 \pi \text{i} \delta_-(q \cdot \mathbf{\hat{e}}_3)
\]

\[
\cdot \mathbf{W}_3 \mathbf{g} \cdot \mathbf{\hat{e}}_{23} \pi \text{i} \delta_-(q \cdot \mathbf{\hat{e}}_{23}) \mathbf{W}_4 \mathbf{g} \cdot \mathbf{\hat{e}}_{24} \pi \text{i} \delta_-(q \cdot \mathbf{\hat{e}}_{24}) \mathbf{W}_4 \mathbf{g} \cdot \mathbf{\hat{e}}_{24}
\]

\[
\delta_-(q \cdot z) \mathbf{P}_{\mathbf{k}_1}(\mathbf{y}_1;\mathbf{t}) \mathbf{P}_{\mathbf{k}_2}(\mathbf{y}_2;\mathbf{t}) \mathbf{P}_{\mathbf{k}_3}(\mathbf{y}_3;\mathbf{t}) \mathbf{P}_{\mathbf{k}_4}(\mathbf{y}_4;\mathbf{t})
\]
When Green's theorem is applied to the velocity integrals of (3.60) it is seen that we can replace $\bar{a}_i$ by $\bar{a}_i$, $\bar{a}_{2i}$ by $\bar{a}_i$, and $\bar{a}_{34}$ by $\bar{a}_i$ where $\bar{a}_i$ is defined by (3.23) and

$$\bar{a}_i \equiv \frac{\partial}{\partial \mathbf{u}_i}$$

In general it can be asserted* that if one of the indices $j$, $n$, say $n$, associated with a vertex does not appear to the left of that vertex then the velocity derivative operator $\bar{a}_i$ can be replaced by $\bar{a}_i$.

We introduce the following compact notations:

$$(3.62a) \quad d_j \equiv \delta n^2 \frac{\mathbf{u}_i}{m} \mathbf{W}_i \mathbf{l} \cdot \mathbf{a}_j$$

$$(3.62b) \quad d_{jn} \equiv \delta n^2 \mathbf{W}_i \mathbf{l} \cdot \mathbf{a}_i$$

and

$$(3.63) \quad \delta^n_i \equiv \pi \delta (\mathbf{l} \cdot \mathbf{a}_i)$$

These quantities have the following symmetry properties

$$(3.64) \quad (d_j)^* = -d_j$$

$$(3.65) \quad (d_{jn})^* = -d_{jn} = d_{nj}$$

and

$$(3.66) \quad (\delta^n_j)^* = \delta^n_j$$

In terms of these (3.60) becomes

* See reference 9, p.50.
The explicit form for the contribution to the collision term from the long range interaction is obtained by inserting the expressions for the terms of the collision operator represented by rings into (3.51). The rings are generated in the manner indicated in Fig. 3.4, each of the diagrams yielding a term similar to (3.67). The result is:

\[
(3.68) \quad \sum_{Q} \left. J_{QJ}(\omega_{1}, \omega_{2}) \right|_{Q,M} = \sum_{Q} \sum_{Q_{3}} \left\{ \frac{d\Phi_{(\delta^{23})}^{(3)}}{\delta_{23}^{(1)}} \frac{d\Phi_{(\delta^{24})}^{(3)}}{\delta_{24}^{(1)}} \right\} \left( \frac{d\Phi_{(\delta^{25})}^{(3)}}{\delta_{25}^{(1)}} \right) \left( \frac{d\Phi_{(\delta^{26})}^{(3)}}{\delta_{26}^{(1)}} \right)
\]

\[
+ \sum_{Q} \sum_{Q_{3}} \left\{ \frac{d\Phi_{(\delta^{23})}^{(3)}}{\delta_{23}^{(1)}} \frac{d\Phi_{(\delta^{24})}^{(3)}}{\delta_{24}^{(1)}} \right\} \left( \frac{d\Phi_{(\delta^{25})}^{(3)}}{\delta_{25}^{(1)}} \right) \left( \frac{d\Phi_{(\delta^{26})}^{(3)}}{\delta_{26}^{(1)}} \right)
\]

\[
+ \sum_{Q} \sum_{Q_{3}} \left\{ \frac{d\Phi_{(\delta^{23})}^{(3)}}{\delta_{23}^{(1)}} \frac{d\Phi_{(\delta^{24})}^{(3)}}{\delta_{24}^{(1)}} \right\} \left( \frac{d\Phi_{(\delta^{25})}^{(3)}}{\delta_{25}^{(1)}} \right) \left( \frac{d\Phi_{(\delta^{26})}^{(3)}}{\delta_{26}^{(1)}} \right)
\]

\[
+ \sum_{Q} \sum_{Q_{3}} \left\{ \frac{d\Phi_{(\delta^{23})}^{(3)}}{\delta_{23}^{(1)}} \frac{d\Phi_{(\delta^{24})}^{(3)}}{\delta_{24}^{(1)}} \right\} \left( \frac{d\Phi_{(\delta^{25})}^{(3)}}{\delta_{25}^{(1)}} \right) \left( \frac{d\Phi_{(\delta^{26})}^{(3)}}{\delta_{26}^{(1)}} \right)
\]

\[
+ \cdots \}
\]

where \( p_{QJ} \) is understood to mean \( p_{QJ}(\omega_{1}, \omega_{2}) \).
The quantity of interest is actually the one particle distribution function, \( f_{1}(\mathbf{z}, \mathbf{y}; t) \), rather than its Fourier coefficient \( \hat{p}_{k}(\mathbf{y}; t) \). Thus we require an expression for

\[
J(z, y; t) \equiv c \sum_{\mathbf{y}_{i}} J_{\mathbf{y}_{i}}(\mathbf{y}; t) e^{\mathbf{z} \cdot \mathbf{y}_{i}}.
\]

Taking the inverse Fourier transform of (3.68) yields

\[
J(z, y; t) = \int d\mathbf{d} \int d\mathbf{u}_{1} \int d_{12} \int d_{2} \int d_{31} \int f(1) f(2)
\]

\[
+ \int d\mathbf{d} \int d\mathbf{u}_{2} \int d_{12} \int d_{2} \int d_{31} \int f(1) f(2) f(3)
\]

\[
+ \int d\mathbf{d} \int d\mathbf{u}_{3} \int d_{12} \int d_{2} \int d_{31} \int f(1) f(2) f(3) f(4)
\]

\[
+ \int d\mathbf{d} \int d\mathbf{u}_{4} \int d_{12} \int d_{2} \int d_{31} \int f(1) f(2) f(3) f(4)
\]

\[
+ \cdots
\]

where

\[
f(\mathbf{d}) \equiv f_{1}(\mathbf{z}, \mathbf{y}; t)
\]

The series (3.70) can be rewritten as

\[
J(z, y; t) \big|_{\mathbf{w}, \mathbf{w}_{s}} = \int d\mathbf{d} \int f(1)
\]

with
\( F(1) = \int d\xi_2 \, \delta_{12} \, d_2 \, f(1) \, f(2) \)

\[ + \int d\xi_2 \, \delta_{12} \, d_2 \, f(2) \int d\xi_3 \, \delta_{13} \, d_3 \, f(1) \, f(3) \]

\[ + \int d\xi_2 \, \delta_{12} \, d_1^* \, f(1) \int d\xi_3 \, (\delta_{12}^{23})^* \, d_2^* \, f(2) \, f(3) \]

\[ + \int d\xi_2 \, \delta_{12} \, d_2 \, f(2) \int d\xi_3 \, \delta_{12} \, d_2 \, f(3) \int d\xi_4 \, \delta_{12} \, d_4 \, f(1) \, f(4) \]

\[ + \int d\xi_2 \, \delta_{12} \, d_2 \, f(2) \int d\xi_3 \, \delta_{12} \, d_1^* \, f(1) \int d\xi_4 \, (\delta_{12}^{34})^* \, d_1^* \, f(3) \, f(4) \]

\[ + \int d\xi_2 \, \delta_{12} \, d_1^* \, f(1) \int d\xi_3 \, (\delta_{12}^{32})^* \, d_1^* \, f(3) \int d\xi_4 \, (\delta_{12}^{34})^* \, d_1^* \, f(2) \, f(4) \]

\[ + \cdots \]

or

\( F(1) = \int d\xi_2 \, \delta_{12} \, d_2 \, f(1) \, f(2) \)

\[ + \int d\xi_2 \, \delta_{12} \, d_2 \, f(2) \int d\xi_3 \, \delta_{12}^{32} \, d_2 \, f(3) \]

\[ + \int d\xi_2 \, \delta_{12} \, d_1^* \, f(1) \int d\xi_3 \, \delta_{12}^{32} \, d_1^* \, f(3) \int d\xi_4 \, (\delta_{12}^{34})^* \, d_1^* \, f(2) \, f(4) \]

\[ + \cdots \]

Introducing the quantities

\( (3.75a) \]

\[ \mathcal{E}(1) = 1 - \int d\xi_1 \, \delta_{12} \, d_2 \, f(2) \]
\((3.75b)\) 
\[ \xi(1) = 1 - i \frac{\delta \gamma V}{m} W \int du_2 \delta_1 \left( \delta \left( \frac{\gamma_{12}}{\delta_2} \right) \delta_2 \cdot \partial_2 \right) f_1 (x_1, y_1; t) \]

\((3.76a)\) 
\[ \varrho(1) \equiv \int du_2 \delta_1^{12} \delta_2 f_1 (1) f(2) \]

\((3.76b)\) 
\[ = -i \pi \frac{\gamma_{12}}{2} \alpha \int du_2 \delta_1 \left( \delta \left( \frac{\gamma_{12}}{\delta_2} \right) \delta_2 \cdot \partial_2 \right) f_1 (x_1, y_1; t) f_1 (x_1, y_1; t) \]

and

\((3.77a)\) 
\[ \delta(1) \equiv \delta \delta_1^{12} f(1) \]

\((3.77b)\) 
\[ = -i \pi \frac{\gamma_{12}}{2} \alpha \int du_2 \delta_1 \left( \delta \left( \frac{\gamma_{12}}{\delta_2} \right) \delta_2 \cdot \partial_2 \right) f_1 (x_1, y_1; t) \]

into \((3.74)\) yields the integral equation

\((3.78)\) 
\[ \xi(1) F(1) = \varrho(1) + i \pi \delta(1) \int du_2 \delta_1 \left( \delta \left( \frac{\gamma_{12}}{\delta_2} \right) \delta_2 \cdot \partial_2 \right) F^{*}(1) \]

The solution of this equation as obtained by Balescu and Taylor\(^{12}\) is

\((3.79)\) 
\[ F(1) \equiv F(\xi, \varrho) = \frac{\varrho(\xi)}{\xi(\varrho)} + \frac{i \pi}{\lambda} \delta(\xi) \int d\lambda \delta_1 \left( \delta_1 - \lambda \right) \frac{\varrho(\lambda)}{|\xi(\lambda)|^2} \]

where

\((3.80)\) 
\[ \lambda \equiv \frac{\xi \cdot \varrho}{\lambda} \]

and

\((3.81)\) 
\[ \varrho(\lambda) \equiv \int du_2 \delta \left( \lambda - \frac{\xi \cdot \varrho}{\lambda} \right) \varrho(\varrho) \]

It must be noted that equation \((3.79)\) is valid only if the quantity \( \xi(\lambda) \), when considered as a function of a complex variable, has no zeros in the upper half-plane. It will be shown later (Chapter III.8) that this requirement is equivalent
to the condition that the system be stable.

The fact that the distribution functions are real and thus \( J(z, \xi; t) \) is also means that only the imaginary part of \( F(l) \) is required to obtain \( J(z, \xi; t) \big|_{\text{rings}} \) from (3.72). The imaginary part of \( F(l) \) is given by

\[
(3.82) \quad \text{Im} \ F(l) = \frac{\text{Im} f(l)}{|\xi(l)|^2}
\]

Noting that

\[
(3.83) \quad \delta_\omega(x) = \delta(x) - \frac{i}{\hbar} P \frac{\lambda}{x}
\]

and using (3.75), (3.76) and (3.82) in (3.72) we obtain

\[
(3.84) \quad J(z, \xi; t) \big|_{\text{rings}} = \hat{n} \left( \frac{z}{m} \right)^2 \int d\lambda \int d\xi \ \lambda \cdot \bar{\omega} \ \frac{\omega_{\xi}}{|\xi(l)|^2}
\]

\[
\delta(\lambda \cdot \bar{\omega}, \lambda \cdot \bar{Q}_2) \ f_{\xi} (x, \xi; t) \ f_{\xi} (x, \xi_2; t)
\]

with \( \xi(l) \) given by (3.75b). This completes the summation of the rings.

In effect, summing over the rings, which involve simultaneous collisions between arbitrary numbers of particles, has resulted in a collision term involving only two particles which interact through an effective potential whose Fourier transform is \( \sim W_{\lambda}/|\xi(l)| \).
5. The Summation of the Chains

The contribution to the collision term of (2.59), \( J_{\frac{1}{2}}(\mathcal{U}, t) \), from the short range interaction will now be determined. According to (3.51) this is obtained by operating on \( \hat{\rho}_{\mathcal{U}'}(\mathcal{U}'; t) \) with the collision operator, letting \( z \rightarrow +i0 \), integrating over \( s'-1 \) velocities and summing over \( \mathcal{U}'_{\mathcal{U}_s} \). The collision operator to be used consists of a series, the terms of which are represented by the class of diagrams called chains. The first few terms of this series are represented by the diagrams of Fig. 3.5.

![Diagram of chains]

The term in the collision operator represented by the second of these diagrams is given by (3.25b). The contribution to the collision term by this diagram is determined by inserting this expression into (3.51). The result is

\begin{equation*}
\end{equation*}
The corresponding contribution to 

\[ \text{(3.69)} \]

\[ \mathcal{J}(x, z; t) \equiv c \sum_{\alpha} J_{\alpha}(z, \tau) e^{i z \cdot x} \]

is given by 

\[ \text{(3.86)} \]

\[ -8 \pi^2 \int \frac{d\omega}{m^2} \left( \frac{\alpha e^2}{m} \right)^2 \int d\omega' \int d\omega'' \mathcal{U}_x \cdot \mathcal{E} \cdot \mathcal{E}' \cdot \mathcal{E}'' \cdot \mathcal{E}''' \cdot \mathcal{E}'''' \cdot \mathcal{E}''''. \]

Each of the chains represents a contribution to the collision term similar to (3.86). The series made up of these contributions is written 

\[ \text{(3.87)} \]

\[ \mathcal{J}(x, z; t) \bigg|_{\text{chains}} = -8 \pi^2 \int \frac{d\omega}{m^2} \left\{ \left( \frac{\alpha e^2}{m} \right)^2 \int d\omega \mathcal{U}_x \cdot \mathcal{E} \cdot \mathcal{E}' \cdot \mathcal{E}'' \cdot \mathcal{E}''' \cdot \mathcal{E}'''' \cdot \mathcal{E}''''. \right\} \]

\[ + \left( \frac{\alpha^2 e^4}{m^2} \right)^2 \int d\omega' \int d\omega'' \mathcal{U}_x \cdot \mathcal{E} \cdot \mathcal{E}' \cdot \mathcal{E}'' \cdot \mathcal{E}''' \cdot \mathcal{E}'''' \cdot \mathcal{E}''''. \]

The summation of the series of (3.87) is accomplished by comparing it term by term with a series describing the scattering of a
beam of particles from a fixed centre of force.*

The Hamiltonian of a particle moving in a central force field is

\[ H = \frac{1}{2} m v^2 + \lambda V(x) \]  

and the Liouville equation appropriate to this simple system is

\[ \frac{\partial}{\partial t} f(x, y; t) = -\nabla \cdot \mathbf{f} + \frac{\lambda}{m} \frac{\partial V}{\partial x} \cdot \frac{\partial \mathbf{f}}{\partial y} \]

Defining the Fourier coefficients of \( f(x, y; t) \) by

\[ f(x, y; t) = \sum_{k} \rho_k(y; t) e^{i\frac{k}{2}(x-y)\cdot z} \]

and of the potential by

\[ V(x) = \int d^2 x \int d^2 y \rho_0(y; t) e^{i\frac{k}{2}(x-y)\cdot z} \]

we can write the following equation for the time evolution of the Fourier coefficient

\[ \frac{\partial}{\partial t} \rho_k = \frac{\lambda}{m} \int d^2 y e^{-i\frac{k}{2}(y-t)\cdot z} V(y) \frac{\partial}{\partial y} \int d^2 x e^{-i\frac{k}{2}(x-y)\cdot z} \rho_k \]

It is assumed that the system is initially homogeneous:

\[ \rho_0(y; 0) \neq 0 ; \quad \rho_k(y, 0) = 0 , \quad k \neq 0 \]

and we consider only the evolution of \( \rho_0 \). Solving (3.92) by iteration with the boundary condition (3.93) we have

* See Chapter 6 of reference 8.
\( (3.94) \quad \rho_0(\mathbf{x}, t) = \rho_0(\mathbf{x}, 0) - \left\{ \left( \frac{3}{m} \right)^{1/2} \int \frac{d\mathbf{p}}{(2\pi)^3} \int_0^t d\tau \int_0^{\tau_f} d\tau', \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} - i \mathbf{V}_i \cdot \mathbf{E}(t - \tau) \right\} \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} \)

\[ + \left( \frac{3}{m} \right)^{3/2} \int d\mathbf{p}' \int d\mathbf{p} \int_0^t d\tau \int_0^{\tau_f} d\tau' \int_0^{\tau_f} d\tau'' \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} e^{-i\mathbf{V}_i \cdot \mathbf{x}(t - \tau)} V_{\mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{x}} \]

Now if \( t \gg (k, x)^{-1} \)

\( (3.95) \quad \int_0^t d\tau \int_0^{\tau_f} d\tau' e^{-i\mathbf{V}_i \cdot \mathbf{x}(t - \tau)} = t \pi \delta_+(\mathbf{x}, t) \)

and thus for times long in comparison with the collision time \( t_c \sim (k, x)^{-1} \), the series of (3.94) becomes

\( (3.96) \quad \rho_0(t) - \rho_0(0) = -t \left\{ \left( \frac{3}{m} \right)^{1/2} \int \frac{d\mathbf{p}}{(2\pi)^3} \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} \delta_+(\mathbf{x}, t) \right\} \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} \)

\[ + \left( \frac{3}{m} \right)^{3/2} \int d\mathbf{p}' \int d\mathbf{p} \int_0^t d\tau \int_0^{\tau_f} d\tau' \int_0^{\tau_f} d\tau'' \mathbf{V}_i \cdot \frac{\partial}{\partial \mathbf{x}} e^{-i\mathbf{V}_i \cdot \mathbf{x}(t - \tau)} V_{\mathbf{k}} \cdot \frac{\partial}{\partial \mathbf{x}} \]

Defining the free particle propagator in phase space by

\( (3.97a) \quad G(\mathbf{x}, \mathbf{y}) = \frac{1}{\mathbf{m}^2} \int \frac{d\mathbf{p}}{(2\pi)^3} \pi \delta_+(\mathbf{x}, \mathbf{y}) e^{i\mathbf{p} \cdot \mathbf{x}} \)
or

\[(3.97b) \quad G(z, \xi) \equiv \int_0^{\infty} d\tau \delta(z - x \cdot \tau)\]

with inverse

\[(3.98) \quad \pi \delta_\perp(z, \xi) = \int dz \quad G(z, \xi) \quad e^{-i \cdot \xi} \]

and noting that

\[(3.99) \quad i \cdot \nabla \chi = \frac{1}{\gamma n^2} \int dz \quad \frac{\partial V}{\partial z} \quad e^{-i \cdot \xi} \]

we can rewrite (3.96) as

\[(3.100) \quad \rho_0(t) - \rho_0(0) = \frac{t}{\gamma n^2} \left\{ \left( \frac{2}{\hbar} \right)^2 \int dz' \quad \frac{\partial V}{\partial z'} \cdot \frac{\partial V}{\partial z} \quad G(z - z', \xi) \quad \frac{\partial V}{\partial z} \cdot \frac{\partial V}{\partial z'} \right. \]

\[+ \left. \left( \frac{2}{\hbar} \right)^2 \int dz' \quad \frac{\partial V}{\partial z'} \cdot \frac{\partial V}{\partial z} \quad G(z - z', \xi) \quad \frac{\partial V}{\partial z} \cdot \frac{\partial V}{\partial z'} \right) + \cdots \right\} \rho_0(0)\]

This is equivalent to the set of two equations:

\[(3.101) \quad \rho_0(t) - \rho_0(0) = \frac{2}{\hbar} \int dz' \quad G(z - z', \xi) \quad \frac{\partial V}{\partial z'} \cdot \frac{\partial V}{\partial z} \quad \bar{F}(z, \xi)\]

and

\[(3.102) \quad \bar{F}(z, \xi) - \rho_0(0) = \frac{2}{\hbar} \int dz' \quad G(z - z', \xi) \quad \frac{\partial V}{\partial z'} \cdot \frac{\partial V}{\partial z} \quad \bar{F}(z', \xi)\]

This latter equation in effect gives the solution of the time independent Liouville equation and hence \(\bar{F}(z, \xi)\) is conserved along the trajectory of motion. It is thus equal to \(\rho_0(\xi', 0)\) for some \(\xi'\) which can be found by tracing back along the trajectory.
When the expression for the propagator in (3.97b) is inserted into (3.102) there results

\[ T(x, y, z, \tau) - P_0(x, y, 0) = \frac{1}{\sqrt{2\pi}} \int dz' \left( \frac{\partial \mathcal{V}}{\partial z} \right) \cdot \frac{\partial}{\partial y} \mathcal{F}(x, y, z', \tau) \]

where the z-axis coincides with \( z' \). If we let \( z \to \infty \) the z' integration then extends from \(-\infty\) to \( \infty \) and (3.103) becomes

\[ T(x, y, z, \tau) - P_0(x, y, 0) = \frac{1}{\sqrt{2\pi}} \int dz' \left( \frac{\partial \mathcal{V}}{\partial z} \right) \cdot \frac{\partial}{\partial y} \mathcal{F}(x, y, z', \tau) \]

Equation (3.101) can be written

\[ P_0(x, y, z'; \tau) - P_0(x, y, 0) = \frac{\tau}{\eta^2} \frac{1}{\sqrt{2\pi}} \int dx' dy' \int dz' \left( \frac{\partial \mathcal{V}}{\partial z} \right) \cdot \frac{\partial}{\partial y} \mathcal{F}(x, y, z', \tau) \]

which then in conjunction with (3.104) yields

\[ P_0(x, y, z'; \tau) - P_0(x, y, 0) = \frac{\tau}{\eta^2} \int dx' dy' \int dz' \left( \frac{\partial \mathcal{V}}{\partial z} \right) \cdot \frac{\partial}{\partial y} \mathcal{F}(x, y, z', \tau) \]

\[ - \mathcal{F}(x, y, \tau, 0) \]

\[ = \frac{\tau}{\eta^2} \int dx' dy' \int dz' \left[ P_0(x, y', 0) - P_0(x, y, 0) \right] \]

We express the element of area \( dx' dy' \) in cylindrical polar coordinates \((r, \phi, z)\)

\[ dx' dy' = b db d\phi \]

and note that \(^{15}\)

\[ b db d\phi = \sigma(\theta, \phi) \sin \theta d\theta d\phi \]

where \( \sigma(\theta, \phi) \) is the cross section for scattering into the element of solid angle \( \sin \theta d\theta d\phi \) at an angle \( \theta \) to the original direction. Equation (3.107) then becomes
(3.109) \[ \rho(U, t) - \rho(U; 0) = \frac{\zeta}{\tilde{\gamma}^2} \int_0^\eta d\phi \sin \phi \sigma(\theta, \phi) \nu [\rho(U'; 0) - \rho(U; 0)] \]

with \( \theta \) being the angle between \( U \) and \( U' \). The quantity on the right of (3.109) is equivalent to the right hand side of (3.96) and we can write the quantity enclosed in the brackets, \( \{ \} \), as a finite displacement operator acting on the velocity, viz.,

(3.110) \[ C(U) = \frac{-1}{\tilde{\gamma}^2} \int_0^\eta d\phi \sin \phi \sigma(\theta, \phi) \nu \left[ e^{-(U' - U)} \frac{2}{\tilde{\gamma}^2} - 1 \right] \]

A direct comparison of the series enclosed in brackets in (3.96) with that of (3.87) reveals that these are identical if we write

(3.111) \[ U = U_1 - U_2 = \Phi_1, \Phi_2 \]

Therefore we can write for the quantity enclosed in the brackets of (3.87)

(3.112) \[ C(U_1 - U_2) = \frac{-1}{\tilde{\gamma}^2} \int_0^\eta d\phi \sin \phi \sigma(\theta, \phi) \Phi_1, \Phi_2 \left[ e^{-(U_1 - U_2)} \frac{2}{\tilde{\gamma}^2} - 1 \right] \]

and thus

(3.113) \[ \bar{J}(x, y; t) \bigg|_{chains} = \int dU_2 \ C(U_1 - U_2) \ f_1(x, y, t) f_1(x, y; t) \]

or

(3.114) \[ \bar{J}(x, y; t) \bigg|_{chains} = \int dU_2 \int_0^\eta d\phi \sin \phi \sigma(\theta, \phi) \Phi_1, \Phi_2 \left\{ f_1(x, y; t) f_1(x, y; t) - f_1(x, y, t) f_1(x, y, t) \right\} \]
where the angle $\Theta$ is that between $\langle \xi'_1 - \xi'_2 \rangle$ and $\langle \xi_1 - \xi_2 \rangle$. This completes the summation of the chains.

The expression (3.114) for the contribution to the collision term by the short range interaction is just the Boltzmann collision term. This is not surprising as the chains essentially represent all possible two body collisions.
6. **Long-time Equations, H-Theorem**

The results of the preceding sections can now be employed to produce an equation describing the development of the one particle distribution function which is valid for times long compared to the collision time. This equation is obtained by Fourier transforming equation (2.59). According to (3.55) the destruction term can be ignored. Writing \( \mu U(r) - \nu W(r) \) for \( \lambda V(r) \) in the self-consistent field term as given by (2.64) we have

\[
\frac{\partial}{\partial t} f_i(z, \xi; t) + \nu_i \cdot \frac{\partial}{\partial x} f_i(z, \xi; t)
\]

\[
- \frac{\rho}{m} \int dz_x \int dz_y \frac{\partial}{\partial z_x} U(|z_x - z_y|) \cdot \frac{\partial}{\partial \xi}, f_i(z_x, \xi; t) f_i(z_x, \xi; t)
\]

\[
+ \frac{\rho}{m} \int dz_x \int dz_y \frac{\partial}{\partial z_x} W(|z_x - z_y|) \cdot \frac{\partial}{\partial \xi}, f_i(z_x, \xi; t) f_i(z_x, \xi; t)
\]

\[
= \left. J(z, \xi; t) \right|_{\text{chains}} + \left. J(z, \xi; t) \right|_{\text{rings}}
\]

with \( J(x_1, v_1; t) \) \( \text{chains} \equiv J_C \) and \( J(x_1, v_1; t) \) \( \text{rings} \equiv J_R \) being given by (3.114) and (3.84) respectively.

Not all the terms in this equation are significant. The contribution from the self-consistent field term to the evolution of the one particle Fourier coefficient is given by (2.63). Putting in \( \mu U_k - \nu W_k \) for \( \lambda V_k \) and noting that for distributions whose half-widths are of the order of the average velocity.

\[
\frac{3}{\nu} \rho_k(u) \sim \frac{1}{\xi v} \rho_k(u) \sim (m \beta)^{\frac{1}{2}} \rho_k(u)
\]

we have that the order of magnitude of (2.63) is,
where, since this will be compared with terms also involving a factor \( \omega \), the Fourier coefficient has been dropped. According to (3.7) \( \mu \ll \omega \) and the first term of (3.117) is therefore negligible. This means that only the long range interaction contributes to the self-consistent field term and

\[
SCF = \frac{\nu c (m\beta)^{1/2}}{m \alpha^{3/2} L_h}
\]

The collision term arising from the short range interaction, \( J_C \), is given in (3.114). Since the cross section for scattering is of the order of \( \chi^{-2} \) this term is clearly of order

\[
\sim \frac{c}{\chi (m\beta)^{1/2}}
\]

and from the definition of \( t^{(s)}_i \) given in (3.31) we have

\[
J_C \sim \sqrt{t^{(s)}_i}
\]

The collision term arising from the long range interaction is given by (3.84). This was obtained by summing all contributions represented by rings. The order of magnitude of an \( n \)th order ring is

\[
R^{(n)} \sim (\nu \omega c \beta)^{n-1} (\nu \omega) \left( \frac{\beta}{m} \right)^{1/2}
\]

and, provided \( \nu \omega c \beta < 1 \), the series converges rapidly. (It will be seen later that this is equivalent to requiring that the system be stable). We therefore estimate the order of magnitude of the collision term, \( J_R \), to be the same as that of
the contribution represented by the second order ring. That is

\begin{equation}
J_R \sim \frac{\nu^2}{m^2} \cdot \mathcal{U} \cdot \alpha^2 \cdot (m\beta)^{3/2}
\end{equation}

and since \( \mathcal{U} \sim \alpha^3 \) this is equivalent to

\begin{equation}
J_R \sim \frac{\nu^2}{\alpha^2} \left( \frac{\beta}{m} \right)^2 \sim \frac{1}{t_r^{(4)}}.
\end{equation}

with \( t_r^{(4)} \) being defined by (3.32). It is then clear from

(3.120) and (3.121b) that the two collision terms will be about

equally effective if \( t_r^{(3)} \sim t_r^{(4)} \), that is, if

\begin{equation}
\nu \sim \frac{1}{\alpha^2}
\end{equation}

The relative magnitudes of the self-consistent field term

and the collision terms can be estimated from (3.118), (3.119)

and (3.121b). We find that the ratios of \( J_C \) and \( J_R \) to the self-

consistent field term are

\begin{equation}
\frac{J_C}{SCF} \sim \frac{\alpha L_h}{\nu^2} \left( \frac{\alpha}{\nu} \right)^2
\end{equation}

and

\begin{equation}
\frac{J_R}{SCF} \sim \nu \alpha L_h
\end{equation}

respectively.

We can distinguish between several possibilities depending

on the relative magnitudes of the combinations of parameters

\( \nu \), \( \alpha \), and \( (\alpha L_h)^{-1} \). These are displayed in Table I.

In the selection of the ring diagrams it was explicitly

assumed that the condition
TABLE I

Relative order of magnitude of the self-consistent field and collision terms.

<table>
<thead>
<tr>
<th>$\nu / \kappa$ vs $\alpha / \kappa$</th>
<th>$(\kappa / \kappa) &lt;&lt; (\alpha L_h)^{-1}$</th>
<th>$(\kappa / \kappa) \sim (\alpha L_h)^{-1}$</th>
<th>$(\kappa / \kappa) &gt;&gt; (\alpha L_h)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu / \kappa &lt; \alpha / \kappa$</td>
<td>(i) $\alpha L_h / \nu \ll 1$ ; SCF $\gg J_c \gg J_R$</td>
<td>(i) $\nu \ll (\alpha L_h)^{-1}$ ; $J_c \gg SCF \gg J_R$</td>
<td></td>
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<tr>
<td></td>
<td>(ii) $\alpha L_h / \nu \sim 1$ ; SCF $\sim J_c \gg J_R$</td>
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<td></td>
</tr>
<tr>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
(3.8a) \[ L_h \gg \alpha^{-l} \]

was satisfied. When it is, all entries in Table I are possible. Relaxation of this restriction to

(3.8b) \[ L_h \sim \alpha^{-l} \]

automatically excludes the second two columns and all but the five entries marked with arrows of column one in Table I. This follows from (3.4) and (3.5).

It will be seen later in the section that the only dissipative terms of (3.115) are \( J_C \) and \( J_R \). Although these terms may be small they are very important as they drive the system to local equilibrium. In order to obtain an irreversible equation then, it is necessary to retain at least one of these collision terms. That is, even if both \( J_C \) and \( J_R \) are much less than SCF they cannot be neglected if the long-time behaviour of the system is of interest. Therefore, only if \( J_C \gg J_R \), i.e. \( \gamma^2 \ll \frac{\alpha}{\mu} \), can \( J_R \) be neglected in the long-time equations and vice versa. Of course if a short-time reversible equation is of interest the collision terms may be neglected if they are very small in comparison with the other terms.

Relaxing the restriction (3.8a) to (3.8b) means that the wave vectors \( k_j^{-l} \sim L_i^{-l} \) can no longer be neglected in comparison with the wave vector \( L \sim \alpha \) in the terms in the expansion of the collision operator represented by rings (see (3.24a, c, f)). However, these terms will still be of the same order of magnitude and, although they cannot be summed exactly, presumably
yield a result of the same order as $J_R$. Equation (3.115) can then still be considered valid provided $J_R$ is negligible. That is, if $J_R \ll J_C$, we can drop $J_R$ from (3.115) and have an equation valid for long times even though the wavelength of the inhomogeneities is comparable to the range of the long range interaction. If on the contrary $J_R \geq J_C$, i.e. $\nu a \geq \frac{\alpha}{h}$, and $L_h \sim \alpha^{-l}$ we do not have an equation valid for long times.

The flow term, $\nu \cdot \frac{\partial f}{\partial x}$, is of the order of $\langle \nu \rangle L_h^{-1}$

If, as according to (3.6), $\frac{\nu c}{\alpha^2} \sim 1$ we see that the self-consistent field term

$$S CF \sim \frac{\nu c}{\alpha^2} L_h^{-1} (m) \frac{1}{\hbar} \sim L_h^{-1} \langle \nu \rangle$$

and therefore the flow term is of the same order as the self-consistent field term.

We can now write the following sets of equations which are valid for long times. First, if the system is weakly inhomogeneous, $L_h \gg \alpha^{-l}$, we have six distinct equations depending on the relative size of the ratio of the strength of the weak interaction to the average kinetic energy, $\nu^2$; the ratio of the wavelength of the inhomogeneities to the range of the long range interaction, $\alpha L_h$; and the ratio of the range of the short range part to the range of the long range part of the interaction, $\frac{\alpha}{L_h}$. These are:

$$\begin{align*}
\frac{\partial f}{\partial t} + \nu \cdot \frac{\partial f}{\partial x} + SCF &= J_C \\
&\text{valid for } \nu \ll \frac{1}{L_h} ; \quad \frac{\alpha L_h \alpha^2}{\nu} \leq 1 .
\end{align*}$$
(3.125b) \[ \frac{\partial f}{\partial t} = J_c \]
valid for \[ \nu \beta \ll \alpha L_h \text{ ; } \frac{\alpha L_h}{\nu} \ll \frac{\alpha^2}{\nu^2} \gg 1 \]

(3.125c) \[ \frac{\partial f}{\partial t} + \nu \cdot \frac{\partial f}{\partial x} + SCF = J_c + J_R \]
valid for \[ \nu \beta \ll \alpha L_h \ll (\alpha L_h)^{-1} \]

(3.125d) \[ \frac{\partial f}{\partial t} = J_c + J_R \]
valid for \[ \nu \beta \gg (\alpha L_h)^{-1} \]

(3.125e) \[ \frac{\partial f}{\partial t} + \nu \cdot \frac{\partial f}{\partial x} + SCF = J_R \]
valid for \[ \alpha L_h \ll \nu \beta \ll (\alpha L_h)^{-1} \]

(3.125f) \[ \frac{\partial f}{\partial t} = J_R \]
valid for \[ \nu \beta \gg \alpha L_h \text{ ; } \nu \beta \gg (\alpha L_h)^{-1} \]

If the system is strongly inhomogeneous, \( L_h \sim \alpha^{-1} \), then the following two equations apply:

(3.126a) \[ \frac{\partial f}{\partial t} + \nu \cdot \frac{\partial f}{\partial x} + SCF = J_c \]
valid for \[ \nu \beta \ll \alpha L_h \text{ ; } \frac{\alpha L_h}{\nu} \ll \frac{\alpha^2}{\nu^2} \ll 1 \]

(3.126b) \[ \frac{\partial f}{\partial t} = J_c \]
valid for \[ \nu \beta \ll \alpha L_h \text{ ; } \frac{\alpha L_h}{\nu} \ll \frac{\alpha^2}{\nu^2} (\frac{\nu}{\alpha})^2 \gg 1 \]

If \( \nu \beta \gg \frac{\alpha}{\nu} \) we have no equation which is valid for long times when the system is strongly inhomogeneous.

It will now be shown that the equations (3.125) and (3.126)
are irreversible. First it will be demonstrated that a quantity which is interpreted as the entropy is a monotone increasing function of time. The homogeneous equilibrium distribution will then be shown to be a stationary solution of the equations (3.125) and (3.126).

The local entropy density is defined by

$$S(x; t) = - k_B \int d\nu \ f_i(x, \nu; t) \ln[f_i(x, \nu; t)]$$

where $k_B$ is Boltzmann's constant. The time rate of change of $S(x; t)$ is

$$\frac{\partial S}{\partial t} = - k_B \int d\nu \ \frac{\partial f}{\partial t} [1 + \ln f]$$

with $\frac{\partial f}{\partial t}$ being given by whichever of the equations (3.125), (3.126) is valid. For example, if $\mathcal{L} \sim \frac{\partial}{\partial x}$, then $\frac{\partial f}{\partial t}$ is determined by (3.125c). All the other equations are simplifications of (3.125c) and can be obtained by dropping one or more terms from it. The time rate of change of $S$, if (3.125c) is valid, is

$$\frac{\partial S}{\partial t} = k_B \int d\nu \left[ \nu \cdot \frac{\partial f}{\partial x} + SCF - \mathcal{L} - \mathcal{R} \right] [1 + \ln f]$$

The first term in the curly bracket gives

$$k_B \int d\nu \ \nu \cdot \frac{\partial f}{\partial x} [1 + \ln f]$$

$$= k_B \frac{\partial}{\partial x} \int d\nu \ \nu \ f \ln f$$

$$= - \frac{\partial}{\partial x} \frac{\mathcal{L}}{2}$$
This expression, the divergence of a vector function \( \mathbf{Y} \), has no definite sign. It represents a flow of entropy from one region to another.

The self-consistent field term yields

\[
\kappa_0 \int dw \int dz' \int dw' \frac{2}{\mathcal{W}} \frac{\partial}{\partial z'} \mathcal{W}(1z' - z') \cdot \frac{2}{\mathcal{M}} f_i(z, u; t) f_{i'}(z', u'; t) \left[ \ln f(z, u; t) \right]
\]

Since \( f_1(x, y; t) \to 0 \) as \( \nu \to \infty \), the integration over \( \nu \) by Green's theorem, gives zero. Therefore, the self-consistent field term does not affect the change of entropy.

The collision term \( J_C \) is displayed in (3.114). It gives a term

\[
Q_C = -\kappa_0 \int \frac{d\theta}{\Delta} \int d\omega \omega \sigma(\theta, \phi) \int dw_1 dw_2 g_{12} \left[ 1 + \ln f_1(x, y; t) \right]
\]

\[
\left\{ f_{1}(x', u'; t)f_{1'}(x, u, t) - f_{1}(x, u, t)f_{1'}(x', u'; t) \right\}
\]

\[
= -\mathcal{F} \int dw_1 dw_2 g_{12} \left[ 1 + \ln f(1) \right] \left\{ f(1') f(2') - f(1) f(2) \right\}
\]

This can be rewritten as

(3.132)

\[
Q_C = -\frac{\mathcal{F}}{\eta} \int dw_1 dw_2 g_{12} \left[ 1 + \ln f(1) + 1 + \ln f(2) - 1 - \ln f(1') - 1 - \ln f(2') \right]
\]

\[
\left\{ f(1') f(2') - f(1) f(2) \right\}
\]

\[
= -\frac{\mathcal{F}}{\eta} \int dw_1 dw_2 g_{12} \ln \frac{f(1) f(2)}{f(1') f(2')} \left\{ f(1') f(2') - f(1) f(2) \right\}
\]

which, since \( \ln \frac{X'}{X} \) is positive or negative as \( x \) is greater than or less than \( y \), shows that
The collision term $J_R$ of (3.84) produces

\begin{equation}
Q_R = -\hbar \epsilon \frac{8\pi^4}{\beta^2} \int \frac{\partial \mathcal{Q}}{\partial \eta} \int \frac{d\mathcal{E}}{d\mathcal{Q}} \left[ 1 + \frac{1}{\epsilon^2} \right] \int \frac{d\ell}{\beta} \frac{\partial}{\partial \ell} \int \frac{d\eta}{\beta^2} \int \frac{d\eta}{\beta^2} \frac{\partial f(1)}{\partial \eta} \frac{\partial f(2)}{\partial \eta} \left[ 2 + \ln f(1) + \ln f(2) \right]
\end{equation}

A partial integration over velocities gives

\begin{equation}
Q_R = \frac{\hbar}{2} \int \frac{d\mathcal{E}}{d\mathcal{Q}} \int \frac{d\ell}{\beta} \frac{\partial f(1)}{\partial \eta} \frac{\partial f(2)}{\partial \eta} \int \frac{d\eta}{\beta^2} \int \frac{d\eta}{\beta^2} \frac{\partial^2 f(1)}{\partial \eta^2} \frac{\partial^2 f(2)}{\partial \eta^2}
\end{equation}

and since by definition $f(1)$ is positive

\begin{equation}
Q_R \geq 0
\end{equation}

It will now be shown that the local equilibrium distribution

\begin{equation}
f^0(z, u) \equiv \left( \frac{m \beta(z)}{2 \pi} \right)^{\frac{3}{2}} n(z) e^{-\frac{m}{2} \beta(z) [u - \mu(z)]^2}
\end{equation}

is both necessary and sufficient for $Q_C$ and $Q_R$ to be zero. It is clear from (3.132) that the equality of (3.133) can hold if and only if
and as is well known\textsuperscript{22} this condition is met only for the local Maxwellian, (3.137). That (3.137) is a sufficient condition for the equality of (3.136) to hold is established by a straightforward substitution of the local Maxwellian into (3.135).

Since

\begin{equation}
\frac{\partial}{\partial \varepsilon} f(\varepsilon, \varepsilon) = -m \beta(\varepsilon) \left[ \varepsilon - u(\varepsilon) \right] f^{0}(\varepsilon, \varepsilon)
\end{equation}

the combination \( \delta(\varepsilon, \varepsilon) e^{2(0 \varepsilon \varepsilon)} \) makes the right hand side of (3.135) identically zero. It is also clear that in order for the right hand side of (3.135) to be identically zero we must have

\begin{equation}
\frac{\partial}{\partial \varepsilon} f(\varepsilon, \varepsilon) = -D(\varepsilon) \left[ \varepsilon + u(\varepsilon) \right] f(\varepsilon, \varepsilon)
\end{equation}

where \( D(\varepsilon) \) is a scalar independent of \( \varepsilon \) and \( u(x) \) is a vector. The solution of this differential equation is

\begin{equation}
f(\varepsilon, \varepsilon) = C(\varepsilon) e^{-\frac{D(\varepsilon)}{2} \left[ \varepsilon + u(\varepsilon) \right]^{2}}
\end{equation}

and since

\( m(\varepsilon) \equiv \int d\nu f(\varepsilon, \nu) \)

\( u(\varepsilon) \equiv \frac{\int d\nu \varepsilon f(\varepsilon, \nu)}{\int d\nu f(\varepsilon, \nu)} \)

and

\( \beta(\varepsilon) \equiv \frac{1}{2} m \frac{\int d\nu \nu^{2} f(\varepsilon, \nu)}{\int d\nu f(\varepsilon, \nu)} \)
D(x) can be identified with \( \varphi(x) \); \( U(x) \) with \(-q(x)\); and \( C(x) \) with \( \left( \frac{m}{2n} \right)^{\frac{3}{2}} n(x) \). This proves that (3.137) is necessary for \( Q_R \) to be zero.

Collecting the results of (3.130), (3.133) and (3.136) we have for the case when (3.125c) describes the evolution of the system that

\[
\frac{\partial}{\partial t} S(x; t) + \frac{\partial}{\partial x} \cdot \mathbf{r} = Q_c + Q_R \geq 0
\]

This shows that the local entropy density may increase or decrease depending on the flow into or out of the region. At the same time the collision terms \( J_C \) and \( J_R \) cause the local entropy density to increase until such time as local equilibrium is reached. This is not a stationary state of the system as the flow term is not necessarily zero. Since the system is isolated there can be no flow across the boundaries and hence the volume integral of (3.142) is

\[
\frac{\partial}{\partial t} \int S \, dx = \int Q_c + \int Q_R \geq 0
\]

where \( \int S \) and \( \int Q \) are the volume integrals of \( S \) and \( Q \). This means that the total entropy of the system is monotone increasing, that is, the system is irreversible.

The flow term of (3.142) is zero for the homogeneous equilibrium distribution

\[
f^0(z, \mathbf{y}) = c \varphi^0(\mathbf{y}) = c \left( \frac{m}{2n \pi^2} \right)^{\frac{3}{2}} \left( \frac{m \nu^2}{2 \pi^2} \right).
\]

and this is therefore a stationary solution of (3.125c) The proof that the system approaches local equilibrium does not
entail an approach to this absolute equilibrium as nothing has been said about the transition from the local to absolute Maxwellian distributions. Grad\textsuperscript{23} has shown that systems described by a linear Boltzmann equation do indeed approach absolute equilibrium. It is therefore taken as plausible that the system described by (3.125c) does evolve until the distribution (3.144) is reached.

This discussion has been concerned with systems whose evolution is controlled by (3.125c). However, since each of the other equations of (3.125) and (3.126) involve one or both of $J_\mathcal{C}$ and $J_\mathcal{R}$, systems controlled by them will behave in the same general manner. That is such systems will evolve in such a way that the entropy is monotone increasing. The local production of entropy will be positive until local equilibrium is reached. The rate at which this state is approached should be proportional to the magnitude of $J_\mathcal{C}$ and/or $J_\mathcal{R}$. According to (3.120) and (3.121b) these are $\sim 1/t_\mathcal{C}^{(s)}$ and $\sim 1/t_\mathcal{R}^{(l)}$, respectively. Thus the system approaches local equilibrium in times of the order of the shorter of $t_\mathcal{C}^{(s)}$ or $t_\mathcal{R}^{(l)}$. 
7. The Short-time Equations. Instability

It will now be shown that the location of the zeros of the quantity $\xi^*(l)$ defined in equation (3.75b) is related to the initial stability of the system. To do this we will require equations describing the short-time behaviour of the system. That is, we consider the development of the system over times short compared to the relaxation time but long compared to the time a particle of average speed takes to cross the range of the short range interaction,

$$\chi^{-1}(m\beta)^{1/2} \sim \tau^{(5)}_c << t << \tau_r$$

This still leaves two possibilities (i) $t \gg \tau^{(5)}_c \sim \chi^{-1}(m\beta)^{1/2}$ and (ii) $t \sim \tau^{(5)}_c$.

The first of these presents no new difficulties in deriving the equations of evolution as the upper limit of integration in (3.18) can still be extended to infinity and the destruction term ignored. This means that the equations (3.125) and (3.126) still describe the development of the system for short times except that it is no longer necessary to insist on irreversibility. Referring back to Table I, we see that in addition to the equations of (3.125) and (3.126) we can distinguish another equation

$$\chi^*(m\beta)^{1/2} = 0$$

which is valid for short times if (a) $\alpha >> \chi$; (b) $\chi >> \alpha L_\perp$; (c) $\alpha L_\perp$ $\chi$ $\perp$. This means also that (3.125a) and (3.126a) are valid for short times only if
\( \frac{\alpha_{L_h}}{\mathcal{M}} \left( \frac{x}{\mathcal{L}} \right)^2 \); (3.125c) is now valid only if \( \frac{x}{\mathcal{L}} \sim (\alpha_{L_h})^{-1} \); and (3.125e) is now valid only if \( \sqrt{\beta} \sim (L_h \omega)^{-1} \). With these additional restrictions, all terms of any particular one of the equations of (3.125) or (3.126) are of the same order of magnitude. That is, each of the terms in any of these equations is of the order of the inverse relaxation time and, since we are interested in much shorter times, the short-time behaviour predicted by the equations (3.125) and (3.126) is the trivial one

\[(3.147) \quad \frac{\partial f}{\partial t} = 0 \]

This together with (3.146) gives the short-time behaviour of the system for all possible values of the parameters \( \sqrt{\beta}, \sqrt{\omega} \) and \( (\alpha_{L_h})^{-1} \) as long as times greater than \( \tau_{\mathcal{L}}(t) \) are of interest.

The second possibility, \( \tau_{\mathcal{L}}(t) \sim t < \tau_r \), makes the extension of the upper limit of integration in (3.18) invalid for the long range interaction and also the destruction term does not decay rapidly enough to neglect it. This latter difficulty is surmounted by invoking (3.17) to argue that the destruction term is much less than the self-consistent field term and is therefore negligible for short times. We can estimate the order of magnitude of the long range collision term for short times by considering the contribution to this term represented by the second order ring. This contribution is given by substituting the expression for the second order term in the collision operator, which is given in equation (B.2) of Appendix B, into (3.18). Writing for the long range potential function
(3.148) \[ W(r) = \frac{e^{-\alpha r}}{\alpha r} \; ; \; r > \kappa^{-1} \]
\[ = 0 \; ; \; r < \kappa^{-1} \]

we have

(3.149) \[ W_l = \frac{1}{2n^2 \alpha l} \; e^{-\frac{\alpha}{l^2} \alpha \sin \frac{\beta h}{l} + \frac{l \cos \frac{\beta h}{l}}{l^2 + \alpha} } \]

For \( l \leq \kappa \)

(3.150) \[ W_l \approx \frac{1}{2n^2 \alpha l} \; \frac{1}{l^2 + \alpha^2} \]

and for \( l > \kappa \) it oscillates rapidly. This means that the integrations, with \( W_l \) written for \( \forall l \), in Appendix B effectively extend over a region \( l \leq \kappa \). We therefore take

(3.151) \[ W_l = \frac{1}{2n^2 \alpha} \; \frac{1}{l^2 + \alpha^2} \; , \; l \leq \kappa \]
\[ = 0 \; ; \; l > \kappa \]

When this is substituted into (B.14) and (B.15) we obtain

(3.152) \[ \chi_1 \left( \frac{\beta}{\kappa}; t \right) = \pi c \left( \frac{\kappa}{m \alpha} \right)^2 \left\{ -\kappa e^{-\kappa \beta t} + \frac{2}{\beta} e^{-\kappa g t} - \frac{2}{\beta} e^{-\kappa g t} \right\} \]

and

(3.153) \[ \chi_2 \left( \frac{\beta}{\kappa}; t \right) = 2 \pi c \left( \frac{\kappa}{m \alpha} \right)^2 \kappa e^{-\kappa \beta t} \]

where, since \( \kappa \gg \alpha \), we have written \( \frac{\beta}{\kappa} = \chi \). The contribution to the collision term from this second order term is
The $\mathcal{P}(\mathcal{U}; t-\tau)$ can be expanded in a Taylor series about $t$ as was done in (3.43) and again only the zero order term in the expansion need be considered. We must then consider the integral over $t$ of $\chi_1$ and $\chi_2$. The first term of $\chi_1$ and $\chi_2$ give

\begin{equation}
\sim c \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \int_0^t d\tau \chi e^{-\alpha \tau} \sim c \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \frac{1}{\alpha}
\end{equation}

(3.155) 

\begin{equation}
\sim c \left( \frac{\mathcal{U}}{m\alpha} \right)^2 (m\beta)^{1/2}
\end{equation}

The second two terms of $\chi_1$ give

\begin{align*}
&\sim \frac{c}{3} \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \int_0^t d\tau \left\{ \frac{e^{-\alpha \tau}}{\tau} - \frac{e^{-\alpha \tau}}{\tau} \right\} \\
&= \frac{c}{3} \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \left\{ \int_0^{\alpha \tau} dx \frac{e^{-x}}{x} - \int_0^{\alpha \tau} dx \frac{e^{-x}}{x} \right\} \\
&= \frac{c}{3} \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \left\{ \int_0^\infty dx \frac{e^{-x}}{x} - \int_0^\infty dx \frac{e^{-x}}{x} \right\} \\
&= \frac{c}{3} \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \left\{ E_1(-\alpha \tau) - E_1(-\alpha \tau) \right\}
\end{align*}

where $E_1(x)$ is the exponential integral. Now $\alpha \tau \sim \alpha (m\beta)^{1/2} \sim t / t_{\xi}$ and $\alpha \tau \gg 1$. Therefore, since $^{24}$ $|E_1(x)| \lesssim 1$ for $x \gg 1$, we have that this term is

\begin{equation}
\lesssim \frac{c}{3} \left( \frac{\mathcal{U}}{m\alpha} \right)^2 \sim \left( \frac{\mathcal{U}}{m\alpha} \right)^2 (m\beta)^{1/4}
\end{equation}

(3.156) 

and

\begin{equation}
\mathcal{J}_{\mathcal{U}}(\mathcal{U}; t)^{(0)} \sim c \left( \frac{\mathcal{U}}{m\alpha} \right)^2 (m\beta)^{1/2} m\beta
\end{equation}

(3.157)
This is precisely the same result as was obtained earlier for the order of magnitude of $J_R$ (see (3.121b)), that is, \( \sim \sqrt{\gamma t} \). This means that, for times of the order of \( t_c \), the collision term due to the long range interaction will be negligible and the behaviour of the system is described by either (3.146) or (3.147). The former being valid if

(a) $\nu \ll \frac{\alpha}{\beta}$, $\frac{\nu L_n}{\nu t_c} \ll 1$

(b) $\nu \sim \frac{\alpha}{\beta} \ll (\alpha L_n)^{-1}$

or (c) $(\alpha L_n)^{-1} \gg \nu \gg \frac{\alpha}{\beta}$ and the latter being applicable otherwise.

Equation (3.147) yields nothing of interest and we consider only (3.146) which when the self-consistent field term is written in its explicit form becomes

\[
\frac{\partial}{\partial t} f_1(x, u; t) + u \cdot \frac{\partial}{\partial x} f_1(x, u; t)
\]

\[
+ \frac{\nu}{m} \int d\tilde{x} \int d\tilde{u} \left( \frac{\partial}{\partial x} W(|\tilde{x} - x|) \cdot \frac{\partial}{\partial \tilde{x}} f_1(\tilde{x}, \tilde{u}; t) f_1(\tilde{x}, \tilde{u}; t) \right) = 0
\]

This is the familiar Vlassov equation. In the form (3.158) it is intractable and therefore we shall consider the linearized form of this equation.

\[
\frac{\partial}{\partial t} f_1(x, u; t) + u \cdot \frac{\partial}{\partial x} f_1(x, u; t)
\]

\[
+ \frac{\nu c}{m} \int d\tilde{x} \int d\tilde{u} \left( \frac{\partial}{\partial x} W(|\tilde{x} - x|) \cdot \frac{\partial}{\partial \tilde{x}} \phi(\tilde{u}; t) f_1(\tilde{x}, \tilde{u}; t) \right) = 0
\]

For times much less than the relaxation time the velocity distribution is essentially constant in time, $\phi(u; t) \equiv \phi(u)$. Using this, and Fourier and Laplace transforming equation (3.159) results in
The Fourier-Laplace transform of the number density \( \eta_k(z) \) is obtained by integrating \( \rho_k(u; z) \) over the velocity

\[
(3.161) \quad \eta_k(z) = \int du \rho_k(u; z) \]

Integrating (3.160) over the velocity, \( u \), iterating the resulting equation and summing the series obtained one finds* that

\[
(3.162) \quad \eta_k(z) = \frac{1}{\mathcal{E}_+(k; z)} \int du \frac{1}{i(\nu \cdot z - z)} \rho_k(u; t=0) \]

where

\[
(3.163) \quad \mathcal{E}_+(k; z) = 1 + \frac{8\pi^2 \nu_C}{m} \mathcal{W}_k \int du \frac{k \cdot \partial \phi}{\nu \cdot z - z} \phi(u) ; \quad \text{Im} \ z > 0
\]

When (3.163) is compared with (3.75b) we see that, if for \( f_1(x_1, x_2; t) \) we write \( \phi(x_2) \) then the quantity there defined is just

\[
\mathcal{E}(t) = \mathcal{E}_+^*(k; z, \nu_2)
\]

Laplace transforming (3.162) yields

\[
(3.164) \quad \eta_k(t) = \frac{1}{2\pi} \int \frac{dz e^{-izt}}{\mathcal{E}_+(k; z)} \int du \frac{1}{i(\nu \cdot z - z)} \rho_k(u; t=0)
\]

* See Chapter 3 of reference 9. Note that, because the interaction here considered is attractive while Balescu is concerned with a repulsive interaction, a trivial change of sign is required.
with it being understood that the analytic continuation of the integrand into the lower half-plane must be used in evaluating the integral.

The behaviour of \( \eta_L(t) \) is determined by the location of the poles of the integrand of (3.164) enclosed within \( \Gamma' \). Since the part of the contour antiparallel to the real axis lies above all singularities of the integrand and the contour is closed at infinity in the lower half-plane it encloses all the singularities of the integrand. We have then

\[
(3.165) \quad \eta_L(t) = -i \sum_j e^{-i \omega_j t} \left\{ \text{Residue } \eta_L(z) \right\}_{z=z_j}
\]

where \( z_j \) is a pole of \( \eta_L(z) \). This means that \( \eta_L(t) \) oscillates with frequencies \( \omega_j = \text{Re } z_j \). The amplitude of these modes is given by the residue of \( \eta_L(z) \) at \( z_j \) and they are either damped, steady or exponentially growing according as \( \text{Im } z_j < 0 \) or \( > 0 \).

The quantity

\[
(3.166) \quad \int_{i(\pi/2, \pi/2 - z)} \rho_L(\varphi; t=0)
\]

is a Cauchy integral. It is regular for \( \text{Im } z > 0 \) but has singularities located in the lower half-plane. The precise location of these singularities depends on \( \rho_L(\varphi; t=0) \) but they always result in damped oscillations. The net effect of these modes is to dissipate an initial disturbance and make the system homogeneous.

The interesting behaviour arises from the singularities of \( \eta_L(z) \) located at the zeros of \( \xi_+(4i z) \). If this function has a zero in the upper half-plane, an exponentially growing mode
results and the system is said to be unstable. It can be shown* that this function has a zero in the upper half-plane and the system is unstable if and only if

\[(3.167) \quad gn^2 \nu c \beta W_k > 1\]

Since \(W_k\) is a sharply peaked function of \(k\) only small values of \(k\) will be important. In particular the value \(k=0\) is of interest as \((3.167)\) then apparently predicts a critical concentration above which a homogeneous system becomes unstable.

This treatment of the short time behaviour of the system predicts that for some situations the number density can oscillate with exponentially growing amplitude. It must be emphasized that this treatment is valid only for short times and that although the system may be initially unstable it will not remain so as eventually the dissipative effects of the collisions will become important.

The Fourier transform of the interaction \(W_k \sim \alpha^2\) and thus the system should be initially stable if

\[(3.168) \quad \nu c \beta \alpha^3 < 1\]

This states that the average interaction energy per particle due to the long range interaction should be less than the average kinetic energy (c.f. \((3.6)\)) for the system to be initially stable.

The inequality of \((3.167)\) is of importance in the summation

* See Section 19, reference 9 and the references cited there.
of the rings discussed in Chapter III.4. It was pointed out there that the solution given for the integral equation obtained by summing the rings is valid only if the zeros $\xi^*(l)$, defined by (3.75b), lie in the lower half-plane. This means that the collision term $\int_R$ is valid only if the inequality of (3.167) is not satisfied or equivalently if the inequality of (3.168) is satisfied.
8. **Equilibrium Two Particle Correlations**

The general equations describing the evolution of the Fourier coefficients of the s-particle correlation function were given in equation (2.68). It was concluded in Chapter III.3 that the destruction term $\mathcal{D}^{(s)}(\xi_d; t)$ defined in (2.67) could be ignored for times long compared with the collision time. The only significant contributions then arise only from the creation term defined in (3.58) if $t >> t_c$. The discussion of Chapter III.2 has provided us with the means of selecting the significant terms in the expansion of the creation operator. In particular Fig. 3.3a and Fig. 3.3b are typical of the two classes of diagrams which represent the significant contributions to the development of the two particle reduced Fourier coefficient. However, even this simplified series cannot in general be summed and as it was shown in section 6 of this chapter that the one particle distribution function approaches the equilibrium distribution for times of the order of the relaxation time we shall consider only two particle correlations at equilibrium.

The two classes of contributions to $\mathcal{C}(\zeta, \zeta'; \xi_d; \xi_d'; z = \pm \alpha)$ represented by the modified rings (see Fig. 3.3a) and the modified chains (see Fig. 3.3b) are summed separately. First the modified rings. These diagrams are just the ordinary rings with the left most vertex split off. Hence the contribution to the creation term from the modified rings is very similar to the collision term $\mathcal{J}_{\xi_d, \xi_d'}(\zeta, \zeta'; t)|_{\xi_d, \xi_d'}$ given in (3.68). In fact, dropping the $\zeta$ and $\xi_d$ integrations and the operator $\mathcal{C}d_t$ from the beginning of this expression and changing the Kronecker delta to $\delta_{\xi_d, \xi_d'} - \Sigma(\xi_d')$ gives the series for $\gamma_{\zeta, \zeta'}(\zeta, \zeta'; t)|_{\zeta, \zeta'}$. Because the system is
assumed to be at equilibrium the \( k' \) wave vectors are all zero and the first few terms of the series are:

\[
\left. \frac{\gamma^{\nu}_{\nu, k_1} (\nu_1, \nu_2) \right|_K = \frac{8 \eta^3}{\kappa c} \left\{ \delta_{+1}^{12} \phi_1 (\nu_1) \phi_1 (\nu_2) \right.

+ \delta_{+2}^{12} \c_i \phi_2 (\nu_1) \phi_2 (\nu_2)

+ \delta_{+3}^{12} c \phi_3 (\nu_1) \phi_3 (\nu_2)

+ \cdots \right\}
\]

where the effect of the Kronecker delta has been taken into account by writing \( \delta_{\nu_3, \nu_4} \) as \( \gamma_{\nu_3, \nu_4} \). The series (3.169) can be rewritten in terms of the quantity \( F(j) \) defined by (3.73) and passing to the thermodynamic limit (2.2) we have

\[
\left. \frac{\gamma^{\nu}_{\nu, k_1} (\nu_1, \nu_2) \right|_K = \delta_{+1}^{12} \left\{ d_1 \phi_1 (\nu_1) \phi_1 (\nu_2) \right.

+ c d_2 \phi_2 (\nu_1) \left[ F^0 (1) + c d_3 \phi_3 (\nu_1) \right] \right\}
\]

with \( F^0 (1) \) being the expression (3.73) when \( C (f_1) \) is written for \( f(j) \). It satisfies an equation obtained by substituting the equilibrium distribution for the one particle distribution function in (3.79). The result is

\[
\left[ 1 + i \frac{8 \eta^3}{\kappa c} \frac{V_c}{\hbar_0 T} \right] \left[ d_1 \phi_1 (\nu_1) \phi_1 (\nu_2) \right] \right\}

= \frac{\nu}{\hbar_0 T} \left[ \phi_1 (\nu_1) \phi_1 (\nu_2) \right] \left[ \delta_{\nu_3, \nu_4} (\nu_3 - \nu_4) \right] \right\}
\]
This integral equation has the solution

\[(3.172) \quad F^*(\nu_j) = \frac{\nu}{\kappa_0} \mathcal{W}_k \frac{1}{1 - 8n^3c \frac{\nu}{\kappa_0} \mathcal{W}_k} \phi^\prime(u_1)\]

Putting (3.172) into (3.170) and using (3.62) and (3.63) yields

\[(3.173) \quad \tilde{\chi}_{k,-k}^0(\xi, \xi_1) \big|_R = \pi \delta_{r,1} [\xi - \xi_1] \frac{1}{\xi_1} \phi^\prime(u_1) \phi^\prime(u_1) \frac{\nu}{\kappa_0} \mathcal{W}_k \frac{1}{1 - 8n^3c \frac{\nu}{\kappa_0} \mathcal{W}_k}\]

Since the two particle correlation function rather than the Fourier transform is of interest the inverse Fourier transform of (3.173) must be taken and we can use the fact that

\[(3.174) \quad \int_{\infty}^{\phi^0} d\zeta \times n_i \delta_-(\zeta) \equiv 1\]

to write

\[(3.175) \quad \tilde{\chi}_{k,-k}^0(\xi, \xi_1) \big|_R = \frac{\nu}{\kappa_0} \mathcal{W}_k \left[1 - 8n^3c \frac{\nu}{\kappa_0} \mathcal{W}_k\right]^{-1} \phi^\prime(u_1) \phi^\prime(u_1)\]

In this calculation we restrict ourselves to the particular form of the potential

\[(3.176) \quad \mathcal{W}(r) = \begin{cases} \frac{e^{-\alpha \kappa r}}{\alpha \kappa} &; \quad r > \kappa^{-1} \\ 0 &; \quad r < \kappa^{-1} \end{cases}\]

in which case

\[\mathcal{W}_k = \frac{1}{\kappa_0^3} \int d\zeta e^{-i k \cdot \zeta} \mathcal{W}(\zeta)\]

* See Section 51, Reference 9
(3.177) \[ \frac{1}{2n^2 \pi^2} e^{-\frac{\hbar}{\alpha \sin \frac{\hbar}{\alpha}} + \frac{\hbar \cos \frac{\hbar}{\alpha}}{\alpha^2}} \]

It can be argued that correlations between particles separated by less than the range of the short range interaction are immaterial and since this corresponds to values of $\hbar \gtrsim$ we are permitted to write for the Fourier transform of the potential

(3.178) \[ \mathcal{W}_k = \frac{1}{2n^2 \pi^2} \frac{1}{\hbar^2 + \alpha^2} \]

When this is substituted into (3.175) there results

(3.179) \[ \tilde{\gamma}^{(0)}_{k} (u_1, u_2) \bigg|_R = \frac{\nu}{2n^2 \pi \hbar \alpha^2} \left[ \hbar^2 + \alpha^2 - \frac{\hbar \nu \alpha}{\alpha \hbar \alpha} \right]^{-1} \tilde{\Phi}^{(0)}(u_1) \tilde{\Phi}^{(0)}(u_2) \]

The two particle correlation function due to the long range interaction is given by

(3.180) \[ \tilde{\gamma}^{(0)}(z_1, z_2; u_1, u_2) \bigg|_R = c^2 \int d\hbar \bar{e}^{i \hbar \cdot (z_1 - z_2)} \tilde{\gamma}^{(0)}_{k} (u_1, u_2) \bigg|_R \]

or writing

(3.181) \[ \bar{z} = z_1 - z_2 \]

(3.182) \[ \tilde{\gamma}^{(0)}(r; u_1, u_2) \bigg|_R = c^2 \int d\hbar \bar{e}^{i \hbar \cdot z} \tilde{\gamma}^{(0)}_{k} (u_1, u_2) \bigg|_R \]

The correlation functions must be everywhere finite. This means that the value $r = 0$ must be excluded in using (3.182). Actually, the passage from (3.177) to (3.178), entails the exclusion of the region $r < \kappa^{-1}$ and we therefore write
where the Heaviside function

\begin{equation}
\mathcal{H}(x) = \begin{cases} 1 & ; \ x > 0 \\ 0 & ; \ x < 0 \end{cases}
\end{equation}

The contribution to the creation term at equilibrium from the modified chains can be determined in the same way as the contribution to the collision term by the chains. The result is

\begin{equation}
\gamma_{k-i}^c(u_i, u_{i'}) \bigg|_c = \left\{ \pi i \delta_{\cdot 12} \frac{\eta^2}{\rho} \frac{m}{\nu} U_{k-i} \phi \phi \right\}_2
\end{equation}

On passing to the thermodynamic limit (2.2) and applying the inverse Fourier transform we obtain
This expression simplifies to

\[(3.187) \quad \varrho_2^0(r, u, u') = c^2 \left\{ - \frac{\mu}{\hbar \omega T} U(r) + \frac{1}{2!} \left[ \frac{\mu}{\hbar \omega T} U(r) \right]^2 \right\} \]

\[\quad - \frac{i}{3!} \left[ \frac{\mu}{\hbar \omega T} U(r) \right]^3 + \cdots \left\{ \phi^0(u) \phi^{*\prime}(u') \right\} \]

Combining this with (3.183) we have the following expression for the equilibrium two particle correlation:

\[(3.188) \quad \varrho_2^0(r; u, u') = c^2 \left\{ \phi^0(u) \phi^{*\prime}(u') \right\} \left\{ e^{-\frac{\mu}{\hbar \omega T} U(r)} - 1 \right\} \]

When the expression for $W_k$ given in (3.178) is substituted into the stability criterion (3.169) it is seen that the system is stable if
(3.189) \[ \frac{4\pi V C}{\hbar_0 T \alpha^2} < 1 \]

It is clear, from examination of the last term in (3.188), that if the parameters of (3.188) are varied so that the system approaches instability, then the range of the correlations becomes infinite. Provided the inequality of (3.189) is satisfied, the range of the correlations will be finite and of the order of $\alpha^{-1}$. In that case we can write

(3.190) \[ g_2^0(r; \xi, \eta, \zeta) = c^2 \phi(y_1) \phi(y_2) \left\{ e^{-\frac{\alpha}{\hbar_0 T} U(r)} - 1 \right\} + \frac{V}{\hbar_0 T} \eta(r-\kappa') \frac{e^{-\alpha r}}{\alpha r} \]

For $r < \kappa'$

(3.191) \[ g_2^0(r; \xi, \eta, \zeta) = -c^2 \phi(y_1) \phi(y_2) \]

and for $r > \kappa'$

(3.192) \[ g_2^0(r; \xi, \eta, \zeta) = \frac{V}{\hbar_0 T} \frac{e^{-\alpha r}}{\alpha r} c^2 \phi'(y_1) \phi'(y_2) \]

These follow from the fact that

(3.193) \[ e^{-\frac{\alpha}{\hbar_0 T} U(r)} \approx 1 \quad ; \quad r > \kappa' \]

\[ \approx 0 \quad ; \quad r < \kappa' \]

The two statements, (3.191) and (3.192), are precisely the same as those given in (3.14) and (3.15) for $g_2^0$ calculated by retaining only the first order term in the cluster expansion.
It should be noted that even if the system approaches instability and the range of the correlations becomes infinite, the order of magnitude of the correlations due to the long range interaction is still of order $\nu_{fr} << |\beta|$. In section 7 of this chapter the effect of the correlations for short times was neglected on the basis that they were of the same order as the correlations at equilibrium. If this is so, it is clear that the correlations are of order $\nu |\beta| << |\beta|$ and can be neglected.

It is important to note that this calculation of the equilibrium correlations is good only if the system is stable. If it is unstable then $\tilde{c}_+(k;z)$ has zeros in the upper half-plane. The solution given in (3.172) for the integral equation (3.171) is then no longer valid.
9. The Equation of State

In this section we shall determine the equation of state of a system whose interactions are given by the following forms for the two parts of the potential:

\[ u(r) = \begin{cases} 1 & ; \ r < \kappa^{-1} \\ 0 & ; \ r > \kappa^{-1} \end{cases} \]

and

\[ \mathcal{W}(r) = \begin{cases} 0 & ; \ r < \kappa^{-1} \\ \frac{\Theta^{-\alpha r}}{\alpha r} & ; \ r > \kappa^{-1} \end{cases} \]

The equilibrium two particle correlation function for this form of interaction is given by (3.188). Using this and the definition (2.41) of the correlation functions we have the following expression for the two-body distribution function at equilibrium.

\[ f^2_z(z',z',\varphi',\varphi; \varphi,\varphi') \equiv c^2 \mathcal{N}_1 (r-\kappa^{-1}) \mathcal{N}_2 (r' \kappa^{-1}) \mathcal{N}(\varphi,\varphi') \mathcal{N}(\varphi',\varphi') \]

\[ \left\{ 1 + \frac{v}{\kappa \delta} \frac{\Theta^{-\alpha r}}{\alpha r} \right\} \]

An expression for the pressure tensor is given in equation (2.32) and since the hydrostatic pressure is just \(1/3 \text{ Tr}_p\) we have

\[ p(z,t) = \frac{1}{2} \int dz',d\varphi', \delta(z'-z) \left( m^2 f_z(z',\varphi') \right) \left( m^2 f_z(z',\varphi') \right) \]

\[ -\frac{1}{2} \int dz',d\varphi',d\varphi,d\varphi' \delta(z'-z) \lambda \frac{\partial \mathcal{V}(z',\varphi)}{\partial z} \left( z',\varphi,\varphi',\varphi' \right) f_z(z',\varphi',\varphi',\varphi'; t) \]
At equilibrium and writing \( r \) for \( x_1 - x_2 \) we have

\[
P_o = \frac{1}{2} m c \int d\nu v^2 \Phi(d\nu)
\]

\[
- \frac{4\pi}{3} \int_0^\infty dr r^2 \frac{\partial V}{\partial r} \int d\nu_1 d\nu_2 \int (x_1, x_2; \nu_1, \nu_2)
\]

With the use of (3.196) and noting that

\[
\frac{\partial \psi(r)}{\partial r} = - \delta(r - \hat{x}')
\]

and

\[
\frac{\partial W(r)}{\partial r} = - \frac{e^{-\alpha r}}{r} - \frac{e^{-\alpha r}}{\alpha r^2}
\]

this becomes

\[
P_o = c \pi \theta^T - \frac{4\pi c^2}{3} \int_0^\infty dr r^3 \left\{ - \mu \delta(r - \hat{x}') + \nu \left( \frac{e^{-\alpha r}}{r} + \frac{e^{-\alpha r}}{\alpha r^2} \right) \right\}
\]

\[
\int (r - \hat{x}') \left\{ 1 + \frac{\nu}{\theta^T} \frac{e^{-\alpha r}}{\alpha r} \right\}
\]

Defining

\[
\Delta^2 \equiv 1 - \frac{4\pi c \nu \theta}{\alpha^3 \pi \theta^T} \sim 1
\]

and employing the fact that \( \alpha \ll \lambda \) the integrations in (3.199) give

\[
P_o = c \pi \theta^T \left\{ 1 + \frac{\pi}{3} \frac{\mu c}{\lambda^2 \theta^T} + \frac{\pi}{3} \frac{\mu \nu c}{\lambda^3 \theta^T} \frac{\lambda}{\alpha}
\]

\[
- 2\pi \frac{\nu c}{\alpha^3 \theta^T} + \frac{2}{3} \pi \frac{\nu c}{\alpha^3 (\theta^T)^2} \left( \frac{\Delta}{(1 + \Delta)^2} \right)
\]
We know from (3.5), (3.6) and (3.7) that

\[ \nu \beta \ll 1 \]

and

\[ \mu c \beta U = \frac{\pi}{3} \frac{\mu c}{\kappa^3} \ll \nu c \beta \varpi = 4n \frac{\nu c}{\alpha^3} \ll 1 \]

Here, \( \beta = \frac{1}{\kappa_0 T} \), and it is immediately obvious that the second and fifth terms of (3.200) are negligible. Therefore

\[ (3.201) \quad \rho_0 = c \kappa_0 T \left\{ 1 + \frac{\pi}{3} \frac{\mu c}{\alpha^3 (\kappa_0 T)^2} - 2\pi \frac{\nu c}{\alpha^3 \kappa_0 T} \right\} \]

Whether or not the second term of this equation is significant depends on the parameters involved. If \( \nu \alpha \ll c \kappa \) it is negligible. If \( \nu \alpha \gg c \kappa \) then it can play an important role provided

\[ \left( \frac{\mu c}{\kappa^3} \right) \left( \nu \beta \varpi \right) \ll 1 \]

The equation of state, (3.201) is of course only valid for those values of the concentration and temperature which make the system stable. This is because the two particle correlation function is good only for stable systems. The concentration must also be much less than \( \chi^2 \) or the selection of the chain diagrams as representing the dominant contributions from the short range part of the interaction is invalidated.
A classical gas whose particles interact through a weak long range attraction and a strong short range repulsion has been studied. It has been determined that, provided the range of the short range interaction, \( \lambda^{-1} \), is much less than the average interparticle distance, i.e. \( \lambda^3 \gg \zeta \), and the range of the long range interaction, \( \alpha^{-1} \), is much greater than the average interparticle distance, i.e. \( \alpha^3 \ll \zeta \), the contributions to the development of the system separate into two classes. The one class, which can be represented by chain diagrams determines the effect of the short range interaction to first order in \( \zeta / \alpha^3 \). The other class, which can be represented by ring diagrams determines to first order in \( \alpha / \zeta \) the effect of the long range interaction, apart from a self-consistent field contribution. Together these contributions yield a set of eight equations, (3.125a-f) and (3.126a,b) each of which is valid for a definite range of the ratio of the strength of the weak interaction to the average kinetic energy per particle, the ratio of a typical wavelength of the inhomogeneities to the range of the long range interaction, and the ratio of ranges of the two parts of the interaction.

Three important restrictions besides that on the ranges of the interaction were placed on the system in order to derive these equations: (i) that the average kinetic energy be much greater than the strength of the weak interaction but much less than the strength of the strong interaction, (3.5); (ii) that
the volume integral of the short range potential be much less than that of the long range potential, (3.7); and (iii) that the system be stable (following (3.81)). It was also required that the wavelength of the inhomogeneities be of the same order or greater than the range of the long range interactions which is not a serious restriction. The correlations were assumed to be of the same range as the interactions. This was shown to be consistent by the calculation of the two body correlation function in Chapter III.8, provided that the system is stable.

The equation of state derived in Chapter III.9,

\[
(3.201) \quad P_0 = c \kappa_0 T \left( 1 + \frac{\pi}{3} \frac{\mu C}{\kappa_0^2 (\kappa_0 T)^3} - \frac{\eta}{2} \frac{C}{\kappa_0 T} \right)
\]

can be compared with the Van der Waals equation of state, namely,

\[
(4.1) \quad P_0 = c \kappa_0 T \left( \frac{1}{1 - \frac{2}{3} \pi \frac{c}{\mu}} - \frac{\eta}{2} \frac{c}{\kappa_0 T} \right)
\]

The first term in brackets of (4.1) is arrived at by considering the reduction in the phase space available to a particle due to the non-zero diameter of the molecules. In this investigation we have asserted that \( C \ll \kappa^2 \) in which case the Van der Waals equation of state is

\[
(4.2) \quad P_0 \approx c \kappa_0 T \left( 1 + \frac{2}{3} \pi \frac{c}{\kappa^3} - \frac{\eta}{2} \frac{c}{\kappa_0 T} \right)
\]

In deriving the two particle correlation function at equilibrium, and indeed throughout this work, we have neglected terms of order \( C/\kappa^2 \) and therefore a term like the second one of (4.2) does not appear in (3.201). The second term of (3.201) arises from the two particle correlations due to the long range interaction.
These are completely neglected in the derivation of the Van der Waals equation of state. The last term in both equations (3.201) and (4.1) are identical. They are due to the mutual attraction of the molecules and involve no effects due to correlations.

That the restrictions mentioned above are not unreasonable can be seen by considering two real gases, Argon and Ethane as examples. We take the interaction potential to be of the form given by (3.194) and (3.195). That is,

\[ \mu U(r) = \begin{cases} \mu, & r \leq \chi^{-1} \\ 0, & r > \chi^{-1} \end{cases} \]

and

\[ \nu W(r) = \begin{cases} 0, & r \leq \chi^{-1} \\ \nu \frac{e^{-\sigma r}}{\alpha r}, & r > \chi^{-1} \end{cases} \]

A more realistic interaction is the Lennard-Jones potential

\[ \lambda \psi(r) = 4E \left[ \frac{a}{r^6} - \left( \frac{a}{r^2} \right)^{12} \right] \]

which fits quite accurately available data such as the viscosity of gases. However, since this does not have a well defined range for the long range part of the interaction, we choose the simpler form above. This is fitted to the Lennard-Jones parameters by taking \( \chi^{-1} = \alpha \), equating the volume integrals,

\[ -\nu \int_{r > \chi^{-1}} dr \frac{e^{-\sigma r}}{\alpha r} = 4E \int_{r > \alpha} dr \left[ \frac{a}{r^6} - \left( \frac{a}{r^2} \right)^{12} \right] \]
and setting the force between particles separated by a distance \(10/\mu\) equal for the two forms of the potential. The 'height' of the repulsive core \(\mu\) is restricted to values such that \(\mu \ll \nu^{2}/\mu\), i.e. \(\mu \ll \nu^{2}/\mu\). This means, because \(\mu\) is finite, that particles colliding with relative velocity \(\nu > (2\mu/m)^{1/2}\) can approach to distances less than \(\chi^{-1}\) from each other.

Table II lists the values of the parameters \(\nu\), \(\alpha\) and \(\chi\) for Argon and Ethane and the range of values specified for \(T\) and \(C\) by the restriction \(\mu \gg \hbar T \gg \nu\) and the stability criterion

\[\frac{4\pi \nu C}{\alpha^{3} \hbar T} < 1.\]

TABLE II

Parameters for Argon and Ethane

<table>
<thead>
<tr>
<th></th>
<th>Argon</th>
<th>Ethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi) cm(^{-1})</td>
<td>2.9x10(^7)</td>
<td>2.3x10(^7)</td>
</tr>
<tr>
<td>(\alpha) cm(^{-1})</td>
<td>4.8x10(^5)</td>
<td>3.7x10(^5)</td>
</tr>
<tr>
<td>(\nu) ergs</td>
<td>6.7x10(^{-20})</td>
<td>1.3x10(^{-19})</td>
</tr>
<tr>
<td>(T)°K</td>
<td>330 &gt;&gt; T &gt;&gt; 5x10(^{-4})</td>
<td>610 &gt;&gt; T &gt;&gt; 9x10(^{-4})</td>
</tr>
<tr>
<td>(C/T) (°K cm(^{3}))(^{-1})</td>
<td>&lt; 1.8x10(^{19})</td>
<td>&lt; 4.5x10(^{18})</td>
</tr>
</tbody>
</table>
The critical concentration for Argon is $8 \times 10^{21} \text{cm}^{-3}$ and for Ethane is $4.2 \times 10^{21} \text{cm}^{-3}$. Thus for concentrations well below the critical concentrations $\chi^2 \gg c$ and provided $c \gg 10^{16}$ the condition $\chi^2 \ll c$ is also satisfied. The requirements on $C/T$ can then be satisfied within the ranges specified for $T$ and $C$.

The values for the parameters above specify which of the equations of (3.125) and (3.126) are applicable. For a homogeneous system, ($\propto L_h^{-1} = 0$), the system will be described by (3.125b), provided $T \gg 6 \times 10^{-2} \text{°K}$ in the case of Ethane or $T \gg 3 \times 10^{-2} \text{°K}$ in the case of Argon. If the system is strongly inhomogeneous, $\propto L_h \sim 1$, the system will be described by (3.126a) if $T \ll 0.3 \text{°K}$ (Ethane) or $T \ll 0.6 \text{°K}$ (Argon) and by (3.126b) otherwise. In neither system is the collision term $J_R$ of any significance. This of course assumes that the system is stable. The order estimate of the term $J_R$, (3.121), is valid only for stable systems. If the system approaches instability the quantity $\xi(1)$ defined in (3.75b) tends to zero for some value of $\xi \cdot \alpha$ and the expression for $J_R$ blows up making the order estimate invalid.

The second term of the equation of state, (3.201), is completely negligible for the above values of the parameters even in comparison to the corresponding term in the Van der Waals equation of state. This indicates that in real gases for the stable region the correlations due to the long range forces can be ignored. Moreover it is apparent that the weak long range interaction is important only in the self-consistent field term. This means that no modification to take into account the correlations due to the long range forces is required and the kinetic
equation used by Sobrino\textsuperscript{5} is adequate in that sense.

The most obvious extension of this work would be to consider higher orders in $\frac{c}{\epsilon^1}$. This would involve summing over diagrams of the type Fig. 3.1g which on the surface appears to be very difficult. Consideration could also be given to systems which have very short wavelength inhomogeneities, that is, wavelengths much less than the range of the long range force. This would entail summing the inhomogeneous chains, e.g. (3.24b) rather than the homogeneous chains, e.g. (3.25b).


APPENDIX A

A simple demonstration of the factorization theorem stated in Chapter II.3 will be given here. Consider the contributions to $\mathcal{P}_{\Xi^2_3}(\{\mu_3; \tau\})$ represented by the diagrams of Fig. A.1. These diagrams constitute

\begin{align*}
\frac{-1}{2n_i} \int d\xi \int d\eta \int d\gamma \sum_{k=3} \left\{ \langle h^k, \xi \gamma | (L_0 - \xi)^- (L_0 - \gamma)^- (L_j - \gamma)^+ \right| \xi^2 \rangle + \langle h^k, \gamma \eta | (L_0 - \gamma)^- (L_0 - \gamma)^- (L_j - \gamma)^+ \right| \eta^2 \rangle \right \} \\
+ \langle h^k, \xi \eta | (L_0 - \xi)^- (L_0 - \gamma)^- (L_j - \gamma)^0 \right| \xi^2 \rangle \right \} \mathcal{P}_{\Xi^2_3}(\{h^3, \gamma \eta; 0\}) \\
= \int d\xi \int d\eta \int d\gamma \sum_{k=3} \left\{ \int_{\xi} \int_{\eta} \left\{ \langle h^k, \xi \gamma | e^{-iL_0 (\xi - \eta)} (-\lambda \delta \lambda^2) e^{-iL_j (\xi - \eta)} \right| \xi^2 \rangle + \langle h^k, \xi \alpha | e^{-iL_0 (\xi - \eta)} (-\lambda \delta \lambda^2) e^{-iL_j (\xi - \eta)} \right| \xi^2 \rangle \right \} \mathcal{P}_{\Xi^2_3}(\{h^3, \gamma \eta; 0\})
\end{align*}

the complete permutation class. The contribution of these diagrams is (see (2.50)}
Using the definitions of the matrix elements of $d\mathbb{L}$ given in (2.27) together with (2.17) and (2.28) this becomes

$\sum_{\delta_{1},\delta_{2}} \left( \frac{\pi n^{2}}{\hbar} \right)^{2} \int d\mathbf{v}_{1} \int d\mathbf{v}_{2} \int_{0}^{t} \int_{0}^{t} \left\{ e^{-i [\mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1}] (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) \right. \\
+ e^{-i [\mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2}] (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2}) \left\} e^{-i [\mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1}] (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) e^{-i [\mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2}] (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2}) \right. \\
+ e^{-i [\mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1}] (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) e^{-i [\mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2}] (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2}) \right. \\
+ e^{-i [\mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1}] (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) e^{-i [\mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2}] (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2})

Since the operators

(2.28) \hspace{1cm} \Theta^{\delta_{1}}(\mathbf{f}) = \frac{2}{m} \mathbf{v}_{f} \cdot \left( \frac{\partial}{\partial \mathbf{v}_{f}} - \frac{\partial}{\partial \mathbf{v}_{f}} \right)

commute with functions of velocities other than $\mathbf{j}$ or $\mathbf{n}$ we can rewrite (A.1) as

\[
\left( \frac{\pi n^{2}}{\hbar} \right)^{2} \sum_{\delta_{1},\delta_{2}} \int d\mathbf{v}_{1} \int d\mathbf{v}_{2} \int_{0}^{t} \int_{0}^{t} \left\{ e^{-i \mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1} (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) \right. \\
+ e^{-i \mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2} (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2}) \right. \\
+ e^{-i \mathbf{b}_{1}, \mathbf{v}_{1} + \theta_{1}, \mathbf{v}_{1} (t - \mathbf{t})} \Theta^{2y_{1}}(\mathbf{b}_{1} - \mathbf{b}_{1}) e^{-i \mathbf{b}_{2}, \mathbf{v}_{2} + \theta_{2}, \mathbf{v}_{2} (t - \mathbf{t})} \Theta^{2y_{2}}(\mathbf{b}_{2} - \mathbf{b}_{2})

\]
The contribution corresponding to the diagram of Fig. A.2 from (2.50) is

\[\begin{align*}
(A.2) & = \left\{ \frac{\gamma n^2}{\mathcal{L}^2} \sum_{\mathbf{k}^*} \int dy_1 \int_0^t d\tau \ e^{-i \mathbf{k}^* \cdot \mathbf{r}_1 (\tau - \tau_0)} \ \Theta^{2\mu}(\mathbf{k}, -\mathbf{k}^*) \ e^{-i [\mathbf{k}^* \cdot \mathbf{r}_1 + (\mathbf{k} - \mathbf{k}^*) \cdot \mathbf{g}_2]} \mathbf{r}_1, \\
& \quad \Theta^{2\mu}(\mathbf{k}, -\mathbf{k}^*) \ e^{-i [\mathbf{k}^* \cdot \mathbf{r}_1 + (\mathbf{k} - \mathbf{k}^*) \cdot \mathbf{g}_2]} \mathbf{r}_1, \\
& \quad \Theta^{2\mu}(\mathbf{k}, -\mathbf{k}^*) \ e^{-i [\mathbf{k}^* \cdot \mathbf{r}_1 + (\mathbf{k} - \mathbf{k}^*) \cdot \mathbf{g}_2]} \mathbf{r}_1, \right. \\
& \left. \Theta^{2\mu}(\mathbf{k}, -\mathbf{k}^*) \ e^{-i [\mathbf{k}^* \cdot \mathbf{r}_1 + (\mathbf{k} - \mathbf{k}^*) \cdot \mathbf{g}_2]} \mathbf{r}_1, \right. \\
& = \int \int_0^t \int d\tau_1 \ e^{-i \mathbf{k} \cdot \mathbf{r}_1 (\tau - \tau_0)} \ (-\lambda \delta L)^t \ (-\lambda \delta L)^{\tau_1} \ e^{-i \mathbf{L}_0 \mathbf{t}_1} \ |\{\mathbf{g}_1^*\}> \ \rho^{(2)}_{\mathbf{g}_1^*}\{|\mathbf{g}_2^*; 0\}
\end{align*}\]
Comparing this with (A.2) it is clear that the sum of the contributions due to diagrams (a) and (b) of Fig. A.1 is just the product of the contributions of the component structures of these diagrams. This is what we wished to demonstrate. A general proof of the factorization theorem is given by Resibois in reference 19.
APPENDIX B

The second order term in the expansion of the collision operator is obtained by applying the inverse Laplace transform to (3.25a). The result is

\begin{equation}
\psi_{(2)}(t) = \frac{1}{2\pi} \int e^{-iz\tau} \left(-i2\pi \mathcal{L} \right)^{2} \frac{\partial}{\partial \tau} \frac{\partial}{\partial \tau} \frac{V_{r}^2 \cdot \mathbf{l}}{l^2 - z^2} \cdot \partial_{12}
\end{equation}

(3.25)

(3.26)

with the tensor function \( \overrightarrow{\mathcal{K}} \) defined by

\begin{equation}
\overrightarrow{\mathcal{K}}(\mathbf{q}, t) = \frac{-i}{2\pi} \int d\mathbf{k} e^{-i\mathbf{k} \cdot \mathbf{q}} \overrightarrow{\mathcal{K}}(\mathbf{k}, 0)
\end{equation}

\begin{equation}
\overrightarrow{\mathcal{K}}(\mathbf{q}, 0) \equiv -i \frac{\mathbf{q} \cdot \mathbf{V}}{\mathcal{L}} \left( \frac{2}{\mathcal{L}} \right)^{2} \mathbf{V} \cdot \mathbf{l} \cdot \mathbf{V}
\end{equation}

For purposes of illustration we assume that the potential is of the form

\begin{equation}
\mathcal{V}(\gamma) = \frac{e^{-\kappa r}}{\kappa r}
\end{equation}

The Fourier transform of this function is (see (2.25))

\begin{equation}
\mathcal{V}_{l} = \frac{i}{2\pi \mathcal{L} \hat{n}} \frac{1}{\hat{n}^{2} + \mathcal{L}^{2}}
\end{equation}

When this is inserted in (B.4) we obtain

\begin{equation}
\overrightarrow{\mathcal{K}}(\mathbf{q}, z) = \frac{-i}{2\pi \mathcal{L} \hat{n}} \left( \frac{2}{\mathcal{L}} \right)^{2} \mathbf{V} \cdot \mathbf{l} \cdot \mathbf{V} \frac{1}{\hat{n}^{2} + \mathcal{L}^{2}}
\end{equation}

If we choose the coordinate system such that \( \mathbf{q} \) and the \( l_{3} \)-axis are parallel it is immediately evident that the tensor \( \overrightarrow{\mathcal{K}} \) is diagonal and moreover the \( l, l_{1}, \) and \( l, l_{2} \) components are equal.
That is,

\begin{equation}
\chi(z; \mathbf{e}) = \chi_1(z; \mathbf{e}) \left[ \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3 \right] + \chi_2(z; \mathbf{e}) \mathbf{e}_2 \mathbf{e}_3,
\end{equation}

where \( \mathbf{e}_1, \mathbf{e}_2, \) and \( \mathbf{e}_3 \) are unit vectors along the \( l_1, l_2, \) and \( l_3 \) axes.

Transforming from rectangular to cylindrical polar coordinates \((b, \phi, \xi)\) we have

\begin{equation}
\chi_1(z; \mathbf{e}) = -i \frac{2}{\pi} c \left( \frac{2}{m \hbar} \right)^2 \int_{-\infty}^{\infty} \frac{1}{\xi g - \bar{z}} \int_{0}^{\infty} \frac{2\pi}{b^2 + \xi^2 + \hbar^2} \frac{b^2 \sin^2 \phi}{(b^2 + \xi^2 + \hbar^2)^2}
\end{equation}

and

\begin{equation}
\chi_2(z; \mathbf{e}) = -i \frac{2}{\pi} c \left( \frac{2}{m \hbar} \right)^2 \int_{-\infty}^{\infty} \frac{1}{\xi g - \bar{z}} \int_{0}^{\infty} \frac{2\pi}{b^2 + \xi^2 + \hbar^2} \frac{1}{(b^2 + \xi^2 + \hbar^2)^2}
\end{equation}

The integral over \( b \) in (B.9) diverges logarithmically as \( b \to \infty \).

The evaluation of the integral is accomplished by taking the upper limit to be \( L, \) a large but finite number. Performing the integrations we obtain*

\begin{equation}
\chi_1(z; \mathbf{e}) = \frac{\pi c}{i} \left( \frac{2}{m \hbar} \right)^2 \left[ \frac{l^2}{\xi} \frac{1}{\bar{z} + i \xi g} + \frac{2i}{9} \ln \frac{z + i \xi g}{z + i \xi g} \right]
\end{equation}

and

\begin{equation}
\chi_2(z; \mathbf{e}) = \frac{4mc}{i} \left( \frac{2}{m \hbar} \right)^2 \left[ \frac{\hbar}{\bar{z} + i \xi g} - \frac{\xi^2}{z + i \xi g} \right]
\end{equation}

where

\begin{equation}
\xi^2 = L^2 + \hbar^2
\end{equation}

Equations (B.11) and (B.12) yield under inverse Laplace transformation

*See Section 28, reference 9.
(B.14) \[ \chi_i(q', t) = \frac{-i}{2\pi} \oint_{\Gamma} d\bar{z} e^{-izt} \chi_i(q', \bar{z}) \]

\[ = \pi c \left( \frac{2}{m\kappa} \right)^2 \left\{ \frac{-L^2}{\xi} e^{-\xi q^*t} + \frac{2}{\eta t} (e^{-\kappa q^*t} - e^{-\xi q^*t}) \right\} \]

and

(B.15) \[ \lambda_i(q, t) = 2\pi c \left( \frac{2}{m\kappa} \right)^2 \left( \frac{e^{-\kappa q^*t} + \xi e^{-\xi q^*t}}{\eta t} \right) \]

Clearly, since \( \xi > \kappa \), all terms in (B.14) and (B.15) decay to zero for times \( t \gg (\kappa q^*)^{-1} \). Thus

(B.16) \[ \chi_i(q, t) \to 0 ; \quad \lambda_i(q, t) \to 0 \quad \text{for} \quad t \gg t_c \]

and therefore

(B.17) \[ \gamma(q, t) \to 0 \quad \text{for} \quad t \gg t_c \]

In general it can be asserted that except for pathological cases the singularities of \( \gamma \) are not real and are located a distance \( \sim \kappa^{-1} \), the inverse of the range of the interaction, from the real axis and that the collision operator therefore tends to zero for times much greater than \( \sim \kappa^{-1}(m\beta)^{1/2} \).