TRANSPORT COEFFICIENTS FOR DENSE GASES

by

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ABSTRACT

A scheme is proposed for calculating the coefficient of self-diffusion in a dense gas of rigid spheres. The method proceeds by deriving and solving a closed equation for the velocity distribution function f associated with a single sphere which has specified initial position and velocity in a system in which the other particles have initial distributions of equilibrium.

At low densities f satisfies a linearized form of Boltzmann's transport equation. It is shown how generalizations of Boltzmann's equation can be obtained which are suitable for describing a gas at any given density. In the derivation of these equations one approximates the many-body dynamical problem by treating the dynamics of a few particles exactly and by also including certain many-body dynamical events. By this approach one can obtain expressions suitable for calculating the coefficient of self-diffusion and at the same time avoid the divergence problem which arises when the gas is analyzed in terms of contributions from finite numbers of isolated particles.

A generalization of Boltzmann's equation is considered which applies to gases dense enough for configurations of three particles in close proximity to be significant. This equation differs from the equation derived by Choh and Uhlenbeck for describing such systems in that it accounts for certain many-body dynamical events as well as three-body collision sequences.

The coefficient of self-diffusion D, as usually defined, is equal to the integral over time of the velocity autocorrelation function which can be calculated from the velocity distribution function f. It is shown how D is obtained from the closed equations for f. Evaluation of D from generalizations of Boltzmann's equation requires detailed numerical analysis.

Thus in order to make a quantitative test of the proposed scheme we consider a one dimensional gas of impenetrable point particles. It is shown that the velocity distribution function and the coefficient of self-diffusion can be determined exactly for this model. A closed equation for f is derived which takes into account three-body dynamics as well as certain many-body events. The latter collision sequences must be included to avoid divergences which also arise in the one dimensional model. The coefficient of self-diffusion as calculated from this equation is found to be very close to the exact value.

A discussion is also presented of an appropriate definition of the coefficient of self-diffusion for dense systems. A modified definition is proposed which takes into account the observed correlations between the velocity of the diffusing particle and other particles of the gas.

STATEMENT

This thesis contains no material which has been accepted for the award of any other degree, and to the best of my knowledge and belief, contains no material previously published or written by another person except where due reference is made in the text.

Geoffrey Richard Anstis

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CHAPTER 1 INTRODUCTION

1.1 THE DEVELOPMENT OF THE THEORY OF DENSE GASES

The principles which were to lead to a rigorous molecular description of a fluid were established through the work of Maxwell, Boltzmann, Liouville and Gibbs[1]. The macroscopic equations of hydrodynamics were shown to be related to averages of microscopic quantities, and when Hilbert, Chapman and Enskog succeeded in solving the well-known transport equation of Boltzmann it became possible to relate the coefficients of viscosity, thermal conduction, diffusion, etc. of dilute gases to the forces between the molecules of the gas[2].

Yet since that early work, no comparable description of gases of moderate or high densities has been developed. Thus one of the outstanding problems in the study of fluids is to derive a scheme for generalizing Boltzmann's equation to describe dense gases and to experimentally verify such a scheme.

Boltzmann's equation describes the time development of the single particle velocity distribution function $f(\underline{x},\underline{v},t)$ which is defined so that $f(\underline{x},\underline{v},t)d\underline{x}d\underline{v}$ is the average number of molecules of the gas in the volume element $d\underline{x}$ moving with velocities in the range $\underline{v},\underline{v}+d\underline{v}$ at the time t. Its derivation depends on the assumption of molecular chaos which states that the average number of collisions between two particles moving with pre-collision velocities v_1 and v_2 is $f(\underline{x},\underline{v}_1,t)$ $f(\underline{x},\underline{v}_2,t)d\underline{x}$. Grad[3] has given a detailed discussion of this and other assumptions used to derive the equation, its range of validity and methods for its solution. The central problem in describing dense gases is to find an appropriate modification to the assumption of molecular chaos.

The possibility of obtaining generalizations to Boltzmann's equation was opened up by the fundamental work of Kirkwood[4], Bogoliubov[5], and Born and Green[6], who obtained an exact equation for the one particle distribution function in terms of a two particle distribution function. This equation is the first of a hierarchy of equations satisfied by distribution functions which depend on the properties of 1,2,3, etc. particles of the system. The assumption of molecular chaos provides a means for truncating the set of equations and leads, as shown by Green[7], to a modification of Boltzmann's equation.

The methods of Bogoliubov have been the most influential in the development of a theory of dense gases. His approach is to assume, for the purposes of calculating the transport coefficients, that the two-, three-, etc. particle velocity distribution functions can be expressed as time-independent functionals of the one-particle distribution functions when sufficiently close to their equilibrium values. By this hypothesis it is possible to obtain from the hierarchy a closed equation for the one-particle distribution function. Furthermore Bogoliubov proposed a scheme for finding a sequence of successive approximations to the actual functional dependence of the higher order distribution functions on the single-particle distribution function. A first approximation to the functional form of the two-particle function yields a modified form of Boltzmann's equation, similar to that derived by Green. The next approximation was investigated by Choh and Uhlenbeck[8] who derived a generalization of Boltzmann's equation which accounts for effects arising from the dynamics of three particles. It therefore applies to gases of sufficient density that configurations of three particles in close proximity to one another commonly occur. Later Hollinger and Curtiss[9] were able to derive the equation by applying the principle of molecular chaos to the precollision velocities of groups of three particles. Sengers[10] has calculated from this equation, transport coefficients for a gas of hard spheres by numerical techniques. It is found that the coefficients differ only slightly from those calculated from an intuitive generalization of Boltzmann's equation due to Enskog[11].

Bogoliubov's work was based on an unproven assumption. M.S. Green[12] and Cohen[13] developed an approach, similar to the cluster expansion methods of equilibrium statistical mechanics, to investigate Bogoliubov's assumption. It was shown how the two-particle distribution function can be expressed as a time-dependent functional of the one particle distribution function. The functional was given as an expansion, each term of which depends on the dynamics of groups of particles isolated from the rest of the system for some length of time. It was conjectured that a time-independent approximation to each term in the expansion could be obtained by taking the length of the time interval to be infinitely long, thus verifying Bogoliubov's hypothesis. Indeed by this approach the first term in the expansion leads to Boltzmann's collision operator and the next term leads to Choh's correction to that operator. However, it soon became evident that the limit, as the length of the time interval approaches infinity, of any other term in the expansion does not exist, since contributions to the functional from groups of four or more isolated particles increase with the length of the time that the group remains separated from the remainder of the fluid[14]. This is not to say that the two-particle function cannot be approximated by a time-independent functional of the one-particle distribution function, but only that the method proposed for finding the functional, if it exists, is inappropriate. It is extremely unlikely that a group of particles will remain isolated for long periods, and this property must be taken into account at each stage in the calculation of the functional.

Cohen[15] has outlined a procedure whereby divergent contribrtions from the dynamics of four or more particles can be modified by accounting for the possibility that the group interacts with other particles of the gas. The cluster expansion method, as developed to investigate Bogoliubov's assumptions, appears to be unsuitable for obtaining a time independent functional relating the one and two particle distribution functions, since a complicated rearrangement of a series is required. It would appear preferable to avoid divergences from the beginning.

Mazenko[16] and van Beijeren[17] have derived formal closed equations for the velocity distribution function. Boltzmann's equation can be derived as an approximation to these equations. To obtain explicit expressions for the operators in their equations, a solution to the many-body problem is required. In seeking approximations which will lead to tractable expressions for transport coefficients, one must take care to avoid divergences of the type discussed earlier.

The work of Opie and Blatt[18], and Prigogine[19] has also been concerned with developing methods for generalizing Boltzmann's equation. The problem of modifying Boltzmann's equation for a system in which bound states can occur has been considered by Green and Hoffman[20]. A somewhat different approach for calculating transport coefficients is to proceed from the correlation formulas first derived by M.S. Green[21]. Green's results were rederived, and sometimes modified, by a number of authors, including Kubo[22], Mori[23] and H.S. Green[24]. A review of this aspect of statistical mechanics is presented by Zwanzig[25]. Direct evaluation of the correlation formulas is achieved by integrating the equations of motion of the particles of an equilibrium system. This has been made feasible for gases at high densities and for liquids by the use of electronic computers. Rahman[26] has studied transport properties of liquids, while Alder, Gass and Wainwright[27] have considered gases composed of rigid spheres.

Approximate evaluation of the correlation formulas leads, to the lowest orders in the density of the system, to the same calculations that arise in solving Boltzmann's equation and the Choh-Uhlenbeck equation[28]. Haines, Dorfman and Ernst[29] have given a method, based on the cluster-expansion techniques of Green and Cohen, for evaluating the formulas at higher densities. Once again divergent terms must be modified to obtain finite values for the transport coefficients. Kawasaki and Oppenheim[30], Cohen[31], Haines[32] and Dorfman[33] have shown how infinite sequences of certain divergent terms can be combined to give a finite contribution to the coefficient of self-diffusion. The analysis of these authors has not been extended beyond removing the divergence arising from the dynamics of four particles. It is found that, because of the geometry of collision sequences involving four particles, the contribution to the transport coefficients from four particle dynamics is a non-analytic function of the density, n. For instance, the coefficient of self-diffusion, D, can be expressed as [34]

$$nD = D_0 + nD_1 + n^2 \log n \, D_2 + n^2 D_2' + \ldots$$

where D_0 is the contribution from Boltzmann's equation, D_1 comes from the Choh-Uhlenbeck equation, and D_2 and D_2' result from 4-body dynamics. Calculations by which D_2, D_2' and corresponding terms for other transport coefficients may be obtained have been made by Gervois, Normand-Alle and Pomeau[35] in the case of rigid spheres. The complexity of many-body dynamics means that only qualitative statements can be made about higher order terms in the expansions for transport coefficients. Haines[32] discusses the possible form of the density dependence of the coefficients.

Experiments[36] have so far failed to confirm or disprove that the transport coefficients are non-analytic functions of the density.

An important problem has arisen from the study of correlation formulas with the result that the microscopic basis for the equations of hydrodynamics is not yet considered as being fully achieved. It seems that for dense gases the correlation functions appearing in the correlation formulas do not, as is assumed in their derivation, decay to zero rapidly in a time interval short enough that macroscopic quantities, such as local density and local temperature, remain almost constant. For a dilute gas the correlation functions exhibit the expected rapid decay. McLaughlin[37] has shown this explicitly for a Maxwellian model of a gas.

Alder and Wainwright[38] have shown, from computer simulations of a dense gas of hard spheres, that the velocity autocorrelation function, which is associated with the coefficient of self-diffusion, decays only slowly with time. Ernst, Hauge and van Leeuwen[39] predict that other correlation functions also decay slowly with time. Their analysis involves a number of unproven assumptions, but nonetheless predicts a long time form of the velocity autocorrelation function in agreement with that found from computer studies. Dorfman and Cohen[40] have studied the decay of correlation functions of moderately dense gases through the use of cluster expansion methods. Their results can be considered as arising from a generalised form of the Choh-Uhlenbeck equation which accounts for the effects of 3-body dynamics exactly and for the effects of many-body dynamics approximately[41]. Another approach, considered by Hauge[42], is to use the full non-linear form of Boltzmann's equation, rather than a linearized form as is usually done when studying steady-state transport phenomena.

As a consequence of the slow decay with time of the correlation functions, it has been suggested that the equations of hydrodynamics, with constant transport coefficients, describe only states of a fluid which vary infinitely slowly in space and time, and not the range of non-equilibrium states to which the hydrodynamic equations are normally applied[43].

The methods of kinetic theory which have been described can be applied to a number of simple models of a gas. The simplest is a one dimensional system of rigid rods since, as Jepsen[44] has shown, all properties of the system can be calculated exactly. The coefficient of self-diffusion is the only important transport coefficient for this system. Lebowitz and Percus[45], Lebowitz, Percus and Sykes[46], and Blum and Lebowitz[48],, have studied this one dimensional system in an attempt to obtain results which are applicable to three dimensional systems. The divergence problem also arises in this model, but because the rods are confined to move in one dimension, the coefficient of self-diffusion does not exhibit the non-analytic dependence on the density found in three dimensional systems.

There is a class of models in which a single moving particle interacts with an infinite array of fixed scatterers. Gates[48] has proposed an exactly solvable model in which a particle moving in two dimensions is scattered by horizontal flat plates. The diffusion coefficient D for the system is such that nD is an analytic function of the density, n. Two and three dimensional Lorentz models in which a particle collides with fixed circular or spherical scatterers have been studied by van Leeuwen and Weyland[49] and Ernst and Weyland[50]. It is predicted that the coefficient of self-diffusion is a non-analytic function of the density and this appears to be confirmed by the numerical work of Bruin[51].

Dorfman, Kuperman, Sengers and McClure[52] have shown that the theory for the drag on a macroscopic object placed in a gas stream is similar to the cluster expansion methods of computing transport properties. Divergent terms arising from collision sequences involving a few particles have to be modified and the drag coefficient displays a logarithmic dependence on the density of the gas.

Another model which is more closely related to real gases is that of a two dimensional gas of rigid discs. Transport coefficient for such a system have been computed from Boltzmann's equation and a first correction to Boltzmann's equation[53]. Computer studies[54] suggest that the time integral of the velocity autocorrelation function diverges which has led to the conjecture that the usual equations of diffusion do not apply to two dimensional systems.

1.2 AN OUTLINE OF THE THESIS

The aim of this thesis is to make some progress towards a general theory of the steady state transport properties of dense gases. The emphasis of the work is on developing a practical method for the calculation of the transport coefficients of a gas, the particles of which interact with known intermolecular forces. The successful completion of a program which gives results beyond those obtained from Boltzmann's equation has implications for the accurate determination of intermolecular forces and for the study of chemical reactions when many-body collisions play an important role.

The scheme which is presented here is applicable to gases with intermolecular potentials which are short-ranged and repulsive. These two requirements avoid the need to consider the complete many-body problem in which a particle may be interacting with several particles simultaneously. Nevertheless it may be possible to adapt the scheme to include the effects of attractive potentials when bound states can occur.

A detailed application of the scheme will be made to determine the coefficients of self-diffusion of gases of rigid spheres, rigid discs and rigid rods.

Chapter 2 presents a discussion of the coefficient of self-diffusion, its relation to the velocity autocorrelation formula and the range of validity of the usual macroscopic equations of diffusion. We show, by considering the theory of Brownian motion based on the Fokker-

Planck equation, that the coefficient of self-diffusion does not necessarily depend on the time integral of the velocity autocorrelation formula alone.

In Chapter 3 a study is made of the velocity distribution function associated with a single particle of a gas in equilibrium. This function which is the first of a hierarchy of n-particle distribution functions, is shown to satisfy a closed equation involving operators which require knowledge of many particle dynamics before they can be explicitly written down. However, the exact equation is derived in such a way that explicit approximations to it are readily derived. Boltzmann's equation is a first approximation; a further approximation takes into account 3-body dynamics exactly and partially accounts for collision sequences involving four or more particles. There are a number of ways in which these many-body interactions can be approximated. Certain equations which have been previously derived may not be the most convenient for calculating transport coefficients.

The solution of the equations is discussed in Chapter 4. The coefficient of self-diffusion is expressed in terms of the solution of an integral equation. To obtain a correction to the values from Boltzmann's equation requires knowledge of 3-body dynamics and hence numerical techniques are needed.

The complexity of many-body dynamics leads us, in Chapter 5, to consider the simple one-dimensional system of a gas of rigid rods. The principle of molecular chaos is formulated exactly for this system and it is shown how the hierarchy of equations for the n-particle velocity distribution functions can be solved directly.

If the coefficient of self-diffusion is evaluated by the approximate methods proposed for a more general model of a gas, we find that a first correction to Boltzmann's equation yields almost the exact value of the coefficient.

CHAPTER 2. THE COEFFICIENT OF SELF-DIFFUSION

2.1 INTRODUCTION

The thesis presents a study of the transport properties of dense gases, the main part of it being concerned with gases of rigid spheres, rigid discs or rigid rods and the transport phenomenon of self-diffusion. It is therefore important to decide on what is meant by self-diffusion and to show how the coefficient of diffusion can be calculated.

From a qualitative point of view, self-diffusion refers to a molecule's slow movement through a fluid. Despite the high average speed of individual molecules, they tend to move only macroscopically small distances in a long time interval because of frequent interactions with other molecules. Theoretical studies of self-diffusion are usually based on theories of Brownian motion. By analogy with Einstein's[55] analysis of Brownian motion, one assumes that, in a sufficiently long time interval t, the mean square displacement of a molecule of a gas in equilibrium is given by

$$\left\langle [\underline{r}(t)]^2 \right\rangle_{eq} = 6Dt \qquad (1.1)$$

Here $r(t)$ is the displacement of some molecule in time t and the brackets $\langle \quad \rangle_{eq}$ denote an average over a statistical ensemble appropriate for describing the state of equilibrium. A time interval long enough for the particle to suffer several collisions is considered suitable for (1.1) to hold. Equation (1.1) then is taken as defining the coefficient of self-diffusion D for a gas in equilibrium.

Yang[56] has shown that in a dilute gas (1.1) is satisfied for macroscopically small time intervals, and therefore that D is just the coefficient of mutual diffusion which appears in the equation

$$n_1(\underset{\sim}{x},t)\underset{\sim}{w}_1(\underset{\sim}{x},t) = -D\frac{\partial n_1}{\partial \underset{\sim}{x}} \qquad (1.2)$$

which describes the diffusion of particles of type 1 in a gas sufficiently close to equilibrium, consisting of particles of two types, labelled 1 and 2, say. $n_1(\underline{x},t)$ is the number density of particles of type 1 at the position $\underline{x}$ at time t, while $\underline{w}_1(\underline{x},t)$ is the diffusion velocity of particles of type 1. Equation (1.2) is valid when the temperature and pressure of the system are constant.

The situation is different in dense fluids. Computer simulations of gases of hard spheres and hard discs suggest that (1.1) is valid only after an infinitely long time interval for a gas of spheres, while in a two dimensional system there is no relation like (1.1) between the mean square displacement of a particle and the time interval in which the displacement occurs. Following on from these observations it has been suggested[43] that, in three dimensions, the generalization for dense gases of equation (1.2), with constant coefficient of diffusion, is valid only when the system is so close to equilibrium that $n_1(\underline{x},t)$ and $\underline{w}_1(\underline{x},t)$ vary infinitely slowly in space and time. For a two dimensional gas equations like (1.2) should not be valid for any non-equilibrium situation. It appears that dense two and three dimensional gases have the characteristics of a fluid with a memory. The modifications to the hydrodynamic equations which are required to describe such fluids are discussed by Storer and Green[57].

This chapter has two purposes. The first is to give the correlation formula for the coefficients of diffusion for a gas consisting of two types of particles. This formula was first given by H.S. Green[24]. If the two types of particles are mechanically identical, the formula reduces to a modification of the velocity autocorrelation formula for the coefficient of self-diffusion which can be applied to systems of finite volume.

The second point we make is that it is possible to modify the definition of the coefficient of self-diffusion so that it is well-defined for both two and three dimensional systems. The relationship between this coefficient and macroscopic equations of diffusion has not been worked out.

We first discuss self-diffusion as a special case of mutual diffusion and give the velocity correlation formulas for the diffusion coefficients given by Green. This is done in Section 2.2.

In Section 2.3 we describe diffusion of a particle by using the Fokker-Planck equation. The coefficient of diffusion is related to the mean square displacement, relative to the mean displacement, of the diffusing particle. We take this relation as defining the coefficient of self-diffusion even if the Fokker-Planck equation is not applicable. For a dilute gas, the definition leads to the same value for the coefficient as does (1.1); however, in a dense gas, correlations between the velocities of colliding particles are important and the definitions do not coincide.

2.2 SELF-DIFFUSION CONSIDERED AS MUTUAL DIFFUSION

From an experimental point of view self-diffusion is not usually studied directly. Rather it is considered as a special case of mutual diffusion in a gas consisting of two types of particles which are mechanically identical but distinguishable in some way. For a dilute gas, one obtains by this approach the same value for the coefficient of self-diffusion as is obtained by considering the diffusion of a single particle.

We give here a brief discussion of diffusion in a gas of two components. We give the correlation formula, due to Green, from which the coefficients of diffusion can be calculated. As will be shown, this formula differs in an important way from other formulas that have been derived.

Consider a gas consisting of two types of mechanically identical particles. The types are called a and b. We define, for $i = a,b$,

$n_i(\underline{x},t)$	as the number density of particles of type i.
$\mu_i(\underline{x},t)$	as the chemical potential of particles of type i.
$\underline{u}(\underline{x},t)$	as the average velocity of particles of both types.
$\underline{w}_i(\underline{x},t)$	as the average velocity, relative to an observer moving with velocity $\underline{u}(\underline{x},t)$, of particles of type i.

If these quantities are close to their equilibrium values, and the temperature of the gas is uniform, the following diffusion equations are valid:

$$m\, n_i(\underline{x},t)\, \underline{w}_i(\underline{x},t) = - \sum_{j=a,b} D_{ij} \frac{\partial \mu_j(\underline{x},t)}{\partial \underline{x}} \qquad i = a,b \tag{2.1}$$

D_{ij} is the transport coefficient appearing in the macroscopic theory of irreversible processes developed by Onsager, de Groot and others[58].

Green[24] has shown that the coefficients appearing in these equations are given by

$$D_{ab} = \frac{m^2}{3kTV} \int_0^\infty dt \left\langle \sum_i^{(a)} \underline{v}_i(o) . \left[\frac{n_a}{n} \sum_j^{(b)} \underline{v}_j(t) - \frac{n_b}{n} \sum_j^{(a)} \underline{v}_j(t)\right] \right\rangle_{eq}$$

$$D_{ab} = D_{ba} = - D_{aa} = - D_{bb} \qquad (2.2)$$

In this equation, n_a and n_b are the equilibrium values of the number densities, $n = n_a + n_b$, the summation $\sum_i^{(k)}$ is restricted to particles of type k $(k = a,b)$ and the average is over an equilibrium ensemble.

Equation (2.2) should be compared with the formula given by M.S. Green[21] and Mori[23].

$$D_{ab} = \frac{m^2}{3kTV} \frac{n_a}{n} \int_0^\infty dt \left\langle \sum_i^{(a)} \underline{v}_i(o) . \sum_j^{(b)} \underline{v}_j(t) \right\rangle_{eq} \qquad (2.3)$$

This latter formula is not correct since the integral with respect to time does not converge. To see this we consider, for the purpose of evaluating the correlation function in (2.3), the subensemble of the grand canonical ensemble of equilibrium in which some particle of the ath type has definite velocity $\underline{v}_a$, say. After an infinite time the momentum of the distinguished particle is shared between particles of type a and type b in the ratio n_a/n_b. Hence for long times the correlation function (2.3) equals $\left\langle \sum_i^{(a)} [\underline{v}_i(o)]^2 \right\rangle_{eq} n_b/n$, a non-zero quantity, and consequently the integral in (2.3) diverges. On the other hand the correlation function in (2.2) is zero for very long times.

Equation (2.2) can be put into a more familiar form. Consider the following expression which appears in that equation:

$$\left\langle \underline{v}_i(o) . \left[\frac{n_a}{n} \sum_j^{(b)} \underline{v}_j(t) - \frac{n_b}{n} \sum_j^{(a)} \underline{v}_j(t)\right] \right\rangle_{eq} \qquad (2.4)$$

Now $$\left\langle \underline{v}_i(o) . \sum_j \underline{v}_j(t) \right\rangle_{eq} = \left\langle [\underline{v}_i(o)]^2 \right\rangle_{eq} \qquad (2.5)$$

since if the momentum of the system is $\underline{v}_i(o)$ at $t = o$, its total momentum $\Sigma_j \underline{v}_j(t)$ at a later time will still be $\underline{v}_i(o)$. Furthermore the particles of type b and of type a, other than particle i, are moving on the average with the same velocities. Hence

$$\left\langle \underline{v}_i(o) . \overset{(b)}{\Sigma_j} \underline{v}_j(t) \right\rangle_{eq} / (n_b V) = \left\langle \underline{v}_i(o) . \overset{(a)}{\underset{j \neq i}{\Sigma}} \underline{v}_j(t) \right\rangle_{eq} / (n_a V - 1) \tag{2.6}$$

Substituting (2.5) and (2.6) into (2.4) we obtain

$$D_{ab} = \frac{m^2}{3kT} \frac{n_a n_b}{n} \int_o^\infty dt \left\langle \underline{v}_i(o) . \left[\frac{\underline{v}_i(o)}{V} - \underline{v}_i(t) \right] \right\rangle_{eq} \tag{2.7}$$

The factor $\underline{v}_i(o)/V$ which appears in this equation is necessary to ensure that the integral converges.

For a dilute gas,

$$\frac{\partial n_a}{\partial \underline{x}} = m \left(\frac{n_a}{kT} \right) \frac{\partial \mu_a}{\partial \underline{x}}$$

If the pressure of the gas is uniform, we obtain from (2.1),

$$n_a \underline{w}_a = - \left(\frac{n}{n_a n_b} \right) \left(\frac{kT}{m^2} \right) D_{aa} \frac{\partial n_a}{\partial \underline{x}}$$

The coefficient of $\partial n_a / \partial \underline{x}$ was denoted by D in equation (1.2). From (2.7) we have

$$D = \frac{1}{3} \int_o^\infty dt \left\langle \underline{v}_i(o) . \left(\underline{v}_i(t) - \frac{\underline{v}_i(o)}{V} \right) \right\rangle_{eq} \tag{2.8}$$

2.3 THE EQUATION OF FOKKER AND PLANCK.

In this section we consider a model of diffusion based on a generalization of an equation derived by Fokker and Planck[59]. The generalization due to Chandrasekhar[60] was developed to describe the diffusion of a Brownian particle in a liquid, while the further generalization by Kirkwood[4] is aimed at providing a molecular description of the macroscopic properties of gases and liquids.

We show that the Fokker-Planck equation relates the coefficient of diffusion to the mean square displacement, relative to the mean displacement, of the diffusing particle. This relation is taken as defining the coefficient of self-diffusion in a fluid, even if the generalized form of the Fokker-Planck is not applicable. Equation (1.1) can be obtained from this definition when the gas is dilute but not when the system is dense since then correlations between the velocities of particles are important.

The equation of Fokker and Planck describes the time evolution of the probability distribution function $f(\underline{x},\underline{v},\underline{t};\underline{x}',\underline{v}')$ which is defined so that

$f(\underline{x},\underline{v},\underline{t};\underline{x}',\underline{v}')d\underline{x}d\underline{v}$ = the probability of finding, at time t, the diffusing particle in the element of volume $d\underline{x}$, about the point $\underline{x}$, and moving with velocity in the range $\underline{v},\underline{v}+d\underline{v}$, given that at $t=o$ it was at position $\underline{x}'$ and had velocity $\underline{v}'$.

The equation which describes the time evolution of f is

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} + \frac{\partial}{\partial \underline{v}}.(\underline{a}f) = 0 \tag{3.1}$$

where $\underline{a}$ is the mean acceleration of the particle. Kirkwood approximated $\underline{a}$ by

$$m\underline{a} = \frac{\partial}{\partial \underline{x}}(nkT - p) - \zeta\left\{\frac{kT}{f}\frac{\partial f}{\partial \underline{v}} + m(\underline{v}-\underline{u})\right\} \tag{3.2}$$

where k is Boltzmann's constant, m the mass of the particle, n

the density of the fluid, T its temperature, p the pressure and $\underline{u}$ the velocity of the fluid. ζ is called the friction constant, and as Kirkwood has shown its exact evaluation depends on solving the many-body dynamical problem. In Chandrasekhar's description of Brownian motion, $\underline{a}$ is taken to be

$$ma = -\zeta_B\left(\frac{kT}{f}\frac{\partial f}{\partial \underline{v}} + m(\underline{v} - \underline{u})\right) \tag{3.3}$$

The friction constant ζ_B, appropriate for Brownian motion, is related to physical properties of the Brownian particle and its fluid environment. In (3.2) and (3.3), the component of force, $-m\zeta(\underline{v} - \underline{u})$, is the frictional force on a particle moving with velocity $\underline{v}$ through a fluid with velocity $\underline{u}$. The component $-\zeta(kT/m)\partial f/\partial\underline{v}$ results from the random molecular collisions which the particle experiences.

In the following we first consider $\underline{a}$ to be given by (3.3) or (3.2) with the term $\partial(nkT - p)/\partial\underline{x}$ neglected. On solving equation (3.1) with this restriction on the form of $\underline{a}$, we find that the density distribution function, defined as

$$n(\underline{x},t;\underline{x}',v') = \int d\underline{v}\; f(\underline{x},\underline{v},t;\underline{x}',\underline{v}') \tag{3.4}$$

is given by[61]

$$n = (4\pi D_1 t)^{-3/2} \exp[-(\underline{x} - \underline{x}' - \underline{r}(t))^2/(4D_1 t)] \tag{3.5}$$

where $$D_1(t) = kT/(mt\zeta^2)\left(\zeta t - 3/2 + 2e^{-\zeta t} - \tfrac{1}{2}e^{-2\zeta t}\right) \tag{3.6}$$

while $\underline{r}(t)$, the displacement of the particle when the effect of molecular collisions is neglected, satisfies

$$d\underline{r}(t)/dt = \underline{c}(t)$$

$$d\underline{c}(t)/dt = -\zeta(\underline{c}(t) - \underline{u}(\underline{r}(t),t)) \quad \underline{c}(o) = v'. \tag{3.7}$$

From (3.5), the mean displacement of the particle in the time interval t is

$$\int d\underline{x}(\underline{x} - \underline{x}')\; n(\underline{x},t;\; \underline{x}',\underline{v}') = \underline{r}(t) \tag{3.8}$$

and its mean square displacement, relative to its mean displacement is

$$\int d\underline{x}[\underline{x} - \underline{x}' - \underline{r}(t)]^2 \; n(\underline{x},t;\underline{x}',\underline{v}') \simeq 6 \; D_1(t)t \tag{3.9}$$

The above calculations assume that the diffusing particle has initial velocity $\underline{v}'$. If an average is taken over all possible initial velocities we obtain

$$\int d\underline{v}'h(\underline{v}') \int d\underline{x} \; [\underline{x}-\underline{x}'-\underline{r}(t)]^2 \; n(\underline{x},t;\underline{x}'\underline{v}') = 6D_1(t) \tag{3.10}$$

where $h(v)$ is the velocity distribution function associated with particles at $\underline{x}'$ at the initial time.

It should be noted that (3.10) leads to the same value of D_1 when the velocity of the fluid is changed by an amount $\underline{u}'(t)$. This expresses the fact that the value of the coefficient of diffusion is independent of the velocity $\underline{u}(t)$ of an observer measuring the coefficient. i.e. is invariant under Galilean transformations.

For times $t >> 1/\zeta$ we may replace $D_1(t)$ by D_1 in (3.10) with negligible error.

To define the coefficient of self-diffusion for a gas, the temperature and density of which are constant, we write

$$\int d\underline{v}'h(\underline{v}') \int d\underline{x}[\underline{x}-\underline{x}' - \overline{\underline{x}(t)}]^2 \; n(\underline{x},t;\underline{x}',\underline{v}') = 6D(t)t \tag{3.11}$$

where $\overline{\underline{x}(t)} = \int d\underline{x}(\underline{x} - \underline{x}') \; n(\underline{x},t;\underline{x}',\underline{v}')$

and assume that $D = \lim_{t\to\infty} D(t)$ exists. D is then taken to be the coefficient of self-diffusion. Note that we are not now assuming that n satisfies the Fokker-Planck equation. If D is related to the coefficient of diffusion in some macroscopic diffusion equation, it is to be expected that, for times t greater than some macroscopically short time

$$D \approx D(t) \tag{3.12}$$

For a dilute gas, which is adequately described by Boltzmann's equation, D can be shown to exist and (3.12) to hold for macroscopically short times. For a dense gas, certain information about many-body dynamics, or equivalently a generalization of Boltzmann's equation, is required to show that the procedure outlined above leads to a well-defined coefficient of diffusion.

Before proceeding to a discussion of diffusion in a dilute gas, and then in a dense gas, we express D in terms of a velocity correlation function. We assume that the gas is in equilibrium and write (3.11), evaluated at a long time t, as

$$\int d\underline{v}' h_o(\underline{v}') < [\underline{x}(t) - <\underline{x}(t)>']^2>' = 6Dt \tag{3.13}$$

The brackets < >' indicate an average over the subensemble of the grand ensemble of equilibrium in which some particle has initial velocity $\underline{v}'$. $\underline{x}(t)$ is the displacement of that particle in time t and $h_o(\underline{v})$ is the equilibrium velocity distribution i.e. the Maxwellian distribution function. Differentiating (3.13) with respect to time, and writing $\underline{v}(t) = d\underline{x}(t)/dt$ we obtain

$$D = \lim_{t\to\infty} \frac{1}{3} \int d\underline{v}' h_o(v') < \int_o^t dt' \left(\underline{v}(t') - <\underline{v}(t')>'\right).\left(\underline{v}(t) - <\underline{v}(t)>'\right)>'$$

and consequently

$$D = \lim_{t\to\infty} \frac{1}{3} \int_o^t dt' \int d\underline{v}' h_o(\underline{v}') \left(<\underline{v}(t').\underline{v}(t)>' - <\underline{v}(t')>' <\underline{v}(t)>'\right) \tag{3.14}$$

Now

$$\begin{aligned} \int d\underline{v}' h_o(\underline{v}') <\underline{v}(t').\underline{v}(t)>' &= <\underline{v}(t').\underline{v}(t)>_{eq} \\ &= <\underline{v}(o).\underline{v}(t - t')>_{eq} \end{aligned} \tag{3.15}$$

since in a gas in equilibrium, the correlation between a particle's velocity at one time with that at another time depends only on the length of the interval between those times. On using the relation (3.15) we obtain the correlation formula

$$D = \frac{1}{3} \lim_{t\to\infty} \int_o^t dt' [<\underline{v}(o).\underline{v}(t')>_{eq} - \int d\underline{v}' h_o(\underline{v}')<\underline{v}(t')>'.<\underline{v}(t)>'] \tag{3.16}$$

which differs from the formula usually given for D by the appearance of the second term on the right side.

In the low density limit, a linearized form of Boltzmann's equation can be used to evaluate (3.16). McLaughlin[37] has evaluated the distribution function f for a Maxwellian model of a gas. From his calculations it can be shown that $\lim_{t\to\infty} \langle \underline{v}(t)\rangle' = o$ while $\int_o^\infty dt \langle \underline{v}(t)\rangle'$ is finite. Hence the coefficient of self-diffusion is given by

$$D = \frac{1}{3}\int_o^\infty dt \langle \underline{v}(o).\underline{v}(t)\rangle_{eq} \qquad (3.17)$$

an expression which can be derived directly from definition (1.1). From Yang's[56] work too, equation (3.17) can be shown to apply to dilute gases.

In a dense gas correlations between the velocities of particles become important. This has been clearly demonstrated in computer simulations of gases of rigid disks carried out by Alder and Wainwright and can be expressed quantitatively by the face that for long times the velocity autocorrelation function is given by[43]

$$\langle \underline{v}(o).\underline{v}(t)\rangle_{eq} = \alpha(n)t^{-d/2} \qquad (3.1\ )$$

where d is the dimension of the system and α is a parameter depending on n, the density of the system. Approximate methods for describing the many-body effects which lead to the slow time decay of the autocorrelation function have been given by Dorfman and Cohen[40], Ernst, Hauge and Van Leeuwen[39] and Hauge[42].

Now the correlation formula (2.2), or equivalently (2.8), for the coefficient of self-diffusion is derived on the assumption that the velocity correlation functions which appear in these formulas decay rapidly compared with the time in which the densities $n_1(\underline{x},t)$ and $n_2(\underline{x},t)$ and the fluid velocity $\underline{u}(\underline{x},t)$ change appreciably. Since the velocity autocorrelation function decays only slowly one expects that the diffusion equations (1.2) and (2.1) apply only when the densities n_1 and n_2 (or μ_1 and μ_2) and the fluid velocity $\underline{u}$ vary infinitely slowly. For a two dimensional system the integral of the velocity autocorrelation function does not exist so that the diffusion equations should not apply to such a gas.

It appears necessary to modify the equations of diffusion (and other equations of hydrodynamics). Storer and Green[57] discuss the form of equations which describe a fluid with memory. Keyes and Oppenheim[62] have proposed a definition of the coefficient of self-diffusion which is finite for two dimensional systems, but they do not attempt to relate it to a coefficient in a diffusion equation.

The definition (3.16) of a coefficient of self-diffusion arose from a consideration of the theory of Brownian motion. An analysis of the data from computer simulations of gases will indicate whether this definition is suitable for describing self-diffusion in dense two and three dimensional systems. The definition attempts to account for correlations between the velocities of neighbouring particles. Computer studies show that the average displacement of a diffusing particle, with given initial velocity, is greater in a dense system than it is in a dilute system. In both cases the diffusing particle rapidly attains the average velocity of surrounding particles, but for dense systems this average depends on the initial velocity of the preferred particle.

The coefficient which is defined in terms of microscopic quantities by equation (3.16) may be related to a constant in a macroscopic equation, just as the velocity autocorrelation function is related to the diffusion coefficient in equation (1.2). Such an equation would differ slightly from (1.2) possibly through the appearance of correlated stream velocity functions, similar to those which were introduced by Green and Hoffman[20].

CHAPTER 3 GENERALIZATIONS OF BOLTZMANN'S EQUATION

3.1 INTRODUCTION

It was shown in Chapter 2, that in order to calculate the coefficient of self-diffusion for a dense gas it is necessary, but not sufficient, to evaluate the time integral of the velocity autocorrelation function. This requires that we consider a gas in equilibrium and determine the velocity of some particle over an infinite length of time. One approach for obtaining such information is to derive and solve an equation for the velocity distribution function $f(\underline{x},\underline{v},t)$ defined in Section 2.3. The derivation of equations for f is the purpose of this chapter. Their solution is considered in Chapter 4.

There is no great difficulty in deriving a formally exact equation for the velocity distribution function, and this has been done in various ways by Cohen[15], Lebowitz, Percus and Sykes[63], van Beijeren[17], and Mazenko[16], as well as by other authors. These equations involve operators which transform the positions and velocities of particles into their values at some later time. Hence to give explicit expressions for these operators and to solve the exact equation requires knowledge of the many-body problem. Therefore it is important to derive the exact equation for f in such a way that approximations to it can be found in a straightforward fashion.

The cluster expansion methods of Green and Cohen have been used to derive a closed equation for the velocity distribution function. By this approach, the effect of collisions on the time development of f is given by an infinite sum of time-dependent collision operators, each depending on the dynamics of some finite number of particles. For the purpose of calculating steady state transport properties, a time-independent approximation to the long-time values of these operators is sought. Apart from Boltzmann's operator, which is time-independent, and the three-body operator, each individual operator is an increasing function of time. In order to obtain a time-independent operator, one must sum certain parts of each operator to obtain a many-body operator which approaches a finite value for long times.

Instead of undertaking a complicated rearrangement of the equation derived by cluster expansion techniques, a more direct approach to finding an equation for the velocity distribution function is to make a rearrangement of the hierarchy equations satisfied by the 1-,2-,... particle distributions functions which describe the gas. Frieman and Goldman[64], Dorfman[33], Pomeau[65] and Mazenko[21] have all shown how to derive a first correction to Boltzmann's equation which incorporates two- and three-body effects exactly, and approximates higher order dynamics.

In this chapter we derive an exact equation for the single particle velocity distribution function. Our derivation is such that approximations, which correctly account for the dynamics of a certain number of particles, can easily be found and furthermore, these approximations are suitable for calculating the coefficient of self-diffusion. The important step in our analysis is to express the hierarchy of equations in a way which clearly brings out the fact that a particle does not remain isolated from other particles for long periods of time.

The contents of this chapter are as follows:

In section 3.2 we define the n- particle velocity distribution function which describes the motion of a diffusing particle and $n-1$ other particles. We derive cluster expansions for the velocity distribution functions by an approach which is more direct than usually given, since we use the grand canonical ensemble of statistical mechanics, rather than the canonical ensemble. We show that when applied to a gas of rigid spheres the hierarchy of equations, which the velocity distribution functions satisfy, can be reformulated to make evident that the gas evolves through a sequence of binary collisions.

In section 3.3 we show that the velocity distribution function $f(\underline{x},\underline{v},t)$ satisfies an equation of the form

$$\left(\frac{\partial}{\partial t} + \underline{v}.\frac{\partial}{\partial \underline{x}}\right)f(\underline{x},\underline{v},t) = U\left(t;f(t)\right) \tag{1.1}$$

where $U(t)$ is a time dependent operator which represents the effect of collisions on the rate of change of $f(t)$. $U(t)$ is expressed as a sum of contributions from 2-,3-,4-,... body dynamics, the first contribution being just the linearized form of Boltzmann's collision operator.

For the purpose of calculating transport properties, $U(t)$ can be replaced by $\overline{U} = \lim_{t\to\infty} U(t)$. Approximations to $\overline{U}$ cannot be calculated easily from the expansion for $U(t)$ since individual terms in the expansion diverge. However, it is possible to obtain transport coefficients directly from (2.1) without the need to first find a time-independent operator.

In section 3.4 we derive an equation of the form

$$\left(\frac{\partial}{\partial t} + \underline{v}.\frac{\partial}{\partial \underline{x}}\right)f(\underline{x},\underline{v},t) = B_E\left(f(\underline{x},\underline{v},t)\right) + \int_0^t dt' \; V\left(t-t';f(t')\right) \tag{1.2}$$

where B_E is Enskog's modification to Boltzmann's collision operator. The time dependent collision operator $V(t)$ can be expressed as a sum of operators each depending on the dynamics of a small group of particles moving in a larger system. It is possible to derive a number of different expansions depending on how the interaction between groups of particles and the rest of the system is treated.

In section 3.5 we consider an approximation to (1.2) which takes into account two- and three-body dynamics exactly and which approximates higher order dynamics. In order to obtain an explicit expression for the three-body collision operator, we present a detailed discussion of the dynamics of three particles.

3.2 THE VELOCITY DISTRIBUTION FUNCTIONS

The object of this chapter is to develop a method by which the velocity autocorrelation function can be evaluated. This function is an average over an equilibrium ensemble, and so in this section we first give a brief description of some standard results of statistical mechanics. The equilibrium ensemble average can be computed by first considering the subensemble of the grand ensemble of equilibrium in which some particle is initially at the origin and is moving with some definite velocity. Velocity distribution functions are defined to describe the time evolution of the subensemble. These satisfy a hierarchy of equations which, for a gas of hard spheres, discs or rods, are put into a form convenient for later use.

In order to describe the properties of a gas we consider, not just one system of particles, but an ensemble of systems. Associated with an ensemble are distribution functions defined on the phase space of a system. A detailed discussion of these ideas is given by Green and Leipnik[66].

Each system in the ensemble is specified by the number of its particles and the position and velocity of each particle at some time. If a system has N particles, they are labelled from 1 through to N. The position of the ith particle is denoted by $\underline{x}^{(i)}$, its velocity by $\underline{v}^{(i)}$. The space containing the points $\underline{z}^{(i)} = (\underline{x}^{(i)},\underline{v}^{(i)})$ is the phase space of the particle. The space of points $(\underline{z}^{(1)},\underline{z}^{(2)},\ldots,\underline{z}^{(N)})$ is the phase space of the N particle system.

We now define the N-particle phase space distribution function. Consider the volume element $d\underline{z}^{(1)}d\underline{z}^{(2)}\ldots d\underline{z}^{(N)}$ about the point $(\underline{z}^{(1)},\underline{z}^{(2)},\ldots,\underline{z}^{(N)})$. The proportion of systems of the ensemble which are represented by a phase space point within this volume element is denoted by

$$\frac{1}{N!}\, F^N(\underline{z}^{(1)},\underline{z}^{(2)},\ldots,\underline{z}^{(N)},t)\; d\underline{z}^{(1)}d\underline{z}^{(2)}\ldots d\underline{z}^{(N)}$$

$F^N(t)$ is the N-particle phase space distribution function. Summing over all possible numbers of particles and over all possible configurations of the system must give unity i.e.

$$\sum_{N=o}^{\infty} \frac{1}{N!} \int d\underline{z}^{(1)}\ldots\int d\underline{z}^{(N)}\; F^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t) = 1$$

Note that here and later we do not indicate the range of integration when for position variables the range is the volume of the system or when for velocity variables the range is unrestricted.

The ensemble average of a function G of phase space points is given by

$$\langle G(\underline{z}^{(1)},\underline{z}^{(2)},\ldots)\rangle_t =$$
$$\sum_{N=o}^{\infty} \frac{1}{N!} \int d\underline{z}^{(1)}\ldots\int d\underline{z}^{(N)}\; F^N(\underline{z}^{(1)},\ldots\underline{z}^{(N)},t)\; G(\underline{z}^{(1)},\underline{z}^{(2)},\ldots) \qquad (2.1)$$

An important example of a phase space distribution function is that which describes an equilibrium ensemble:

$$F_o^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)}) = \frac{1}{Z}\exp\big(\beta(\mu N - H^N)\big) \qquad (2.2)$$

Z, a normalization constant, is the grand partition function. μ is the chemical potential. $\beta = 1/(kT)$ is related to Boltzmann's constant k and the temperature T of the system. H^N is the hamiltonian of the system.

Next we consider the time dependence of the phase space distribution functions. Consider N particles which at time t_o are at phase space points $\underline{z}_o^{(i)}$ $(i = 1,..,N)$. They will move in such a way that at time t particle i is at the point $\underline{z}^{(i)}$. We define the N particle streaming operator $S^N(t-t_o)$ by

$$S^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t-t_o)\; f\big(\underline{z}^{(1)},\ldots,\underline{z}^{(N)} = f(\underline{z}_o^{(1)},\ldots,\underline{z}_o^{(N)})\big) \tag{2.4}$$

where f is some function of $2N$ variables.

Liouville's equation states that

$$F^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t) = F^N(\underline{z}_o^{(1)},\ldots,\underline{z}_o^{(N)},t_o) \tag{2.5}$$

Equation (2.5) can be put into the differential form

$$\left(\frac{\partial}{\partial t} + L^N\right) \; F^N(t) = o \tag{2.6}$$

where

$$L^N = \sum_{i=1}^{N} \left[\underline{v}^{(i)}\cdot\frac{\partial}{\partial\underline{x}^{(i)}} - \frac{1}{m}\,\frac{\partial\overline{V}^N}{\partial\underline{x}^{(i)}}\cdot\frac{\partial}{\partial\underline{v}^{(i)}}\right] \tag{2.7}$$

and $\overline{V}^N$ is the potential energy of a N particle system. $\overline{V}^N$ is the sum of all interparticle potentials $V(r)$ which depend only on the separation r of the pair of particles.

$$\overline{V}^N = \sum_{i<j} \; V(|\underline{x}^{(i)} - \underline{x}^{(j)}|)$$

We are interested in the velocity autocorrelation function $<\underline{v}^{(1)}(o).\underline{v}^{(1)}(t)>_{eq}$, which on using the definition (2.1) of the ensemble average and the equilibrium distribution F_o^N, may be expressed as

$$\sum_{N=o}^{\infty} \frac{1}{N!} \int d\underline{z}_o^{(1)}\ldots \int d\underline{z}_o^{(N)} \; F_o^N(\underline{z}_o^{(1)},\ldots,\underline{z}_o^{(N)})\underline{v}_o^{(1)} \; \underline{v}^{(1)}(t) \tag{2.8}$$

where $\underline{v}^{(1)}(t)$ is a function of the variables $\underline{z}_o^{(1)},\ldots,\underline{z}_o^{(N)}$.

It is convenient to introduce into this expression the three dimensional delta functions $\delta(\underline{x}_o^{(1)} - \underline{x}_o)$ and $\delta(\underline{v}_o^{(1)} - \underline{v}_o)$ to obtain

$$\int d\underline{x}_o \int d\underline{v}_o \; \underline{v}_o.\sum_{N=o}^{\infty}\frac{1}{N!}\int dz_o^{(1)}\ldots\int d\underline{z}_o^{(N)} \; \delta(\underline{x}_o^{(1)}-\underline{x}_o)\;\delta(\underline{v}_o^{(1)}-\underline{v}_o)\; F_o^N\,\underline{v}^{(1)}(t) \tag{2.9}$$

One can define a new phase space distribution $F_1^N(t)$ which at time $t_o = 0$ is

$$F_1^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t_o) = \frac{V}{N}\frac{1}{h_o(\underline{v}_o)}\delta(\underline{x}^{(1)}-\underline{x}_o)\delta(\underline{v}^{(1)}-\underline{v}_o)\; F_o^N(\underline{z}^{(1)},..\underline{z}^{(N)}) \tag{2.10}$$

V is the volume of the system, and

$$h_o(\underline{v}) = \left(\beta m/(2\pi)\right)^{3/2} \exp(-\tfrac{1}{2}\beta m v^2) \tag{2.11}$$

is the equilibrium velocity distribution function for a single particle of mass m.

At later times F_1^N is given by the solution (2.5) of Liouville's equation, with (2.10) as initial condition. $F_1^N(\underline{z}^{(1)};\underline{z}^{(2)}..,\underline{z}^{(N)},t)$ is symmetric in the arguments $\underline{z}^{(2)},\ldots,\underline{z}^{(N)}$. It describes the subensemble of the equilibrium ensemble in which particle 1 is at position $\underline{x}_o$ and moving with velocity $\underline{v}_o$ at the time t_o. The average over this ensemble of a function G is defined by

$$<G>^1_t = \sum_{N=1}^{\infty}\frac{1}{(N-1)!}\int d\underline{z}^{(1)}..\int d\underline{z}^{(N)}\; F_1^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t)\; G(\underline{z}^{(1)},\underline{z}^{(2)}\ldots) \tag{2.12}$$

Then by using Liouville's Theorem:

$$d\underline{z}^{(1)}\ \ldots\ d\underline{z}^{(N)} = d\underline{z}_o^{(1)}\ \ldots\ d\underline{z}_o^{(N)}$$

where $\underline{z}_o^{(i)}$ and $\underline{z}^{(i)}$ were defined immediately prior to equation (2.4), we may combine (2.9), (2.10) and (2.12) to obtain

$$<\underline{v}^{(1)}(o).\underline{v}^{(1)}(t)>_{eq} = \frac{1}{V}\int d\underline{x}_o \int d\underline{v}_o\; h_o(\underline{v}_o)\underline{v}_o<\underline{v}^{(1)}>^1_t \tag{2.13}$$

To facilitate the evaluation of $<\underline{v}^{(1)}>^1_t$ we introduce a set of velocity functions $f_n(t)$; $n = 1,2,\ldots$ defined so that

$$f(\underline{z}_1;\underline{z}_2,..,\underline{z}_n,t)\; d\underline{z}_1 \Big/ \int d\underline{z}_1\; f(\underline{z}_1;\underline{z}_2,..,\underline{z}_n,t)$$

is the probability that particle 1 will be in the phase space element $\underline{z}_1$, when some other particles are at the phase space points $\underline{z}_2,..,\underline{z}_n$

The n-particle velocity distribution function is calculated from an ensemble average of delta functions

$$f_n(\underline{z}_1;\underline{z}_2,\ldots,\underline{z}_n,t) = \Big\langle\delta(\underline{z}_1-\underline{z}^{(1)}) \sum_{j_2\neq\ldots\neq j_n} \delta(\underline{z}_2-\underline{z}^{(j_2)})\ldots\delta(\underline{z}_n-\underline{z}^{(j_n)})\Big\rangle_t^1 \qquad (2.14)$$

The notation $\sum\limits_{j_2\neq\ldots\neq j_n}$ indicates a summation over the $(N-1)!/(N-n)!$ different $(n-1)$ - tuples that can be chosen, having regard to order, from N-1 particles.

From (2.14) and the definition (2.12) of the ensemble average, we have

$$f_n(\underline{z}_1,\ldots,\underline{z}_n t) = \sum_{N=1}^{\infty}\frac{1}{(N-1)!}\int d\underline{z}^{(1)}\ldots\int d\underline{z}^{(N)}\;\delta(\underline{z}_1-\underline{z}^{(1)})$$

$$\sum_{j_2\neq\ldots\neq j_n} \delta(\underline{z}_2-\underline{z}^{(j_2)})\ldots\delta(\underline{z}_n-\underline{z}^{(j_n)})\;F_1^N(\underline{z}^{(1)},\ldots,\underline{z}^{(N)},t) \qquad (2.15)$$

Using the symmetry of F_1^N, and integrating over the delta functions, leads to

$$f_n(\underline{z}_1,\ldots,\underline{z}_n,t) = \sum_{N=1}^{\infty}\frac{1}{(N-n)!}\int d\underline{z}_{n+1}\ldots\int d\underline{z}_N\;F_1^N(\underline{z}_1,\ldots,\underline{z}_N,t) \qquad (2.16)$$

Those terms for which $N<n$ do not contribute to (2.16). On putting $j = N-n$, we have

$$f_n(\underline{z}_1,\ldots,\underline{z}_n,t) = \sum_{j=0}^{\infty}\frac{1}{j!}\int d\underline{z}_{n+1}\ldots\int d\underline{z}_{n+j}\;F_1^{n+j}(\underline{z}_1,\ldots,\underline{z}_{n+j},t) \qquad (2.17)$$

We may solve this set of equations for F_1^n :

$$F_1^n(\underline{z}_1,\ldots,\underline{z}_n,t) = \sum_{j=0}^{\infty}\frac{(-1)^j}{j!}\int d\underline{z}_{n+1}\ldots\int d\underline{z}_{n+j}\;f_{n+j}(\underline{z}_1,\ldots,\underline{z}_{n+j},t) \qquad (2.18)$$

Verification of this expression is achieved by direct substitution of (2.18) into (2.17).

The velocity distribution functions satisfy the following hierarchy of equations.

$$\left(\frac{\partial}{\partial t} + L_n\right) f_n(\underline{z}_1,\ldots,\underline{z}_n,t) =$$

$$\sum_{k=1}^{n} \int d\underline{z}_{n+1} \frac{1}{m} \frac{\partial V_{k,n+1}}{\partial \underline{x}_k} \cdot \frac{\partial}{\partial \underline{v}_k} f_{n+1}(\underline{z}_1,\ldots,\underline{z}_{n+1},t) \qquad (2.19)$$

where L_n is the Liouville operator defined by (2.7) $V_{i,j}$ is the potential energy arising from the interaction of particles i and j, which are at positions $\underline{x}_i$ and $\underline{x}_j$. The derivation of equations (2.19) proceeds by differentiating (2.17) with respect to time and using Liouville's equation (2.6).

For a gas of rigid spheres, rigid discs or rigid rods of diameter a the hierarchy equations can be written as

$$\left(\frac{\partial}{\partial t} + L_n\right) f_n(\underline{z}_1,\ldots,\underline{z}_n,t) = \sum_{i=1}^{n} J_{i,n+1}\left(f_{n+1}(\underline{z}_1,\ldots,\underline{z}_{n+1},t)\right) \qquad (2.20)$$

$J_{i,n+1}(f_{n+1})$ is the contribution to the rate of change of f_n due to collisions between the particle with coordinates $\underline{z}_i = (\underline{x}_i,\underline{v}_i)$ and some other particle of the system. $J_{i,n+1}$ acts on functions of $\underline{z}_i$ and $\underline{z}_k$ as follows:

$$J_{i,k}\left(g(\underline{x}_i,\underline{v}_i,\underline{x}_k,\underline{v}_k)\right) =$$

$$\int d\underline{v}_k \int d\underline{a}\cdot\underline{v}_{ki}\ \varepsilon(\underline{a}\cdot\underline{v}_{ki})\ \left(g(\underline{x}_i,\underline{v}_i',\underline{x}_i+\underline{a},\underline{v}_k') - g(\underline{x}_i,\underline{v}_i,\underline{x}_i-\underline{a},\underline{v}_k)\right) \qquad (2.21)$$

The integration with respect to $\underline{a}$ in this expression is over the surface of a sphere (for a three dimensional system) of radius $\underline{a}$. $d\underline{a}$ is a vector with direction $\underline{a}$ and magnitude an element of surface area. For a two dimensional system the integration is over a circle and $d\underline{a}$ is an element of arc. In one dimension, the integration region is simply two points. $\underline{v}_i'$ and $\underline{v}_k'$ are the precollision velocities leading to postcollision velocities $\underline{v}_i$ and $\underline{v}_k$ when the vector from the centre of particle k to the centre of particle i is $\underline{a}$ at the time of collision between these particles. The integration in (2.21) is limited to regions in which $\underline{a}\cdot(\underline{v}_k-\underline{v}_i) > 0$.

Hence we have introduced the step function $\varepsilon(x)$ defined by

$$\begin{aligned}\varepsilon(x) &= 0 \quad x < 0\\ &= 1 \quad x > 0\end{aligned} \tag{2.22}$$

$\underline{v}_i'$ and $\underline{v}_k'$ are given in terms of $\underline{a}$ and $\underline{v}_{ki} = \underline{v}_k - \underline{v}_i$

$$\begin{aligned}\underline{v}_i' &= \underline{v}_i - (\underline{v}_{ki}\cdot\underline{a})\underline{a}/a^2\\ \underline{v}_k' &= \underline{v}_k + (\underline{v}_{ki}\cdot\underline{a})\underline{a}/a^2\end{aligned} \tag{2.23}$$

Furthermore, if $\underline{v}_{ki}' = \underline{v}_k' - \underline{v}_i'$, we have

$$\underline{a} = a(\underline{v}_{ki} - \underline{v}_{ki}')/|\underline{v}_{ki} - \underline{v}_{ki}'| \tag{2.24}$$

Equation (2.20) is a consequence of assuming that in a gas of rigid particles, configurations in which a particle interacts simultaneously with two or more particles can be neglected. The derivation of equation (2.20) is given in Appendix A.

$f_n(t)$ may be obtained in terms of the velocity distributions at some earlier time, t_0, by direct integration of the hierarchy equations. However a more convenient form of the solution is obtained by first applying Liouville's equation to (2.17) so that

$$f_n(\underline{z}_1,\ldots,\underline{z}_n,t) =$$

$$\sum_{j=0}^{\infty} \frac{1}{j!} \int d\underline{z}_{n+1} \ldots \int d\underline{z}_{n+j}\, S(\underline{z}_1,\ldots,\underline{z}_{n+j},t-t_0)\, F_1^{n+j}(\underline{z}_1,\ldots,\underline{z}_{n+j},t_0) \tag{2.25}$$

and then expressing $F_1^n\,(t_0)$ in terms of $f_n(t_0)$ through (2.18).

We obtain

$$f_n(t) = \sum_{j=0}^{\infty} \frac{1}{j!} \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \int d\underline{z}_{n+1} \ldots \int d\underline{z}_{n+j+k}$$

$$\times\ S(\underline{z}_1,\ldots,\underline{z}_{n+j},t-t_0)\, f_{n+j+k}(\underline{z}_1,\ldots,\underline{z}_{n+j+k},t_0)$$

which on defining $\ell = j + k$, becomes

$$f_n(t) = \sum_{\ell=0}^{\infty} \frac{1}{\ell!} \sum_{j=0}^{\ell} (-1)^{\ell-j} \binom{\ell}{j} \int d\underline{z}_{n+1} \ldots \int d\underline{z}_{n+\ell}$$

$$\times\ S(\underline{z}_1,\ldots,\underline{z}_{n+j},t-t_0)\, f_{n+1}(\underline{z}_1,\ldots,\underline{z}_{n+\ell},t_0) \tag{2.26}$$

These equations are precisely the cluster expansions of the velocity distribution functions first given by Cohen[13]. By describing the gas in terms of a grand canonical ensemble, rather than a canonical ensemble, we arrive at these expansions in a far more direct manner. The velocity distribution functions f_n differ from those defined by Cohen, but the analysis given above still applies.

Equation (2.26) expresses the time development of $f_n(t)$ as contributions from those configurations of the system at time t_o which are such that in the interval (t_o,t) particle 1 suffers no collision, no more than one collision, no more than two collisions, etc. The dynamics of a many-particle system has been expressed in terms of the dynamics of finite numbers of particles.

To complete this section of preliminary results, we discuss the initial values of the velocity distribution functions. From the definition (2.14) of f_n, the definition (2.12) of the average $< >^1_t$ and the initial conditions (2.10), we find

$$f_n(\underline{z}_1,\ldots,\underline{z}_n,o) = \left(V/h_o(\underline{v}_o)\right)\,\delta(\underline{z}_1-\underline{z}_o)$$

$$\times <\delta(\underline{z}^{(1)}-\underline{z}_1)\sum_{j_2\neq\ldots\neq j_n}\delta(\underline{z}^{(j_2)}-\underline{z}_2)\ldots\delta(\underline{z}^{(j_n)}-\underline{z}_n)>_{eq} \tag{2.27}$$

These averages can be partially evaluated by using the equilibrium phase space distribution function given by (2.2).

$$f_1(\underline{z}_1,o) = \delta(\underline{z}_1-\underline{z}_o)$$

$$f_q(\underline{z}_1,\ldots,\underline{z}_q,o) = n_q(\underline{x}_2,\ldots,\underline{x}_q;\underline{x}_1)\;h_o(\underline{v}_2)\ldots h_o(\underline{v}_q)\;f_1(\underline{z}_1,o) \tag{2.28}$$

h_o was defined by (2.11). We define n_q as

$$n_q(\underline{x}_2,\ldots,\underline{x}_q;\underline{x}_1) =$$

$$V<\delta(\underline{x}^{(1)}-\underline{x}_1)\sum_{j_2\neq\ldots\neq j_q}\delta(\underline{x}^{(j_2)}-\underline{x}_2)\ldots\delta(\underline{x}^{(j_q)}-\underline{x}_q)>_{eq} \tag{2.29}$$

which is the equilibrium density of particles at $\underline{x}_2,\ldots,\underline{x}_q$ given that particle 1 is at $\underline{x}_1$.

The initial conditions (2.28) play an important part in the next sections when we derive closed equations for $f_1(t)$.

The distribution functions n_k can be written as a power series in the density by using the expansion methods of Mayer[67]. We note here that

$$n_2(\underline{x}_2;\underline{x}_1) = n\, e^{-V_{12}} + n^2 \int d\underline{x}_3 (e^{-V_{13}}-1)(e^{-V_{23}}-1)e^{-V_{12}} + \ldots$$

$$n_q(\underline{x}_2,\ldots,\underline{x}_q;\underline{x}_1) = n^{q-1} e^{-V_{1,\ldots,q}} + \ldots \tag{2.30}$$

where

$$n = \langle \textstyle\sum_j \delta(\underline{x} - \underline{x}^{(j)}) \rangle \tag{2.31}$$

is the equilibrium density of the system and where

$$\exp\,[V_{1,2,\ldots,q}] = \exp\,[\sum_{i<j=1}^{j} V_{ij}]$$

3.3 THE GENERAL TRANSPORT EQUATION

In order to evaluate the velocity autocorrelation function, we are required to find a solution to the hierarchy of equations (2.19) subject to the initial conditions (2.28). In this section we derive a closed equation for $f(\underline{x},\underline{v},\underline{t})$ of the form

$$\frac{\partial f}{\partial t} + \underline{v}.\ \frac{\partial f}{\partial \underline{x}} = U(t;f) \tag{3.1}$$

where $U(t)$ is a time-dependent operator, and we discuss some qualitative features of this equation.

Derivation of (3.1) proceeds by substituting the initial conditions (2.28) into the expansions (2.26); thus f_2, f_3, etc. can be expressed in terms of $f(o)$ and equilibrium distribution functions.

If we write t_o for $t = 0$, f and f_2 are given by

$$f(\underline{z}_1,t) = S(\underline{z}_1,t-t_o)\, f(\underline{z}_1 t_o) + \sum_{j=1}^{\infty} \frac{1}{j!} \int d\underline{z}_2 \ldots \int d\underline{z}_{j+1} \sum_{k=o}^{j} (-1)^{j-k} \binom{j}{k} S(\underline{z}_1,\ldots,\underline{z}_{k+1},t) \times n_{j+1}(\underline{x}_2,\ldots,\underline{x}_{j+1};\underline{x}_1)\, h_o(\underline{v}_2)\ldots h_o(\underline{v}_{j+1})\, f(\underline{z}_1 t_o) \qquad (3.2)$$

$$f_2(\underline{z}_1,\underline{z}_2 t) = S(\underline{z}_1,\underline{z}_2,t-t_o)\, n_2(\underline{x}_2;\underline{x}_1)\, h_o(\underline{v}_2)\, f(\underline{z}_1,t_o) + \sum_{j=1}^{\infty} \frac{1}{j!} \sum_{k=o}^{j} (-1)^{j-k} \binom{j}{k} S(\underline{z}_1,\ldots,\underline{z}_{k+2},t-t_o) \times n_{j+2}(\underline{x}_2,\ldots,\underline{x}_{j+2};\underline{x}_1)\, h_o(\underline{v}_2)\ldots h_o(\underline{v}_{j+2})\, f(\underline{z}_1,t_o) \qquad (3.3)$$

These are equations of the form

$$f(\underline{z}_1,t) = T(\underline{z}_1,t-t_o)\, f(\underline{z}_1,t_o) \qquad (3.4)$$

and

$$f_2(\underline{z}_1\underline{z}_2,t) = T(\underline{z}_1,\underline{z}_2,t-t_o)\, f(\underline{z}_1,t_o) \qquad (3.5)$$

where $T(\underline{z}_1,t-t_o)$ and $T(\underline{z}_1,\underline{z}_2,t-t_o)$ are operators.

To obtain a closed equation for f we first eliminate $f(t_o)$ from (3.4) and (3.5) to obtain f_2 as a functional of f which is then substituted into the first hierarchy equation (2.19). To eliminate $f(t_o)$ we must find the inverse $T^{-1}(\underline{z}_1,t-t_o)$ of the operator $T(\underline{z}_1,t-t_o)$. This requires that we have a solution to the many-body problem. However, it is possible to calculate the inverse, correct to some power of the density, by solving (3.4) by iteration.

Expanding (3.2) and (3.3) in powers of the density, we obtain

$$f(\underline{z}_1,t) = S(\underline{z}_1,t-t_o)\, f(\underline{z}_1,t_o) + n \int d\underline{z}_3 [S(\underline{z}_1,\underline{z}_3,t-t_o) - S(\underline{z}_1,t-t_o)]\, e^{-V_{13}}\, h_o(\underline{v}_3)\, f(\underline{z}_1,t_o) + \ldots \qquad (3.6)$$

$$\begin{aligned} f_2(\underline{z}_1,\underline{z}_2,t) = {} & S(\underline{z}_1,\underline{z}_2,t-t_o)[n + n^2 \int d\underline{z}_3 \, (e^{-V_{13}} - 1) \\ & \times (e^{-V_{23}} - 1) \, h_o(\underline{v}_3)] \, h_o(\underline{v}_2) \, f(\underline{z}_1,t_o) \\ & + n^2 \int d\underline{z}_3 \, [S(\underline{z}_1,\underline{z}_2,\underline{z}_3,t-t_o) - S(\underline{z}_1,\underline{z}_2,t-t_o)] \\ & \times e^{-V_{123}} \, h_o(\underline{v}_2) \, h_o(\underline{v}_3) \, f(\underline{z}_1,t_o) + \ \ldots \end{aligned} \tag{3.7}$$

We have used the expansions (2.30) of n_2 and n_3 to derive these expressions. (3.6) is solved for $f(t_o)$ by iteration:

$$\begin{aligned} f(\underline{z}_1,t_o) = {} & S(\underline{z}_1,t_o-t) \, f(\underline{z}_1,t) - n \, S(\underline{z}_1,t_o-t) \int d\underline{z}_3 \, [S(\underline{z}_1,\underline{z}_3,t-t_o) \\ & - S(\underline{z}_1,t-t_o)] \, e^{-V_{13}} \, h_o(\underline{v}_3) \, S(\underline{z}_1,t_o-t) \, f(\underline{z}_1,t) + \ldots \end{aligned} \tag{3.8}$$

and when this is substituted into (3.7) there results

$$\begin{aligned} f_2(\underline{z}_1,\underline{z}_2,t) & = T(\underline{z}_1,\underline{z}_2,t-t_o) \, T^{-1}(\underline{z}_1,t-t_o) \, f(\underline{z}_1,t) \\ & = S(\underline{z}_1,\underline{z}_2,t-t_o) \, [n + n^2 \int d\underline{z}_3 (1 - e^{-V_{13}})(1 - e^{-V_{23}}) h_o(\underline{v}_3)] \\ & \quad \times h_o(\underline{v}_2) \, S(\underline{z}_1,t_o-t) \, f(\underline{z}_1,t) + n^2 \int d\underline{z}_3 [S(\underline{z}_1,\underline{z}_2,\underline{z}_3,t-t_o) \\ & \quad - S(\underline{z}_1,\underline{z}_2,t-t_o)] \, e^{-V_{123}} \, h_o(\underline{v}_2) \, h_o(\underline{v}_3) \, S(z_1,t_o-t) \, f(z_1,t) \\ & \quad - n^2 \int d\underline{z}_3 \, S(\underline{z}_1,\underline{z}_2,t-t_o) \, S(\underline{z}_1,t_o-t)[S(\underline{z}_1,\underline{z}_3,t-t_o) \\ & \quad - S(\underline{z}_1,t-t_o)] \, e^{-V_{13}} \, h_o(\underline{v}_2) \, h_o(\underline{v}_3) \, S(\underline{z}_1,t_o-t) \, f(\underline{z}_1,t) + \, .. \end{aligned} \tag{3.9}$$

If we consider a gas of hard spheres or hard discs, when the hierarchy equations can be written as in (2.20), f_2 need only be evaluated for precollision configurations of two particles i.e. for $(\underline{x}_1-\underline{x}_2)\cdot(\underline{v}_1-\underline{v}_2) < o$. In this case (3.9) becomes, after some rearrangement of terms

$$
\begin{aligned}
f_2(\underline{z}_1,\underline{z}_2,t) = {} & [n + n^2 \int d\underline{x}_3\ (e^{-V_{13}} - 1)\ (e^{-V_{23}} - 1)]\ h_o(\underline{v}_2)\ f(\underline{z}_1,t) \\
& + n^2 \int d\underline{z}_3\ e^{-V_{123}}\ [S(\underline{z}_1,\underline{z}_2,\underline{z}_3,t-t_o) - S(\underline{z}_1,\underline{z}_3,t-t_o)] \\
& \times h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ S(\underline{z}_1,t_o-t)\ f(\underline{z}_1,t) + n^2 \int d\underline{z}_3\ e^{-V_{13}} \\
& \times (1 - e^{-V_{23}})\ [1 - S(\underline{z}_1,\underline{z}_3,t-t_o)\ S(\underline{z}_1,t_o-t)] \\
& \times h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,t) + \ldots
\end{aligned}
\qquad (3.10)
$$

Here and in (3.9) we have explicitly indicated the first two terms in the density expansion of the functional relationship between f and f_2. This expansion is similar to one derived by Cohen[31]. It differs from Cohen's in the choice of initial conditions. Cohen, in effect, takes

$$f_k = (n)^{k-1}\ h_o(\underline{v}_2) \ldots h_o(\underline{v}_k)\ f$$

i.e. n_{k-1} is replaced by $(n)^{k-1}$ in (2.28).

The first term in (3.10) involves the first two terms in the density expansion of $n_2(\underline{x}_2;\underline{x}_1)$. It is the contribution to f_2 from pairs of particles, the velocities of which are uncorrelated. The next term is a "three-body" term. It vanishes unless at least two collisions take place in the time interval (t_o,t); a third collision is about to occur at time t. For instance if particle 2 does not interact with 1 or 3 then

$$S(\underline{z}_1,\underline{z}_2,\underline{z}_3,t-t_o) = S(\underline{z}_1,\underline{z}_3,t-t_o)\ S(\underline{z}_2,t-t_o)$$

or if only particles 2 and 3 interact, then

$$S(\underline{z}_1,\underline{z}_2,\underline{z}_3,t-t_o)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3) = S(\underline{z}_1,t-t_o)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)$$

since the 3-particle operator transforms the velocities of particles 2 and 3 to precollision values and by conservation of energy, the product of the equilibrium velocity distribution functions remains unchanged.

The collision sequences which do contribute to the 3-body term have been characterized by Sengers^{10}. The sequence in which 1 and 2 collide, followed by an interaction between 1 and 3 and then between 1 and 2 is such a sequence. There are, in addition to sequences of 3 collisions, sequences involving 4 collisions but no higher number.

Contributions to the third term of (3.9) come from configurations in which particles 2 and 3 are overlapping at time t i.e. $|\underline{x}_2-\underline{x}_3| < a$, and in which particles 1 and 3 interact in the interval (t_o, t).

Our derivation of a closed equation for f essentially results from integrating the equations of motion from a time t_o at which the n-particle velocity distribution functions can be expressed in terms of the one-particle distribution function. Because of the special ensemble which was constructed to evaluate the velocity autocorrelation function, we have taken $t_o = o$. However, there may be other choices for t_o. For instance, if the gas is of sufficiently low density, it will be a good approximation to neglect the possibility that two particles which are on collision trajectories have interacted either directly or indirectly in the past. We may then neglect all terms in (3.10) apart from those corresponding to uncorrelated pre-collision velocities, or what is equivalent take $t_o = t$. We then obtain

$$f_2(\underline{z}_1,\underline{z}_2 t) = n\, h_o(\underline{v}_2)\, f(\underline{z}_1 t)$$

$$(\underline{x}_1-x_2).(\underline{v}_1-\underline{v}_2) < o \qquad (3.11)$$

and hence a linearized form of Boltzmann's equation.

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} =$$

$$n \int d\underline{w} \int d\underline{a}.(\underline{w}-\underline{v})\ \varepsilon[(\underline{w}-\underline{v}).\underline{a}]\ [h_o(\underline{w}')\ f(\underline{x},\underline{v}',t) - h_o(\underline{w})\ f(\underline{x},\underline{v},t)] \qquad (3.12)$$

We may suppose that as the density of the gas increases configurations of three particles in close proximity to each other will occur more frequently. We might then consider the correction to Boltzmann's equation which arises from the second and third terms of the expansion (3.10). The time t_o is then chosen to be before the three particles interact, since if they have not interacted previously, the factorization (2.28) will apply. If the time t is sufficiently long it will be a good approximation to take the limit as $|t-t_o| \to \infty$ of those terms of (3.10) under consideration. The resultant time independent functional relating f_2 to f leads to a linearized form of the Choh-Uhlenbeck equation.

One cannot continue this process by taking into account the four-body term of (3.10). It is found that there are certain collision sequences involving four particles which cause the four-body operator to diverge as $|t-t_o| \to \infty$. The same effect occurs for higher order terms in the expansion (3.10). These divergences are a result of the method of analysing the dynamics of the complete system by considering the dynamics of small groups of particles isolated from the rest of the system for long periods of time.

Thus it is not possible to verify Bogoliubov's assumption about the functional form of f_2 by considering in succession two-, three-.. body effects. A rearrangement of (3.10) is required, to take into account that particles frequently collide. A partial resummation, which removes the divergence due to four particle dynamics, has been carried out by Kawasaki and Oppenheim[30], Cohen[31], Haines[32] and Dorfman[33].

However, the use of cluster expansions does not seem a very practical way of obtaining a time-independent functional relationship between f and f_2. In the next section we shall re-examine the hierarchy equations to obtain more useful expansions for the one- and two-particle distribution functions.

It should be mentioned that corrections to Boltzmann's equation may be obtained which involve time dependent functionals. An equation such as

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = n_2(a)\ B(f) + U_3(t;f) + \ldots + U_n(t;\ f) \tag{3.13}$$

where B is a linearized form of Boltzmann's collision operator, and $U_k(t)$ are time-dependent operators depending on the dynamics of k particles, is obtained by retaining the first few terms of the expansion (3.10) and substituting into the hierarchy equation for f. While the functionals $U_4(t), U_5(t)$ etc. are divergent functions of time, $U_k(t;f(t))$ may approach zero for long times, provided the solution of (3.13) approaches the equilibrium value of f rapidly enough. This is because $U_k(t;f) = o$ when $f \propto h_o$.

To prove that solutions of (3.13) have this property would seem a difficult task. However the properties of Boltzmann's operator B are such that if the effects of the other operators are small, the rapid approach to equilibrium exhibited by the solutions of Boltzmann's equation may be seen in the solutions of (3.10). In Chapter 5 we calculate the coefficient of self-diffusion for a one dimensional system with an equation of the form (3.13), with $n = 3$. A small correction only to the value predicted by Boltzmann's equation is obtained, suggesting that it is necessary to solve (3.13) for large values of n to obtain accurate values of the coefficient of self-diffusion for dense gases.

3.4 ALTERNATIVE FORM OF THE TRANSPORT EQUATION

The equation for f derived in the previous section involved a sum of terms associated with groups of particles separated from the remainder of the system for some period of time. Such configurations of the fluid should provide only small contributions to the time development of f since they have only a small probability of occurring. While equation (3.13) may take into account this property of the fluid, it is preferable to derive equations for f where the high probability of collisions occurring is made explicit from the beginning.

We now derive an equation of the form

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = n_2(a)\ B(f) + \int_0^t dt'V\big(t-t';f(t')\big) \qquad (4.1)$$

in such a way that approximations to the functional V(t) can be calculated readily.

Equation (4.1) is not difficult to derive in a formal fashion. It can be obtained readily by Laplace transformation.of equations (3.4) and (3.5) which express f(t) and $f_2(t)$ as functionals of $f(t_o)$. The derivation of Lebowitz, Percus and Sykes[63] is closest to ours. However we have proceeded further than their formal derivation of (4.1) in that we obtain a systematic sequence of approximations to V(t).

Divergences appear in this approach if approximations to V(t) do not approach zero rapidly enough with time. For not only does the second term of the right side have to remain finite for all times, it must also approach zero sufficiently rapidly so that for large times f attains a stationary form.

These conditions lead us to seek expansions of the functionals in the equations

$$f(\underline{z}_1,t) = T(\underline{z}_1,t)\ f(\underline{z}_1,o) \qquad (4.2)$$

$$f(\underline{z}_1,\underline{z}_2,t) = T(\underline{z}_1,\underline{z}_2,t)\ f(\underline{z}_1,o) \qquad (4.3)$$

in which each term of the expansions approaches zero with increasing time. In physical terms, this corresponds to ensuring that contributions from the dynamics of particles isolated for long periods are small. There are a number of ways by which this can be achieved and these lead to equations of varying suitability for calculating transport properties.

A large class of expansions of the operators $T(\underline{z}_1,t)$ and $T(\underline{z}_1,\underline{z}_2,t)$ can be generated by the following simple procedure. We first write the hierarchy equations (2.20) for a gas of rigid spheres, discs or rods as

$$\left(\frac{\partial}{\partial t} + L_n + \lambda_n\right) f_n(t) = \sum_{i=1}^{n} J_{i,n+1}[f_{n+1}(t)] + \lambda_n\ f_n(t) \qquad (4.4)$$

We have added the term $\lambda_n f_n$ to both sides of the hierarchy equations. λ_n may be chosen to be a number, function or operator. However, Holtzmann's equation should be obtained as the first of a series of approximate equations for the single particle distribution function. Furthermore, a first correction to Boltzmann's equation should give a value of the coefficient of self-diffusion in sufficiently good agreement with experiment.

Equation (4.4) is integrated next to obtain

$$\begin{aligned} f_n(t) &= I(\underline{z}_1,..,\underline{z}_n,t)f_n(o) \\ &+ \int_o^t dt_1\ I(\underline{z}_1,..,\underline{x}_n,t-t_1)\ [\sum_{i=1}^{n} J_{i,n+1}[f_{n+1}(t_1)] + \lambda_n f_n(t_1)] \end{aligned} \qquad (4.5)$$

where

$$I(\underline{z}_1,..,\underline{z}_n,t) = \exp[-(L_n+\lambda_n)t] \qquad (4.6)$$

By a series of successive substitutions we obtain from (4.5) the following expansions for f and f_2:

$$f(t) = I(\underline{z}_1,t)\ f(o) + \int_0^t dt_1\ I(\underline{z}_1,t-t_1)\ \{J_{12}[I(\underline{z}_1,\underline{z}_2,t_1)\ f_2(o)]$$

$$+ \lambda_1\ I(\underline{z}_1,t_1)\ f_1(o) + J_{12}[\int_0^{t_1} dt_2\ I(\underline{z}_1,\underline{z}_2,t_1-t_2)(J_{13} + J_{23})$$

$$[I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_2)\ f_3(o)]] + \lambda_2\ I(\underline{z}_1,\underline{z}_2,t_2)\ f_2(o) + \ldots \} \qquad (4.7)$$

$$f_2(t) = I(\underline{z}_1,\underline{z}_2,t)\ f_2(o) + \int_0^t dt_1\ I(\underline{z}_1,\underline{z}_2,t-t_1)\ \{(J_{13} + J_{23})$$

$$[I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1)\ f_3(o)] + \lambda_2\ I(\underline{z}_1,\underline{z}_2,t_1)\ f_2(o) + \ldots \} \qquad (4.8)$$

We mention at this point that we need consider only those configurations of particles 1 and 2 for which $(\underline{x}_1-\underline{x}_2).(\underline{v}_1-\underline{v}_2) < o$.

On substitution of initial conditions (2.30) into (4.7) and (4.8) we obtain expansions for f and f_2 in terms of $f(o)$. Before showing how $f(o)$ can be eliminated from these expansions, we express the first term in the expansion (4.8) in the form

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ I(\underline{z}_1,t)\ f(o) + \ldots \qquad (4.9)$$

It is then possible to obtain Enskog's modification to Boltzmann's equation. For the purpose of deriving (4.9), define

$$y(\underline{z}_1,\underline{z}_2,t) = \exp[-(L_2+\lambda_1+\lambda')t]\ n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(z_1,o) \qquad (4.10)$$

where

$$\lambda' = \lambda_2 - \lambda_1$$

If the operators L_2, λ_1 and λ' do not commute, the evaluation of $y(t)$ is not straightforward. Here we describe an iterative scheme for its evaluation.

We note that $n_2(\underline{x}_2;\underline{x}_1)$ is a function of the single variable $\underline{r} = \underline{x}_1 - \underline{x}_2$ (which we write as $\overline{n}(r)$) and that y satisfies the equation

$$\left(\frac{\partial}{\partial t} + \underline{v}_1.\frac{\partial}{\partial \underline{x}_1} + \lambda_1 + (\underline{v}_1-\underline{v}_2).\frac{\partial}{\partial \underline{r}} - \frac{1}{m}\frac{\partial V}{\partial \underline{r}}.\left(\frac{\partial}{\partial \underline{v}_1} - \frac{\partial}{\partial \underline{v}_2}\right) + \lambda'\right)$$

$$\times\ y(\underline{x}_1,\underline{v}_1,\underline{r},\underline{v}_2,t) = 0 \qquad (4.11)$$

where $V(r)$ is the interparticle potential for rigid particles. Equation (4.11) can be solved by iteration as follows.

$$y(t) = e^{-(L_1+\lambda_1)t}\,\bar{n}(r)\,h_o(\underline{v}_2)\,f(\underline{z}_1,o)$$

$$-\int_o^t dt_1\,e^{-(L_1+\lambda_1)(t-t_1)}\left[(\underline{v}_1-\underline{v}_2).\frac{\partial}{\partial\underline{r}} - \frac{1}{m}\frac{\partial}{\partial\underline{r}}\,.\left(\frac{\partial}{\partial\underline{v}_1}-\frac{\partial}{\partial\underline{v}_2}\right) + \lambda'\right]$$

$$x\;e^{-(L_1+\lambda_1)t_1}\,\bar{n}(r)\,h_o(\underline{v}_2)\,f(\underline{z}_1,o) + \ldots$$

$$= \bar{n}(r)\,h_o(\underline{v}_2)\,I(\underline{z}_1,t)\,f(\underline{z}_1,o)$$

$$-\int_o^t dt_1\,I(\underline{z}_1,t-t_1)\left[(\underline{v}_1-\underline{v}_2).\frac{\partial}{\partial\underline{r}} - \frac{1}{m}\frac{\partial V}{\partial\underline{r}}\left\{\frac{\partial}{\partial\underline{v}_1}-\frac{\partial}{\partial\underline{v}_2}\right\} + \lambda'\right]$$

$$x\;\bar{n}(r)\,h_o(\underline{v}_2)\,I(\underline{z}_1,t_1)\,f(\underline{z}_1,o) + \ldots \tag{4.12}$$

This expansion contains the term

$$n_2(\underline{x}_2;\underline{x}_1)\,h_o(\underline{v}_2)\,I(\underline{z}_1,t)\,f(\underline{z}_1,o)$$

which we were seeking. On substitution of (4.12) into (4.8) we obtain an equation of the form

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\,h_o(\underline{v}_2)\,I(\underline{z}_1,t)\,f(\underline{z}_1,o) + K_2\left(\underline{z}_1,\underline{z}_2,t;f(o)\right) \tag{4.13}$$

where $K_2(t)$ is an operator.

We also write (4.7) as

$$f(t) = I(\underline{z}_1,t)\,f(o) + K_1\left(\underline{z}_1,t;f(o)\right) \tag{4.14}$$

and we now show how to eliminate $f(o)$ from equations (4.13) and (4.14).

Since $K_1(o) = K_2(o) = o$ we may write, using $K(t)$ to denote either $K_1{}'t)$ or $K_2(t)$,

$$K(t) = \int_o^t dt_1\,\frac{d}{dt_1}\left[K(t_1)\,e^{-(L_1+\lambda_1)(t-t_1)}\right]$$

$$= \int_o^t dt_1\left[K'(t-t_1)\,e^{-(L_1+\lambda_1)t_1} + K(t-t_1)\,(L_1+\lambda_1)\,e^{-(L_1+\lambda_1)t_1}\right] \tag{4.15}$$

$K'(t)$ denotes the time derivative of the operator $K(t)$.

Using (4.15), equations (4.14) and (4.13), can be written as

$$f(t) = e^{-(L_1+\lambda_1)t}\, f(o) + \int_o^t dt'\; M_1(\underline{z}_1, t-t')\; e^{-(L_1+\lambda_1)t'} f(o) \tag{4.16}$$

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\; f(t) + \int_o^t dt'\; M_2(\underline{z}_1,\underline{z}_2, t-t')\; e^{-(L_1+\lambda_1)t'}\; f(o) \tag{4.17}$$

where $M_1(t)$ and $M_2(t)$ are operators.

To eliminate $f(o)$ from these equations, we solve (4.16) iteratively.

$$e^{-(L_1+\lambda_1)t}\, f(o) = f(t) - \int_o^t dt_1\; M_1(t-t_1)\; f(t_1)$$

$$+ \int_o^t dt_1\; M_1(t-t_1) \int_o^{t_1} dt_2\; M_1(t_1-t_2)\; f(t_2) + \ldots \tag{4.18}$$

On substitution of (4.18) into (4.17) we obtain the desired relationship between f and f_2.

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\; h_o(\underline{v}_2)\; f(t) + \int_o^t dt_1\; M_2(t-t_1)[f(t_1)$$

$$- \int_o^{t_1} dt_2\; M_1(t_1-t_2)\; f(t_2) + \ldots] \tag{4.19}$$

Terms such as

$$\int_o^t dt_1 \int_o^{t_1} dt_2 \ldots \int_o^{t_{n-1}} dt_n\; M_2(t-t_1)\; M_1(t_1-t_2) \ldots M_1(t_{n-1}-t_n)\; f(t_n)$$

which occur in (4.19) may be rewritten as

$$\int_o^t dt_1 \; [\int_o^{t_1} dt_2 \ldots \int_o^{t_{n-1}} dt_n\; M_2(t_1-t_2)\; M_1(t_2-t_3) \ldots M_1(t_{n-1}-t_n)] f(t-t_1)$$

Hence (4.19) is an expression of the form

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\; h_o(\underline{v}_2)\; f(t) + \int_o^t dt'\; \tilde{M}(\underline{z}_1,\underline{z}_2, t-t')\; f(t') \tag{4.20}$$

With this relationship and the hierarchy equation for f we obtain a closed equation for f, of the form (4.1). Our derivation is longer than other derivations but this is because we intend to derive explicit approximations to the operator $\breve{M}$. The approach of this section enables us to do this. We next consider various first corrections to Boltzmann's equation which result from different choices of λ_n.

3.5 CORRECTIONS TO BOLTZMANN'S EQUATION

We continue our discussion of the scheme proposed in the previous section. We derive closed equations for f which fully take into account two and three body collision sequences and which approximate the dynamics of four or more particles. We consider two choices of the factors λ_n. These correspond to two different ways of approximating many-body dynamics.

The first choice is

$$\lambda_k = n\alpha(\underline{v}) \qquad k = 1,2,\ldots \tag{5.1}$$

where

$$n\alpha(\underline{v}) = n \int d\underline{w} \int d\underline{a}.(\underline{w}-\underline{v})\ \varepsilon[\underline{a}.(\underline{w}-\underline{v})]\ h_o(\underline{w}) \tag{5.2}$$

is the frequency of collisions experienced by a particle moving with a velocity $\underline{v}$ through an equilibrium environment.

A second choice is the operator λ_k, defined on functions of $z_1,\ldots,z_k$, by

$$\lambda_k = -nB(\underline{v}_1) - \ldots - nB(\underline{v}_k) \tag{5.3}$$

where $B(\underline{v})$ is the Lorentz-Boltzmann collision operator, defined on functions of $\underline{v}$ by

$$B(\underline{v})\ g(\underline{v}) = \int d\underline{w} \int d\underline{a}.(\underline{w}-\underline{v})\ \varepsilon[\underline{a}.(\underline{w}-\underline{v})]\ [h_o(\underline{w}')\ \ g(\underline{v}') - h_o(\underline{w})\ g(\underline{v})]$$

The motivation for choosing λ_k as in (5.3) is that the approximation

$$f_{k+1}(\underline{z}_1,..,\underline{x}_i,\underline{v}_i,..,\underline{z}_k,\underline{x}_i-\underline{a},\underline{v}_{K+1},t) = n\, h_o(\underline{v}_{k+1})\, f_k(\underline{z}_1,..,\underline{z}_k,t)$$

$$\text{when } \underline{a}.(\underline{v}_{k+1}-\underline{v}_i) > o \tag{5.4}$$

is good for dilute gases and small values of k. It is a consequence of assuming that the velocities of particles i and $k+1$, which are in a precollision configuration, are uncorrelated. When (5.4) is substituted into the hierarchy equation for f_k, we obtain

$$\left(\frac{\partial}{\partial t} + L_k\right) f_k = -\lambda_k f_k + \ldots \tag{5.5}$$

For a dilute gas we have isolated the most important part of the collision term in the equation for f_k. Therefore, in the study of moderately dense gases, the operator λ_k, defined by (5.3), should fairly accurately represent the effect of the rest of the system on the dynamics of a small group of particles. The choice of $\lambda_k = n\alpha(\underline{v})$ is a cruder approximation of many-body effects. However the simplicity of this choice leads to equations which are easier to analyse than those derived from (5.3).

The case when λ_k is given by equation (5.3) is treated in Appendix B.

In this section we consider the latter choice for λ_k. We first note that, when $(\underline{x}_2-\underline{x}_1).(\underline{v}_2-\underline{v}_1) < o$

$$\exp[-(L_2+ n\alpha(\underline{v}_1))t]\, n_2(\underline{x}_2;\underline{x}_1)\, h_o(\underline{v}_2)\, f(\underline{z}_1,o)$$

$$= \exp\{-n\alpha(\underline{v}_1)t\}\, \bar{n}\{\underline{x}_1-\underline{x}_1-(\underline{v}_2-\underline{v}_1)t\}\, h_o(\underline{v}_2)\, f(\underline{x}_1-\underline{v}_1t,\underline{v}_1,o)$$

$$= [n_2(\underline{x}_2;\underline{x}_1) + \int_o^t dt' \frac{\partial}{\partial t'} \bar{n}(\underline{x}_2-\underline{x}_1-(\underline{v}_2-\underline{v}_1)t')]\, h_o(\underline{v}_2)$$

$$\times\, I(\underline{z}_1,t)\, f(\underline{z}_1,o) \tag{5.6}$$

Now to second order in the density

$$\frac{\partial}{\partial \underline{r}} \bar{n}(r) = n^2 \int d\underline{a}\, (e^{-V(\underline{r}-\underline{a})} - 1) \tag{5.7}$$

which is a consequence of the density expansion (2.30) for n_2.

Hence (5.6) becomes

$$\begin{aligned} I(\underline{z}_1,\underline{z}_2,t)\, f_2(o) = {} & n_2(\underline{x}_2;\underline{x}_1)\, h_o(\underline{v}_2)\, I\, (\underline{z}_1,t)\, f(o) \\ & + n^2 \int_o^t dt' \int d\underline{a}.(\underline{v}_1-\underline{v}_2)\, I(\underline{z}_1,\underline{z}_2,t-t') \\ & x\, (e^{-V(\underline{x}_1-\underline{x}_2-a)} - 1)\, h_o(\underline{v}_2)\, I(\underline{z}_1,t')\, f(\underline{z}_1,o) \end{aligned} \tag{5.8}$$

Furthermore, with $\lambda_k = n\alpha(\underline{v})$,

$$\begin{aligned} f(\underline{z}\;;t) = {} & I(\underline{z}_1,t)\, f(o) + n\int_o^t dt_1\, I(\underline{z}_1,t-t_1) \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{31} \\ & x\, \varepsilon(\underline{a}.\underline{v}_{31})\, h_o(\underline{v}_3)\, I(\underline{x}_1,\underline{v}_1',t_1)\, f(\underline{x}_1,\underline{v}_1',o) + \ldots \end{aligned} \tag{5.9}$$

and

$$\begin{aligned} f_2(\underline{z}_1,\underline{z}_2\; t) = {} & I(\underline{z}_1,\underline{z}_2,t)\, f(o) + n^2\int_o^t dt_1\, I(\underline{z}_1,\underline{z}_2 t-t_1) \\ & x\, \Big\{\int d\underline{v}_3 \int d\underline{a}.\underline{v}_{31}\, \varepsilon(\underline{a}.\underline{v}_{31})\, I(\underline{x}_1,\underline{v}_1',\underline{x}_2,\underline{v}_2,\underline{x}_1+\underline{a},\underline{v}_3',t_1) \\ & x\, h_o(\underline{v}_2)\, h_o(\underline{v}_3')\, f(\underline{x}_1,\underline{v}_1',o) \\ & + J_{23}[I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1)\, h_o(\underline{v}_2)\, h_o(\underline{v}_3)\, f(\underline{z}_1,o)]\Big\} + \ldots \end{aligned} \tag{5.10}$$

These equations follow from (4.7) and (4.8).

From equations (5.8 - 5.10) we obtain

$$\begin{aligned} f_2(t) = {} & n_2(\underline{x}_2;\underline{x}_1)\, h_o(v_2)\, f(t) + n^2 \int_o^t dt_1\, I(\underline{z}_1,\underline{z}_2,t-t_1) \\ & x\, \Big\{ \int d\underline{a}.\underline{v}_{12}\, (1 - e^{-V(\underline{x}_1-\underline{x}_2-\underline{a})})\, h_o(\underline{v}_2)\, f(\underline{z}_1,t_1) \\ & + J_{13}\, \big[\big(I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1) - I(\underline{z}_1,\underline{z}_3,t_1)\big)\, h_o(\underline{v}_2)\, h_o(\underline{v}_3)\, f(\underline{z}_1,o)\big] \\ & + J_{23}\, [I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1) h_o(\underline{v}_2)\, h_o(\underline{v}_3)\, f(\underline{z}_1,o)] + \ldots \Big\} \end{aligned} \tag{5.11}$$

To obtain from this equation a suitable relationship between f and f_2 requires that we analyse the dynamics of three particles.

If we examine equations (5.11) and the definition of the operators J_{13} and J_{23}, we see that we must evaluate the expressions

$$I(\underline{z}_1, \underline{z}_2, \underline{x}_1 - \underline{a}, \underline{v}_3, t)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1, o) \qquad (5.12a)$$

$$I(\underline{x}_1, \underline{v}_1', \underline{z}_2, \underline{x}_1 + \underline{a}, \underline{v}_3', t)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3')\ f(\underline{x}_1, \underline{v}_1', o) \qquad (5.12b)$$

$$\text{with } \underline{a}\cdot(\underline{v}_3 - \underline{v}_1) > o$$

and

$$I(\underline{z}_1, \underline{z}_2, \underline{x}_2 - \underline{a}, \underline{v}_3, t)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1, o) \qquad (5.13a)$$

$$I(\underline{z}_1, \underline{x}_2, \underline{v}_2', \underline{x}_2 + \underline{a}, \underline{v}_3', t)\ h_o(\underline{v}_2')\ h_o(\underline{v}_3')\ f(\underline{z}_1, o) \qquad (5.13b)$$

$$\text{with } \underline{a}\cdot(\underline{v}_3 - \underline{v}_2) > o$$

Collision sequences involving three isolated discs or spheres have been considered by Sandri, Sullivan and Norem[68] and by Cohen, Murphy and Foch[69]. It has been shown that no more than four collisions are possible and that the fraction of collision sequences with three collisions for which a fourth collision can occur is of the order of one or two parts in a thousand. Hence we shall consider only the possibility that three collisions occur among three particles.

There are two different sets of configurations which we must consider. The first set, which occurs in the evaluation of (5.12a) and (5.13a), is that at time t_1 particle 3 is about to collide with either of particles 1 or 2 which would otherwise have collided at time t. The second set, applying to (5.12b) and (5.13b), consists of those configurations in which particle 3 is about to collide with 1 or 2 at time t_1 thus causing 1 and 2 to collide at time t.

Denoting a collision between particles i and j by (ij) and a collision which would have occurred, if an earlier collision had not taken place by $(\overline{ij})$, we need consider the following sequences.

(A collision written to the left of another indicates it occurred earlier.)

For $I(\underline{z}_1,\underline{z}_2,\underline{x}_1-\underline{a},\underline{v}_3,t)$ consider $(23)(13)(\overline{12})$.

For $I(\underline{x}_1,\underline{v}_1',\underline{z}_2,\underline{x}_1-\underline{a},\underline{v}_3',t_1)$ consider $(23)(13)(12')$ and $(12)(13)(12)$

For $I(\underline{z}_1,\underline{z}_2,\underline{x}_2-\underline{a},\underline{v}_3,t_2)$ consider $(13)(23)(\overline{12})$

For $I(\underline{z}_1,\underline{x}_2,\underline{v}_2',\underline{x}_2+\underline{a},\underline{v}_3',t_1)$ consider $(13)(23)(12)$ and $(12)(23)(12)$

To characterize the configurations which lead to a particular sequence of collisions, we introduce the expression

$$\int_o^t dt' \int d\underline{a}.\underline{v}_{jk}\, \varepsilon(\underline{a}.\underline{v}_{jk})\, \delta\{\underline{x}_j - \underline{v}_j(t-t') + \underline{a} - \underline{x}_k + \underline{v}_k(t-t')\} \tag{5.14}$$

which equals one if particles j and k have collided in the time interval (o,t) and zero if they have not.

To see that this is appropriate we transform the integration in (5.14), which is over the surface of a hemisphere, into an integration over a disc of radius a in a plane perpendicular to the relative velocity $\underline{v}_j - \underline{v}_k$. (See Figure 5.1)

Then

$$\int d\underline{a}.\underline{v}_{jk}\, \varepsilon(\underline{a}.\underline{v}_{jk}) = \int_o^a db\, b \int_o^{2\pi} d\phi\, |\underline{v}_{jk}|$$

$$\delta(\underline{x}_j - \underline{x}_k - \underline{v}_{jk}(t-t') + \underline{a}) = \delta[(\underline{x}_j - \underline{x}_k + \underline{a}).\underline{v}_{jk}/|\underline{v}_{kj}| - |\underline{v}_{jk}|(t-t')]$$
$$\times \frac{1}{b}\delta[(\underline{x}_j - \underline{x}_k)_\perp - b]\; \delta(\tilde{\phi} - \phi)$$

We have written the three dimensional delta function of (5.14) as a product of one dimensional delta functions. We have denoted the projection of the vector $\underline{x}_j - \underline{x}_k$ on to a plane perpendicular to the vector $\underline{v}_{jk}$ by the polar coordinates $\left((\underline{x}_j - \underline{x}_k)_\perp, \tilde{\phi}\right)$.

The delta function $\delta[(\underline{x}_j - \underline{x}_k)_\perp - b]$ limits the configurations

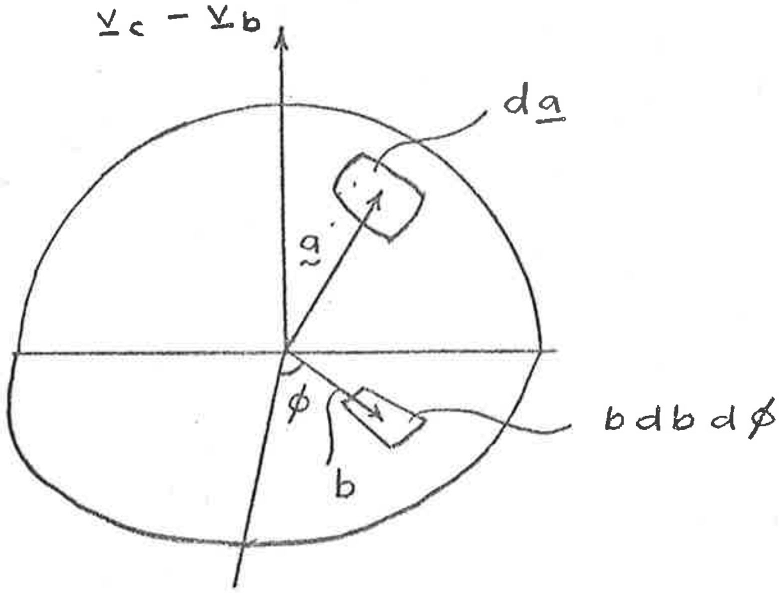

Figure 5.1. Relation between $\underline{a}$ and (b,ϕ).

of j and k which contribute to (5.14) to those for which j and k would have collided sometime in the past. The delta function $\delta\,[(\underline{x}_j - \underline{x}_k + \underline{a})\cdot\underline{v}_{jk}/|\underline{v}_{jk}| - |\underline{v}_{jk}|(t-t')]$ specifies the collision time as t'.

Using (5.14) we may write, to take (5.12a) as an example,

$$I(\underline{z}_1,\underline{z}_2,\underline{x}_2-\underline{a},\underline{v}_3,t_1)\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; f(\underline{z}_1,o) = I(\underline{z}_1,t_1)\; h_o(\underline{v}_2)\; h_o(\underline{v}_3) \times f(\underline{z}_1,o)$$

$$+ \int_o^{t_1} dt_2 \int d\underline{b}\cdot\underline{v}_{31}\; \varepsilon(\underline{b}\cdot\underline{v}_{31})\; \delta\big(\underline{x}_2 - \underline{a} - \underline{v}_3(t_1-t_2) - \underline{b} - \underline{x}_1$$

$$+ \underline{v}_1(t_1-t_2)\big)\; [I(\underline{z}_1,\underline{z}_2,\underline{x}_2-\underline{a},\underline{v}_3,t_1) - I(\underline{z}_1,t_1)]\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; f(\underline{z}_1,o) \tag{5.15}$$

The first term of the right side is the value of the expression for those configurations in which no interaction among the three particles occurs in the time interval (o,t). The second term results from all configurations in which particles 1 and 3 collided at time t_2, the collision being specified by the vector $\underline{b}$.

If the configuration of particles 1,2 and 3 at time t_1 is such that at the earlier time t_2, particles 1 and 3 collided, then

$$I(\underline{x}_1,\underline{v}_1,\underline{x}_2,\underline{v}_2,\underline{x}_2-\underline{a},\underline{v}_3,\underline{t}_1)\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; f(\underline{z}_2,o)$$

$$= \exp[-n\alpha(\underline{v}_1)(t_1-t_2) - n\alpha(\underline{v}_1')t_2]\; h_o(\underline{v}_2)\; h_o(\underline{v}_3')$$

$$\times f(\underline{x}_1-\underline{v}_1(t_1-t_2) - \underline{v}_1' t_2,\underline{v}_1',o)$$

where $\underline{v}_1'$ and $\underline{v}_3'$ are the velocities of particles 1 and 3 prior to their collision at time t_2.

Hence (5.15) can be written

$$I(\underline{z}_1,\underline{z}_2,\underline{x}_2-\underline{a},\underline{v}_3,t_1)\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; f(\underline{z}_1,o) = I(\underline{z}_1,t_1)\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)$$

$$\times f(\underline{z}_1,o) + \int_o^{t_1} dt_2 \int d\underline{b}\cdot\underline{v}_{31}\; \varepsilon(\underline{b}\cdot\underline{v}_{31})\; I(\underline{z}_1,\underline{x}_2-\underline{a},\underline{v}_3,t_1-t_2)\; \delta(\underline{x}_2-\underline{a}-\underline{x}_1-\underline{b})$$

(cont.)

$$\times\ h_o(\underline{v}_2)\ [h_o(\underline{v}_3')\ I(\underline{x}_1,\underline{v}_1',t_2)\ f(\underline{x}_1,\underline{v}_1',o) - h_o(\underline{v}_3)\ I(\underline{x}_1,\underline{v}_1,t_2)\ f(\underline{x}_1,\underline{v}_1,o)] \tag{5.16}$$

The expressions (5.12b) and (5.13a,b) can be analysed in a similar fashion. On substitution of the approximation

$$I(\underline{x}_1,\underline{v}_1,t_2)\ f(\underline{x}_1,\underline{v}_1,o) = f(\underline{x}_1,\underline{v}_1,t_2)$$

into (5.16) we obtain

$$I(\underline{z}_1,\underline{z}_2,\underline{x}_2-\underline{a},\underline{v}_3,t_1)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o) = I(\underline{z}_1,t_1)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)$$

$$+ \int_o^{t_1} dt_2 \int d\underline{b}.\underline{v}_{31}\ \varepsilon(\underline{b}.\underline{v}_{31})\ I(\underline{z}_1,\underline{x}_2-\underline{a},\underline{v}_3,t_1-t_2)\ \delta(\underline{x}_2-\underline{a}-\underline{x}_2+\underline{b})$$

$$\times\ h_o(\underline{v}_2)\ [h_o(\underline{v}_3')\ f(\underline{x}_1,\underline{v}_1',t_2) - h_o(\underline{v}_3)\ f(\underline{x}_1,\underline{v}_1,t_2)] \tag{5.17}$$

When (5.17) and similar expressions are substituted into (5.11) there results

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(t) + n^2 \int_o^t dt_1\ \exp[-n\alpha(\underline{v}_1)(t-t_1)]$$

$$\times\ S(\underline{z}_1,\underline{z}_2,t-t_1)\ \{C_1(f(t_1)) + \int_o^{t_1} dt_2\ (C_2(t_1-t_2) + \ldots + C_4(t_1-t_2)$$

$$- C_5(t_1-t_2))\ f(t_2)\} \tag{5.18}$$

where the collision operators $C_1, .., C_5$ are given as follows:

$$C_1(f) = \int d\underline{a}.\underline{v}_{12}\ (1 - e^{-V(\underline{x}_{12}-\underline{a})})\ h_o(\underline{v}_2)\ f(\underline{z}_1,t_1)$$

$$+ \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{31}\ \varepsilon(\underline{a}.\underline{v}_{31})\ h_o(\underline{v}_2)\ [(e^{-V(\underline{x}_{12}+\underline{a})} - 1)\ h_o(\underline{v}_3')$$

$$\times\ f(\underline{x}_1,\underline{v}_1',t_1) - (e^{-V(\underline{x}_{12}-\underline{a})} - 1)\ h_o(\underline{v}_3)\ f(\underline{x}_1,\underline{v}_1,t_1)] \tag{5.19}$$

The first term of the right side of this expression for C_1 already appears in (5.11). The other terms are a consequence of the fact that operators such as $I(\underline{z}_1,\underline{z}_3,t)$ are non-zero when $|\underline{x}_2-\underline{x}_3| < a$ whereas $I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t)$ is zero for such values.

$$C_2(t_1-t_2)\ f(t_2) = \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{31}\ \varepsilon(\underline{a}.\underline{v}_{31}) \int d\underline{b}.(\underline{v}_2-\underline{v}_1')\ \varepsilon[\underline{b}.(\underline{v}_2-\underline{v}_1')]$$

$$\times\ I(\underline{x}_1,\underline{v}_1',\underline{x}_2,\underline{v}_2,t_1-t_2)\ \delta(\underline{x}_2-\underline{x}_1-\underline{b})\ h_o(\underline{v}_3')$$

$$\times\ [h_o(\underline{v}_2')\ f(\underline{x}_1,\underline{v}_1'',t_2) - h_o(\underline{v}_2)\ f(\underline{x}_1,\underline{v}_1',t_2)] \qquad (5.20)$$

This is the contribution from collision sequences, in which particles 1 and 2, with initial velocities $\underline{v}_1''$ and $\underline{v}_2'$, collide at time t_2 ($\underline{b}$ specifies the collision). They then move with velocities $\underline{v}_1'$ and $\underline{v}_2$ until 1 and 3 collide at time t_1 ($\underline{a}$ specifies this collision) so that particles 1,2 and 3 have final velocities $\underline{v}_1$, $\underline{v}_2$ and $\underline{v}_3$ respectively. Symbolically we write this sequence as

$$(\underline{v}_1'', \underline{v}_2', \underline{v}_3') \xrightarrow[t_2]{\underline{b}} (\underline{v}_1', \underline{v}_2, \underline{v}_3') \xrightarrow[t_1]{\underline{a}} (\underline{v}_1, \underline{v}_2, \underline{v}_3)$$

$$C_3(t_1-t_2)\ f(t_2) = \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{32}\ \varepsilon(\underline{a}.\underline{v}_{32}) \int d\underline{b}.(\underline{v}_3'-\underline{v}_1)\ \varepsilon[\underline{b}.(\underline{v}_3'-\underline{v}_1)]$$

$$\times\ I(\underline{x}_1,\underline{v}_1,\underline{x}_2+\underline{a},\underline{v}_3',t_1-t_2)\ \delta(\underline{x}_2+\underline{a}-\underline{x}_1-\underline{b})$$

$$\times\ h_o(\underline{v}_2')\ [h_o(\underline{v}_3')\ f(\underline{x}_1,\underline{v}_1',t_2) - h_o(\underline{v}_3')\ f(\underline{x}_1,\underline{v}_1,t_2)] \qquad (5.21)$$

This is the contribution from collision sequences

$$(\underline{v}_1', \underline{v}_2', \underline{v}_3') \xrightarrow[t_2]{\underline{b}} (\underline{v}_1, \underline{v}_2', \underline{v}_3') \xrightarrow[t_1]{\underline{a}} (\underline{v}_1, \underline{v}_2, \underline{v}_3)$$

$$C_4(t_1-t_2)\ f(t_2) = \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{32}\ \varepsilon(\underline{a}.\underline{v}_{32}) \int d\underline{b}.(\underline{v}_2'-\underline{v}_1)\ \varepsilon[\underline{b}.(\underline{v}_2'-\underline{v}_1)]$$

$$\times\ I(\underline{x}_1,\underline{v}_1,\underline{x}_2,\underline{v}_2',t_1-t_2)\ \delta(\underline{x}_2-\underline{x}_1-\underline{b})$$

$$\times\ h_o(\underline{v}_3')\ [h_o(\underline{v}_2'')\ f(\underline{x}_1,\underline{v}_1',t_2) - h_o(\underline{v}_2')\ f(\underline{x}_1,\underline{v}_1,\ t_1)] \qquad (5.22)$$

is the contribution from sequences

$$(\underline{v}_1',\underline{v}_2'',\underline{v}_3',) \xrightarrow[t_2]{\underline{b}} (\underline{v}_1,\underline{v}_2',\underline{v}_3') \xrightarrow[t_1]{\underline{a}} (\underline{v}_1,\underline{v}_2,\underline{v}_3)$$

$$C_5(t_1-t_2)\; f(t_2) = \int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{32}\; \varepsilon(\underline{a}\cdot\underline{v}_{32}) \int d\underline{b}\cdot\underline{v}_{31}\; \varepsilon(\underline{b}\cdot\underline{v}_{31})$$

$$\times\; I(\underline{x}_1,\underline{v}_1,\underline{x}_2-\underline{a},\underline{v}_3,t_1-t_2)\; \delta(\underline{x}_2-\underline{a}-\underline{x}_1-\underline{b})$$

$$\times\; h_o(\underline{v}_2)\; [h_o(\underline{v}_3')\; f(\underline{x}_1,\underline{v}_1',t_2) - h_o(\underline{v}_3)\; f(\underline{x}_1,\underline{v}_1,t_2)] \quad (5.23)$$

is the contribution from sequences

$$(\underline{v}_1',\underline{v}_2,\underline{v}_3') \xrightarrow[t_2]{\underline{b}} (\underline{v}_1,\underline{v}_2,\underline{v}_3) \xrightarrow[t_1]{\underline{a}} (\underline{v}_1,\quad,\quad)$$

The collision at time t_1 between 2 and 3 interupts the path of particle 2 so that no collision between 1 and 2 occurs at time t. Hence C_5 is subtracted in equation (5.18).

Equation (5.18) expresses $f_2(t)$ as a functional of f. When substituted into the first hierarchy equation it yields a generalization of Boltzmann's equation which accounts for 3-body interactions. In the next chapter we show how the velocity autocorrelation formula may be obtained from this equation.

In Appendix B we derive an equation similar to (5.18) in which the Boltzmann collision operator is used to take into account the interaction between three particles and other particles in the gas.

CHAPTER 4 CALCULATION OF THE COEFFICIENT OF SELF-DIFFUSION

4.1 INTRODUCTION

In Chapter 3 we derived an exact equation for the distribution function $f(\underline{x},\underline{v},t)$ associated with a specified particle of a gas. That equation was written in two ways:

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = n_2(a)\ B(f) + n^2 U_3(t;f) + n^3 U_4(t;f) + \ldots \tag{1.1}$$

and

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = n_2(a)\ B(f) + \int_0^t dt'\ [V_3\big(t-t';f(t')\big)+V_4\big(t-t';f(t')\big)+\ldots] \tag{1.2}$$

In (1.1) the interaction between the preferred particle and other particles is represented by a sum of operators, each depending on the dynamics of a small number of isolated particles. In equation (1.2) the operators V_3, V_4, etc. depend on the dynamics of 3,4, etc. particles interacting with other particles in the system. As explained in Section 3.5 there are a number of ways in which these many-body effects can be accounted for. In this chapter the operators V_3, V_4, etc. will be taken as the operators arising from equation (5.18) of Chapter 3. In this equation, the effect of interactions between a few specified particles and the other particles is approximated by the factor $\exp(-n\alpha t)$.

In this Chapter we show how the coefficient of self-diffusion can be calculated from approximations to equations (1.1) and (1.2). One must be careful to avoid divergent terms when seeking approximations to the exact closed equation for f. Suitable approximations to (1.1) and (1.2) can be obtained by simply neglecting terms U_{k+1}, $U_{k+2}, \ldots$ or V_{k+1}, $V_{k+2}, \ldots$ for some finite value of k. It should be noted that this is a suitable method for approximating (1.2) only because certain many-body dynamical effects are included in each of the operators

V_3, V_4, etc.

The simplest approximation to these equations is

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = n_2(a)\ B(f) \tag{1.3}$$

an equation which has been studied in great detail. We present a brief discussion on how the coefficient of self-diffusion is calculated from this equation. Approximations which involve three-body dynamics are much more difficult to study because of the complexity of the dynamics of three particles. However the required techniques have been developed by Sengers[10,53,70] and we will show how our work is related to the Choh-Uhlenbeck equation as analysed by Sengers.

4.2 CALCULATIONS

In Chapter 2 we proposed a definition of the coefficient of self-diffusion with the aim of avoiding difficulties which arise if one simply applies Einstein's definition of the coefficient of diffusion for Brownian motion to the process of self-diffusion. This definition takes into account the small, but observable, correlations between the velocity of the diffusing particle and those of other particles. In a dilute gas these correlations decay nearly exponentially with time so that the formula

$$D = \frac{1}{3}\int_o^\infty dt < \underline{v}(o).\underline{v}(t) >_{eq} \tag{2.1}$$

is adequate. It is to be expected that the generalizations of Boltzmann's equation considered in this section also predict that the correlations decay rapidly with time. This is because many-body dynamical events which are the cause of the actual slow decay of the velocity autocorrelation function are accounted for in only an approximate fashion through the factor $\exp(-n\alpha t)$. Hence equation (2.1) will be suitable for calculating the coefficient of self-diffusion from the generalizations of Boltzmann's equation considered here.

On the other hand if one requires a more accurate description of the diffusing particle, the generalization of Boltzmann's equation discussed in Appendix B should be suitable. In this equation many-body contributions are contained in the term

$\exp\left[-\left(\underline{v}.\frac{\partial}{\partial \underline{x}} - nB(\underline{v})\right)t\right]$ Dorfman and Cohen[40] have shown that by including this factor the long time behaviour of the velocity autocorrelation function can be predicted. The coefficient of self-diffusion will be somewhat more difficult to evaluate from this generalization of Boltzmann's equation than from the simpler generalizations considered here, but since the correlations between velocities of particles are small it is probably not necessary to use the equation of Appendix B to obtain a value of the coefficient of self-diffusion suitably close to experimental values.

To calculate D as defined by equation (2.1), we first note that the velocity autocorrelation function is related to the velocity distribution function f by

$$< \underline{v}(o).\underline{v}(t) >_{eq} = \int d\underline{v}_o\, h_o(\underline{v}_o)\underline{v}_o . \int d\underline{x} \int d\underline{v}\, f(\underline{x},\underline{v},t)\underline{v} \qquad (2.2)$$

where

$$f(\underline{x},\underline{v},o) = \delta(\underline{x} - \underline{x}_o)\, \delta(\underline{v} - \underline{v}_o)$$

It is convenient to introduce the functions h and $\underline{\phi}$ defined by

$$h(\underline{v},t) = \int d\underline{x}\, f(\underline{x},\underline{v},t)$$

$$\underline{\phi}\,(\underline{v}) = \int_o^\infty dt \int d\underline{v}_o\, h_o(\underline{v}_o)\underline{v}_o\, h(\underline{v},t) \qquad (2.4)$$

so that

$$D = \frac{1}{3}\int d\underline{v}\, \underline{\phi}(\underline{v}).\underline{v} \qquad (2.5)$$

We now consider the evaluation of D when f satisfies equation (1.3). Then h obeys

$$\frac{\partial h}{\partial t} = n_2 \int d\underline{w} \int d\underline{a}.\ (\underline{w}-\underline{v})\ \varepsilon[a.(\underline{w}-\underline{v})][h_o(\underline{w}') \ h(\underline{v}',t) - h_o(\underline{w}) \ h(\underline{v},t)] \qquad (2.6)$$

Now the solution of (2.6) is such that the time integral defining $\underline{\phi}$ is certainly finite. This is best seen by an examination of the eigenvalues and eigenfunctions of the collision operator B(v) which appears in (2.6). The spectrum of the operator B is discussed by Foch and Ford[71]. The function h_o is an eigenfunction corresponding to the eigenvalue 0. All other eigenvalues λ_i are negative. The solution to (2.6) is of the form

$$h(\underline{v},t) = \Sigma_i \ a_i \ e^{n_2\lambda_i t} \ \psi_i(\underline{v}) \qquad (2.7)$$

where ψ_i is the eigenfunction corresponding to λ_i. The constants a_i are determined from the initial value of h. We shall write equation (2.7) in the compact form

$$h(\underline{v},t) = e^{n_2 B(\underline{v})t} \ h(\underline{v},o) \quad , \qquad (2.8)$$

These considerations show that the time integral in (2.4) is finite and thus $\underline{\phi}$ is well-defined when h satisfies (2.6).

To obtain the equation which $\underline{\phi}$ satisfies, multiply both sides of (2.6) by $h_o(\underline{v}_o)\underline{v}_o$ and integrate with respect to $\underline{v}_o$ and t.

Now

$$\int_o^\infty dt \int d\underline{v}_o \ h_o(\underline{v}_o)\underline{v}_o \frac{\partial h}{\partial t} = -\ \underline{v}h_o(\underline{v})$$

since $h(\underline{v},o) = \delta(\underline{v}-\underline{v}_o)$ and $h(t) \rightarrow h_o$ as $t \rightarrow \infty$. Hence $\underline{\phi}$ satisfies the integral equation

$$-\ \underline{v}\ h_o(\underline{v}) = n_2(a)\ B[\underline{\phi}(\underline{v})] \qquad (2.9)$$

We note that this equation can also be obtained from equation (1.3) for f by using the methods of Chapman and Enskog[2]. One substitutes into (1.3)

$$f(\underline{x},\underline{v},t) = n(\underline{x},t)\ [h_o(\underline{v}) - \underline{\phi}(\underline{v}) . \frac{\partial n}{\partial \underline{x}} + \ldots] \tag{2.10}$$

where

$$n(\underline{x},t) = \int d\underline{v}\ f(\underline{x},\underline{v},t)$$

to obtain

$$\frac{\partial f}{\partial t} + \underline{v}.\frac{\partial f}{\partial \underline{x}} = -\ n_2(a)\ B(\underline{\phi}).\frac{\partial n}{\partial \underline{x}} + \ldots \tag{2.11}$$

Writing

$$\frac{\partial f}{\partial t} + \underline{v}.\ \frac{\partial f}{\partial \underline{x}} = \left(\frac{\partial n}{\partial t} + \underline{v}.\ \frac{\partial n}{\partial \underline{x}}\right) h_o(\underline{v}) + \ldots$$

and writing the continuity equation as

$$\begin{aligned}\frac{\partial n}{\partial t} &= -\ \frac{\partial}{\partial \underline{x}.} \int d\underline{v}\ \underline{v}\ f(\underline{x},\underline{v},t) \\ &= -\ \frac{\partial}{\partial \underline{x}.} \int d\underline{v}\ \underline{v}\ [n(\underline{x},t)\ h_o(\underline{v}) + \ldots]\end{aligned}$$

we have to a first approximation that

$$\frac{\partial f}{\partial t} + \underline{v}.\ \frac{\partial f}{\partial \underline{x}} = \underline{v}\ h_o(\underline{v})\ \frac{\partial n}{\partial \underline{x}}$$

which when substituted into (2.11) yields (2.10).

The usual method of solving this equation is to expand the functions $\underline{\phi}$ and $\underline{v}$ in terms of the Sonine polynomials[2]. One then obtains an infinite set of simultaneous equations for the coefficients of the expansions. If the infinite set of equations is replaced by a finite set one can obtain approximations to the coefficient of self-diffusion.

An alternative method of solving (2.6) is to transform the equation into a differential equation. This approach has been considered by Pekeris[72], Brooker and Green[73]. Kumar[74] has reformulated the method of Chapman and Enskog in terms of irreducible tensors and matrices. By this approach one does not require any of the theory of integral equations.

The solution to (2.9) will be written as

$$\underline{\phi}\ (\underline{v}) = - \frac{1}{n_2(a)}\ B^{-1}\ [\underline{v}\ h_o(\underline{v})] \tag{2.12}$$

where we have introduced the inverse operator B^{-1}.

The value of the coefficient of self-diffusion that is obtained from this equation is[72]

$$D = 1.019\ \frac{3}{8a^2} \left(\frac{kT}{\Pi m}\right)^{1/2} \frac{1}{n_2(a)}$$

Using the density expansion of $n_2(a)$ given by equation (2.30) of Section 3.2 we find[10]

$$n\ D = 1.019\ \frac{3}{8a^2} \left(\frac{kT}{\Pi m}\right)^{1/2} \left(1 - \frac{5}{12}\ \Pi a^3 n + \ldots\right) \tag{2.13}$$

The first term of the right hand side of (2.13) is consistent with the value of nD at low densities which Alder and Wainwright[38] obtained from a computer simulation of a gas of rigid spheres. The next term, according to the computer studies is

$$- 0.8 \times \frac{5}{12}\ \Pi a^3 n$$

Hence the most important part of the first correction to the results from Boltzmann's equation comes from the equilibrium distribution function n_2. Further corrections arise from considering three-body dynamics, and we now consider how these can be calculated.

Consider first the approximation to equation (1.1) which results when the operators $U_{k+1}, U_{k+2}, \ldots$ are neglected. On integrating the resultant equation with respect to the variable $\underline{x}$, we find that h satisfies an equation of the type

$$\frac{\partial h}{\partial t} = n_2(a)\ B(h) + n^2 C_3(t;h) + \ldots + n^{k-1}\ C_k(t;h) \tag{2.14}$$

where C_3, C_4, ... are operators. We propose that this equation provides a suitable description of the gas even though the operators C_k may diverge. To see this, we put (2.14) into the integral form

$$h(\underline{v},t) = e^{n_2Bt}\, h(\underline{v},o) + \int_o^t dt'\, e^{n_2B(t-t')}$$

$$\times\, [n^2C_3(t') + \ldots + n^{k-1}\, C_k(t')]\, h(v,t') \tag{2.15}$$

This equation can be solved by iteration:

$$h(\underline{v},t) = e^{n_2Bt} h(\underline{v},o) + \int_o^t dt'\; e^{n_2B(t-t')}$$

$$\times\, [n^2C_3(t') + \ldots + n^{k-1}\, C_k(t')]\; e^{n_2Bt'}\; h(\underline{v},o) \pm \ldots \tag{2.16}$$

It should be noted that

$$C_k(t)\ [h_o(\underline{v})] = 0$$

so that

$$C_k(t)\ e^{n\ Bt}\ h(\underline{v},o) \to 0 \quad \text{as} \quad t \to \infty$$

provided $C_k(t)$ does not increase too rapidly with time. Hence each term in (2.16) approaches zero for long times, apart from the first term which approaches the equilibrium value h_o. To show that the solution to (2.14) is well-behaved requires that the sum of all terms in (2.16) approaches zero. A detailed analysis of the operators C_k is required to decide whether that property is true. However solutions to (2.14) obey

$$\int d\underline{v}\ h(\underline{v},t) = 1,$$

for all times t, which suggests that h is well-behaved. This identity follows from the fact that (2.14) is of the form

$$\frac{\partial h}{\partial t} = J_{12}\ [C(\underline{v}_1,\underline{v}_2,t;h)]$$

where C is a functional and that J_{12} has the property

$$\int d\underline{v}_1\ J_{12}\ [g(\underline{v}_1,\underline{v}_2)] = 0$$

Thus it seems likely that finite values of the coefficient of self-diffusion can be obtained from equation (2.14) even though the operators $C_k(t)$ may diverge for large times. It is the operator B which provides the necessary modification to divergent terms and there is no need to consider many-body dynamics.

$\underline{\phi}(\underline{v})$ is given immediately by equation (2.16). From the definition (2.4) of $\underline{\phi}$ we obtain

$$\underline{\phi}(\underline{v}) = \int_0^\infty dt\ e^{n_2Bt}[\underline{v}\ h_o(\underline{v})] + \int_0^\infty dt \int_0^t dt'\ e^{n_2B(t-t')}$$

$$\times\ [n^2C_3(t') + \ldots + n^{k-1}\ C_k(t')]\ e^{n_2Bt'}\ [\underline{v}\ h_o(\underline{v})] + \ldots$$

$$= -\frac{1}{n_2}\ B^{-1}\ [\underline{v}\ h_o(\underline{v})] - \frac{1}{n_2}\ B^{-1}\int_0^\infty dt\ [n^2C_3(t) + \ldots$$

$$\ldots + n^{k-1}\ C_k(t)]\ e^{n_2Bt}\ [\underline{v}\ h_o(\underline{v})] + \ldots \tag{2.17}$$

The factor e^{n_2Bt} represents a sum of exponentially decaying terms. Hence each term in (2.17) is finite and so corrections to D beyond the value predicted by Boltzmann's equation can be obtained.

We will briefly consider the next two terms which take into account three and four particle interactions. If the operaotr $C_3(t)$ is replaced by $\overline{C}_3 = \lim_{t\to\infty} C_3(t)$, one obtains from (2.17), on neglecting C_4, C_5,...

$$\underline{\phi}(\underline{v}) = -\frac{1}{n_2}\ B^{-1}[\underline{v}\ h_o(\underline{v})] + \left(\frac{n}{n_2}\right)^2\ B^{-1}\ \overline{C}_3\ B^{-1}[\underline{v}\ h_o(\underline{v})] + \ldots \tag{2.18}$$

This is the iterated solution to the integral equation derived from the Choh-Uhlenbeck equation . $\overline{C}_3$ is given by equation (3.10) of Section 3.3.

One can make some qualitative statements about the contribution to $\underline{\phi}$ from the operator C_4 by drawing upon the results from an analysis of four-body dynamics made by Pomeau and others[35].

If one defines $\overline{C}_4$ by

$$C_4(t) = \int_o^t dt' \, \overline{C}_4 \, (t')$$

we see that

$$\int_o^\infty dt \; C_4(t) \; e^{n \, Bt} = \int_o^\infty dt' \; \overline{C}_4(t') \; e^{n \, Bt'} \int_{t'}^\infty dt \; e^{n \, Bt}$$

$$= \int_o^\infty dt \; \overline{C}_4(t) \; e^{n \, Bt} \; \left(- \frac{1}{n} B^{-1}\right)$$

so that (2.17) can be written

$$\underline{\phi}(\underline{v}) = - \frac{1}{n_2} \; B^{-1} \; [\underline{v} \; h_o(\underline{v})] + \frac{1}{n^2} \; B^{-1} \; [n^2 \overline{C}_3$$

$$+ n^3 \int_o^\infty dt \; \overline{C}_4(t) \; e^{n \, Bt}] \; B^{-1} \; [\underline{v} \; h_o(\underline{v})] \tag{2.19}$$

For small values of n, we expect from the work on the dynamics of four particles that the operator

$$\int_o^\infty dt \; \overline{C}_4(t) \; e^{n \, Bt}$$

is proportional to ln n. This implies that the self-diffusion coefficient D depends on the density n in the following way

$$nD = D_o + D_1 + n \ln n \; D_2 + \ldots \tag{2.20}$$

The form of higher order terms in the expansion is discussed by Haines[32]. To conclude our discussion of equation (2.14) we remark that such an equation is used in Chapter 5 to provide a finite correction to the value of D from Boltzmann's equation for a one dimensional gas.

We now consider the calculation of D from approximations to (1.2) which are obtained by neglecting V_{k+1}, V_{k+2}, etc. With such an approximation n obeys an equation of the type

$$\frac{\partial h}{\partial t} = n_2 B(h) + \int_o^t dt' \; \{A_3(t-t') + \ldots + A_k(t-t')\} \; h(t') \tag{2.20}$$

with $A_k(t)$ time-dependent operators.

The equation satisfied by $\underline{\phi}$ is obtained from (2.20) by multiplying both sides of the equation by $\underline{v}_o\ h_o(\underline{v}_o)$ and integrating with respect to $\underline{v}_o$ and t.

Thus

$$- v\ h_o(\underline{v}) = n_2 B[\underline{\phi}(\underline{v})] + \int_o^\infty dt \int_o^t dt' \ \{A_3(t-t') + \ldots + A_k(t-t')\}$$

$$x \int d\underline{v}_o\ h_o(\underline{v}_o)\ \underline{v}_o\ h(\underline{v},t')$$

which on changing the order of integration with respect to t and t′ becomes

$$-\underline{v}\ h_o(\underline{v}) = n_2 B[\underline{\phi}(\underline{v})] + \int_o^\infty dt\ \{A_3(t) + \ldots + A_k(t)\}\ \underline{\phi}(\underline{v}) \tag{2.21}$$

$\underline{\phi}$ then, is the solution to this integral equation. It has already been mentioned that the operators A_k contain contributions from certain many-body collision sequences and that these must be included if the time integrals in (2.21) are to converge.

The operator $\int_o^\infty dt\ A_3(t)$ can be obtained from equation (5.18) of Section 3.5:

$$\int_o^\infty dt\ A_3(t)\ \underline{\phi}(\underline{v}_1) = n^2 J_{12}\ [\int_o^\infty e^{-n\alpha(\underline{v}_1)t} \int d\underline{a}.\underline{v}_{12} (1-e^{-V(\underline{x}_{12}-\underline{v}_{12}t-\underline{a})})$$

$$x\ h_o(\underline{v}_2)\ \underline{\phi}(\underline{v}_1)\ dt]$$

$$+ n^2 J_{12}\ [\int_o^\infty dt\ e^{-n\alpha(\underline{v}_1)t}\ S(\underline{z}_1,\underline{z}_2,t)\ h_o(\underline{v}_2)$$

$$x\ J_{13}[(e^{-V_{23}} -1)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)\}]$$

$$+ n^2 J_{12}\ \{ \int_o^\infty dt\ e^{-n\alpha(\underline{v}_1)t}\ S(\underline{z}_1,\underline{z}_2,t)$$

$$x \int dv_3 \int d\underline{a}.\underline{v}_{31}\ \varepsilon(\underline{a}.\underline{v}_{31})$$

$$x \int_o^\infty dt\ e^{-n\alpha(\underline{v}_1')t} S(\underline{x}_1\ \underline{v}_1,\underline{x}_2,\underline{v}_2,t)$$

$$\times \int db.\ (\underline{v}_2-\underline{v}_1')\ \epsilon[\underline{b}.(\underline{v}_2-\underline{v}_1')]$$

$$\times\ \delta(\underline{x}_{21}-\underline{b})\ h_o(\underline{v}_3')[h_o(\underline{v}_2')\ \underline{\phi}(\underline{v}_1'')\ -\ h_o(\underline{v}_2)\underline{\phi}(\underline{v}_1)]\}$$

$$+ \ldots \tag{2.22}$$

Further terms can be obtained directly from equation (5.18).

The collision sequences which contribute to the various terms in this expression were described in Section 3.5. Because of the factor $\exp(-n\alpha t)$ each of the terms is certainly finite, although the inclusion of these factors is not essential to obtain finite values of D. This is because of the particular geometry of collision sequences involving three particles. If the exponential terms are replaced by 1 i.e. if many-body collision sequences are neglected we obtain from (2.22) an integral equation which has also been derived by Sengers, Ernst and Gillespie[75] by using Laplace transformation techniques developed by Zwanzig. This is demonstrated in Appendix E. The equation is of the form

$$-\underline{v}\ h_o(\underline{v}) = (n_2 B + n^2\ \overline{A})\ \ \underline{\phi}(\underline{v})$$

and can be solved by iteration

$$\underline{\phi}(\underline{v}) = -\frac{1}{n_2}\ (1 - n\ B^{-1}\ \overline{A} + \ldots)\ B^{-1}\ [\underline{v}\ h_o(\underline{v})] \tag{2.23}$$

Sengers[70] has developed numerical methods for evaluating the result of the operator $\overline{A}$ acting on a function of $\underline{v}$. It is found that the first two terms of (2.23) lead to

$$nD = \frac{3}{8a^2}\left(\frac{kT}{\Pi m}\right)^{1/2}\ [1.019 - r\,\frac{5}{12}\,\Pi a^3\ n + \ldots] \tag{2.24}$$

where[10]

$$r = 0.9150 \pm 0.0018$$

This expression should be compared with equation (2.13), with $r=1$, which is a consequence of considering only two-body dynamics and with the value $r=0.8$ obtained from computer studies. This difference between the calculated and observed values of r may be a consequence of considering only the first two terms of (2.23). Alternatively it may be necessary to include many-body effects as well as three-body collision sequences to explain the difference. A detailed analysis of the operator $\int_0^\infty dt\, A_3(t)$ as given by (2.23) would seem worthwhile. From a physical point of view it is to be expected that accounting for the possibility of interactions between three particles and other particles would give a more accurate description of the gas.

CHAPTER 5 A STUDY OF A ONE-DIMENSIONAL GAS[76]

5.1 INTRODUCTION

In the earlier chapters of this thesis we have developed a theory of self-diffusion in a dense gas of rigid spheres or discs. Some discussion of numerical predictions from this theory has already been presented. However the complications of even three-body dynamics requires that elaborate numerical analysis be performed if accurate corrections to results from Boltzmann's equation are to be obtained. The scheme which we have developed can be adapted to describe a one-dimensional gas of rigid rods, a system for which the dynamics are comparatively simple. Indeed, in this case the coefficient of self-diffusion can be calculated exactly.

In this chapter we present the theory of a gas of point particles. The techniques used in previous chapters can also be applied to this model of a gas. Divergences arise from the usual methods and are even more severe than in two or three dimensions. A form of Boltzmann's equation can be derived. However, unlike the situation in higher dimensions, this is an approximate equation even when the density of the gas is low. The coefficient of self-diffusion as derived from Boltzmann's equation is always 16% off the exact value irrespective of the density of the system. We derive a generalization of Boltzmann's equation by considering three-body and certain many-body dynamical events. The latter are required to modify divergences due to the dynamics of three isolated particles. The value of the coefficient of self-diffusion as calculated from this equation is close to its exact value.

In Section 5.2 we define velocity distribution functions appropriate for describing a single particle in the one-dimensional gas when the other particles have an initial distribution of equilibrium. These distribution functions are shown to satisfy a set of equations, analogous to the hierarchy developed for two and three dimensional gases. It is possible to find the exact relationship between two-particle and one-particle distribution functions which enables the hierarchy to be solved exactly.

In Section 5.3 we apply the methods developed in previous chapters, to derive approximate closed equations for the one-particle velocity distribution function. The coefficient of self-diffusion is calculated from these equations by numerical techniques, in order to demonstrate the efficacy and accuracy of these methods.

5.2 THE DISTRIBUTION FUNCTIONS

In this section we examine the behaviour in time of a specified particle in a system of impenetrable point particles, constrained to move along an infinite line. The statistical ensemble which describes the state of the gas in which we are interested is the subensemble of the grand canonical ensemble of equilibrium in which some particle has specified position and velocity. The specified particle is labelled as particle o and other particles are labelled according to their order along the line, with particles labelled by negative numbers to the left of the distinguished particle.

The distribution function $F^{M,N}(z_{-M},..,z_N,t)$ describes the sub-ensemble with M particles to the left and N particles to the right of particle o, and obeys the M+N+1 Louiville equation

$$\left(\frac{\partial}{\partial t} + L^{M,N}\right) F^{M,N} = 0 \tag{2.1}$$

where $L^{M,N}$ is the Liouville operator for the system. The ensemble average $\langle G\rangle$ of any property G is then given by the

$$\langle G\rangle = \sum_{M=0}^{\infty} \sum_{N=0}^{\infty} \underset{x_{-M} < \,...\, < x_N}{\int dz_{-M} \cdots \int dz_N} F^{M,N}(o)\, G^{M,N}\left(z_{-M}(t),..,z_N(t)\right) \tag{2.2}$$

where $z_i(t) = \{x_i(t), v_i(t)\}$ denotes the position and velocity of particle i at time t, and $z_i = z_i(o)$. The initial distribution function $F^{M,N}(o)$ is given by

$$F^{M,N}(z_{-M},\dots,z_N,o) = \delta(z_o - z')\exp\{\beta[\mu(M+N) - H^{M,N}]\}/(Z_L Z_R) \qquad (2.3)$$

$z' = (x', v')$ specifies the initial position and velocity of the test particle. $H^{M,N}$ is given by

$$H^{M,N} = \sum_{\substack{j=-M \\ j\neq o}}^{N} \left(\tfrac{1}{2} m v_j^2 - \sum_{k\neq j} V_{kj}\right)$$

where $V_{kj} = V(x_k - x_j)$ is the interaction potential between a particle at x_k and one at x_j. Z_L is the equilibrium grand ensemble partition function for particles to the left of particle o, and Z_R is defined similarly for those to the right. β is the statistical temperature and μ the chemical potential.

Velocity distribution functions $f_j^{(n)}$ are defined as follows:

$$f_j^{(n)}(z_1;z_2,\dots,z_n,t) =$$

$$\langle\delta(z_j(t) - z_1) \sum_{j_2\neq\dots\neq j_n} \delta(z_{j_2}(t) - z_2)\dots\delta(z_{j_n}(t) - z_n)\rangle \qquad (2.4)$$

so that $f_j^{(1)}(z_1,t)\,dz_1$ is the probability of finding particle j in the phase space volume dz_1 about the point z_1 at time t, and $f_j^{(2)}(z_1;z_2,t)$ is a distribution function associated with finding particle j at z_1 and any other particle at z_2. The higher order distribution functions have a similar interpretation.

The distribution functions obey a hierarchy of equations similar to the hierarchy applicable to two and three dimensional fluids.

$$\left(\frac{\partial}{\partial t} + L^n\right) f_j^{(n)}(z_1,\dots,z_n,t) = \sum_{i=1}^{n} \int dz_{n+1} \frac{1}{m}\frac{\partial V_{i,n+1}}{\partial x_{n+1}} \frac{\partial}{\partial v_{n+1}} f_j^{(n+1)}(t) \qquad (2.5)$$

where m is the mass of a particle, and

$$L^n = \sum_{i=1}^{n} \left(v_i \frac{\partial}{\partial x_i} - \frac{1}{m} \left(\frac{\partial}{\partial x_i} \sum_{\substack{j=1 \\ j\neq i}}^{n} V_{ij}\right) \frac{\partial}{\partial v_i}\right) \tag{2.6}$$

is the n-particle Liouville operator.

The hierarchy (2.5) can be put into a form similar to the hierarchy of equations for the distribution functions describing a gas of rigid spheres or discs. We will consider in detail the first hierarchy equation, which contains the term

$$\frac{1}{m} \int dz_2 \frac{\partial V_{12}}{\partial x_1} \frac{\partial}{\partial v_1} f_j^{(2)} (z_1, z_2, t) \tag{2.7}$$

Now for the interaction under consideration, the integration range in this expression can be limited to an arbitrarily small line segment containing x_1 and in the limit where this range becomes vanishingly small, only terms in the integrand involving δ-functions contribute to the integral. The terms involving δ-functions in the equation for $f_j^{(2)}$ are explicitly displayed in

$$[(v_1-v_2) \frac{\partial}{\partial(x_1-x_2)} - \frac{1}{m} \frac{\partial V_{12}}{\partial x_1} (\frac{\partial}{\partial v_1} \quad \frac{\partial}{\partial v_2}] f_j^{(2)}(z_1, z_2, t) \tag{2.8}$$

$$= \text{other terms}$$

which is a consequence of the second hierarchy equation. Substitution of (2.8) into (2.7) leads to

$$\left(\frac{\partial}{\partial t} + v_1 \frac{\partial}{\partial x_1}\right) f_j^{(1)} (z_1, t)$$

$$= \lim_{\varepsilon \to 0} \int_{x_1-\varepsilon}^{x_1+\varepsilon} dx_2 \int dv_2 (v_2 - v_1) \frac{\partial}{\partial(x_2-x_1)} f_j^{(2)} (z_1, z_2, t)$$

$$= \lim_{\varepsilon \to 0} \int dv_2 \, |v_2 - v_1| \, [f_j^{(2)}(x_1, v_1, x_1^+, v_2, t) - f_j^{(2)}(x_1, v_1, x_1^-, v_2, t)] \tag{2.9}$$

where

$$x_1^{\pm} = x_1 \pm \varepsilon \operatorname{sgn} (v_2 - v_1) \tag{2.10}$$

The variables x_1, v_1, x_1^+, v_2 are postcollision variables whereas x_1, v_1, x_1^-, v_2 are precollision variables. But from (2.8)

$$\lim_{\varepsilon\to 0} f_n^{(2)} (x_1,v_1,x_1^+,v_2,t) = \lim_{\varepsilon\to 0} f_j^{(2)}(x_1^-,v_2,x_1,v_1,t) \tag{2.11}$$

since in the limit $\varepsilon\to 0$, the "other terms" of (2.8) can be neglected. We have also used the fact, that for this system, two particles simply exchange velocities upon collision. From (2.9) and (2.11) we obtain

$$\left(\frac{\partial}{\partial t} + v_1 \frac{\partial}{\partial x_1}\right) f_j^{(1)}(z_1,t) = \lim_{\varepsilon\to 0} \int dv_2 \ |v_1-v_2|$$

$$x \ [f_j^{(2)}(x_1^-,v_2,x_1,v_1,t) - f_j^{(2)}(x_1,v_1,x_1^-,v_2,t)] \tag{2.12}$$

We can make use of the fact that the particles are impenetrable. The j^{th} particle is always next to the $(j+1)^{th}$ and $(j-1)^{th}$ particles and so

$$\lim_{\varepsilon\to 0} f_j^{(2)} (x_1^-,v_2,x_1,v_1,t) = \lim_{\varepsilon\to 0} f_{(j)}^{(2)}(x_1,v_1,x_1^-,v_2,t) \tag{2.13}$$

where

$$(j) = j + \text{sgn}\ (v_2-v_1) \tag{2.14}$$

Equation (2.12) can then be written in the form

$$\left(\frac{\partial}{\partial t} + v_1 \frac{\partial}{\partial x_1}\right) f_j^{(1)} (z_1,t) = \lim_{\varepsilon\to 0} \int dv_2 \ |v_2-v_1|$$

$$x \ [f_{(j)}^{(2)} (x_1,v_2,x_1^-,v_2,t) - f_j^{(2)}(x_1,v_1,x_1^-,v_2,t)] \tag{2.15}$$

By a similar procedure we can express the hierarchy equations for $f_j^{(2)}$, $f_j^{(3)}$, etc. in forms similar to (2.12) and (2.15). In these equations it is not necessary to take into account any interactions other than those of the j^{th} particle with the unlabelled particles since $f_j^{(n)}$ is symmetric with respect to unlabelled particle interchange. This is because particles exchange velocities upon collision and so the unlabelled particles behave, as far as the motion of particle j is concerned, like an ideal gas.

The equations governing $f_j^{(n)}$ then are

$$\left(\frac{\partial}{\partial t} + L_j^n\right) f_j^{(n)}(z_1;..,z_n,t)$$

$$= \lim_{\varepsilon\to 0} \int dv_{n+1}\, |v_{n+1} - v_1|\, [f_j^{(n+1)}(x_1^-,v_{n+1};..,x_1,v_1,t)$$

$$- f_j^{(n+1)}(x_1,v_1;..,x_1^-,v_{n+1},t)] \tag{2.16}$$

where L_j^n is the n-particle Liouville operator which includes only interactions between particle j and the unlabelled particles. Equations similar to (2.15) can also be obtained.

The initial values of the distribution functions can be found from equations (2.2), (2.3) and (2.4). Assume that the particles are initially constrained to an interval $(-L,L)$ with particle 0 at the origin so that

$$F^{M,N}(o) = \delta(x_o)\,\delta(v_o - v')\,\exp\{\beta[\mu(M+N) - H^{M,N}]\}/(Z_L Z_R)$$

$$\text{if for } i = -M,..,N \qquad |x_i| < L$$

$$= 0 \text{ otherwise}$$

Then,

$$\text{for } j = 0: \qquad f_o^{(1)}(z,0) = \delta(x)\,\delta(v-v')$$

$$\text{for } j > 0: \qquad f_j^{(1)}(z,0) = \frac{n(nx)^{j-1}}{(j-1)!}\, e^{-nx}\, h_o(v) \qquad 0 < x < L$$

$$= 0 \qquad \text{otherwise}$$

$$\text{for } j < 0: \qquad f_j^{(1)}(z,0) = f_{-j}^{(1)}(-x,v,0) \tag{2.17}$$

where n is the initial density of particles other than particle 0 and

$$h_o(v) = \left(\beta m/(2\pi)\right)^{\frac{1}{2}} \exp(-\tfrac{1}{2}\beta m v^2) \tag{2.18}$$

The higher order distribution functions $f_j^{(n)}$ satisfy

$$f_j^{(n+1)}(z_1;..,z_{n+1},0) = f_{j'}^{(n)}(z_1;..,z_n0)\ h(x_{n+1},v_{n+1}) \tag{2.19}$$

where

$$\begin{aligned} j' &= j - 1 && 0 < x_{n+1} < x_1 \\ &= j + 1 && x_1 < x_{n+1} < 0 \\ &= j && \text{otherwise} \end{aligned}$$

and

$$\begin{aligned} h(x,v) &= nh_o(v) + \delta(x)\ \delta(v-v') && |x| < L \\ &= 0 && \text{otherwise} \end{aligned}$$

It is shown in Appendix C, that for later times a similar factorization of $f_j^{(n+1)}$ occurs for configurations of $n+1$ particles for which particle j has not previously interacted with any of these particles. For instance, if $(x_1 - x_2)(v_1 - v_2) < 0$

$$\begin{aligned} f_j^{(2)}(z_1;z_2,t) &= f_{j-1}^{(1)}\ (z_1,t)\ h(z_2,t) && 0 < x_2-v_2t < x_1-v_1t \\ &= f_{j+1}^{(1)}\ (z_1,t)\ h(z_2,t) && x_1-v_1t < x_2-v_2t < 0 \\ &= f_j^{(1)}\ (z_1,t)\ h(z_2,t) && \text{otherwise} \end{aligned} \tag{2.20}$$

where

$$\begin{aligned} h(x,v,t) &= n\ h_o(v) + \delta(x_2-v_2t)\ \delta(v-v') && |x_2-v_2t| < L \\ &= 0 && \text{otherwise.} \end{aligned}$$

When (2.20) is substituted into (2.15) we obtain an infinite set of equations for $f_{\pm k}^{(1)}$ $(k = 0,1,2,...)$ which can be solved as described in Appendix C.

The velocity distribution functions $f_j^{(n)}$ can be written in terms of functions $F_j^{(n)}$ defined by

$$F_j^{(n)}(z_1;..,z_n,t) = f_j^{(n)}(z_1;..,z_n,t) - \int dz_{n+1}\, f_j^{(n+1)}(z_1;...,z_{n+1},t) + ..$$

$$= \sum_{k=0}^{\infty} \frac{(-1)^k}{k!} \int dz_{n+1} ... \int dz_{n+k}\, f_j^{(n+k)}(z_1;..,z_{n+k},t) \tag{2.21}$$

It can be shown that

$$\left(\frac{\partial}{\partial t} + L_j^n\right) F_j^{(n)} = 0 \tag{2.22}$$

and

$$f_j^{(n)}(t) = \sum_{k=0}^{\infty} \frac{1}{k!} \int dz_{n+1} ... \int dz_{n+k}\, F_j^{(n+k)}\ (z_1;..,z_{n+k},t) \tag{2.23}$$

(2.22) can be obtained by using the hierarchy equations (2.5) and (2.23) can be verified by direct substitution into (2.21). Similar sets of equations have already been derived for systems of higher dimension.

In the next section we shall use the scheme proposed in Chapters 3 and 4 to calculate approximate values of the coefficient of self-diffusion defined by

$$D = \int_0^{\infty} dt \int dv'\, h_o(v')v' \int dv\, h(v,t) \tag{2.24}$$

where

$$h(v,t) = \int dx\, f_o^{(1)}\ (x,v,t) \tag{2.25}$$

To simplify matters, we assume that the initial distribution of particles is over an infinite interval. On taking the limit L→∞ of the expression (C17) (Appendix C) for $f_o^{(1)}$, we calculate D as

$$D = (2\pi\beta m)^{-\frac{1}{2}}\, n^{-1} \tag{2.26}$$

From equation (2.11) and the property

$$\lim_{\varepsilon\to o} f_j^{(2)}(x,v_1,x\pm\varepsilon,v_2,t) = \lim_{\varepsilon\to o} f_j^{(2)}(x,v_2,x\pm\varepsilon,v,t)$$

we see that $h(t)$ satisfies

$$\frac{\partial}{\partial t} h(v_1,t) = \int dv_2\ |v_1-v_2|[h_2(v_2,v_1,t) - h_2(v_1,v_2,t)] \tag{2.27}$$

where

$$h_2(v_1,v_2,t) = \lim_{\varepsilon\to o} \int dx\ f_o^{(2)}\left(x,v_1,x-\varepsilon\ \mathrm{sgn}\ (v_2-v_1),v_2,t\right) \tag{2.28}$$

5.3 GENERALIZATIONS OF BOLTZMANN'S EQUATION FOR THE ONE DIMENSIONAL MODEL

The work of Chapters 3 and 4 can be applied directly to a one dimensional system. Besides the simplification due to the dynamics of point particles, there is the additional benefit of simple initial conditions. We find that

$$f_1(z,o) = \delta(x)\ \delta(v-v')$$

$$f_k(z_1;..,z_k,o) = n^{k-1} h_o(v_2)\ldots h_o(v_n)\ f_1(z,o) \tag{3.1}$$

where we will use the notation $f_k = f_o^{(k)}$ from now on.

We will calculate the coefficient of self-diffusion from three different closed equations for the distribution function $h(t)$. The first is Boltzmann's equation

$$\frac{\partial h}{\partial t} = nB[h]$$

$$= n \int dw\ |v-w|\ [h_o(v)\ h(w,t) - h_o(w)\ h(v,t)] \tag{3.2}$$

which results from substituting the approximation

$$h_2(v,w,t) = n\ h_o(w)\ h(v,t) \tag{3.3}$$

into equation (2.27). Equation (3.2) can be solved exactly; its solution is given in Appendix D. The coefficient of self-diffusion is found to be 16% off its exact value (2.26) irrespective of the density of the system.

We then consider two corrections to Boltzmann's equation which account for correlations between the velocities of colliding particles caused by three body collision sequences.

One equation is of the form

$$\frac{\partial h}{\partial t} = nB[h] + n^2 t\, C[h] \tag{3.4}$$

where C is a time-independent integral operator which is derived by the methods described in Section 3.3 by considering the dynamics of three isolated particles. We obtain from this equation a small correction to the value of the coefficient of diffusion.

The other equation is of the form

$$\frac{\partial h}{\partial t} = nB[h] + n^2 \int_0^t dt' V\left(e^{-n\alpha(t-t')};\ h(t')\right) \tag{3.5}$$

The operator V as well as including three-body effects, introduces many-body dynamics through the term $e^{-n\alpha t}$ where

$$n\,\alpha(v) = n \int dw\ |v-w|\ h_o(w)$$

is the rate of collisions experienced by a particle moving with velocity v through an equilibrium environment. Equation (3.4) is derived by the approach of Sections 3.4 and 3.5. The coefficient of self-diffusion as calculated from this equation is within 1% of its exact value.

The factorization condition (3.3) which leads to Boltzmann's equation is exact at the initial time as well as when the velocity distribution function h(t) has reached its equilibrium value. Hence we expect equation (3.2) to give a reasonably good approximation to D.

If we define $\phi(v)$ by

$$\phi(v) = \int_0^\infty dt \int dv'\ h_o(v')\ v'\ h(v,t) \tag{3.6}$$

so that

$$D = \int dv\ \phi(v)\ v \tag{3.7}$$

we obtain, by the methods of Chapter 4, the integral equation

$$-vh_o(v) = n \int dw\ |v-w|\,[h_o(v)\ \phi(w) - h_o(w)\ \phi(v)] \tag{3.8}$$

the solution of which is given by equations (D9) and (D10) with $\varepsilon = o$. Numerical evaluation of the integral in (3.7) then gives

$$D_B = 0.328/n \tag{3.9}$$

We have taken $\beta m = 2$ in these calculations, in which case the exact value of the coefficient of self-diffusion is

$$D_{exact} = 0.282/n \tag{3.10}$$

We now consider generalizations of Boltzmann's equation. From the expansion (2.23) for the distribution function $f_j^{(n)}$ and the initial conditions (3.1) we can obtain the expression

$$f_k(z_1;\ldots,z_k,t) = n^{k-1} \sum_{j=o}^{\infty} \frac{1}{j!} n^j \sum_{\ell=o}^{j} (-1)^{j-\ell} \binom{j}{\ell}$$

$$\times \int dz_{k+1} \ldots \int dz_{k+j}\ S^{(k+\ell)}(t)\ h_o(v_2)\ldots h_o(v_{k+j})\ f_1(x_1,v_1,o) \tag{3.11}$$

in exactly the same manner that equation (2.26) of Chapter 3 was derived. In equation (3.11)

$$S^{(n)}(z_1,\ldots,z_n,t) = e^{-L^n t} \tag{3.12}$$

is the n-particle streaming operator. $f_1(o)$ can be eliminated from the expansions for $f_1(t)$ and $f_2(t)$ obtained from (3.11). For precollision configurations, i.e. $(x_1-x_2)(v_1-v_2) < o$

$$\begin{aligned} f_2(z_1,z_2,t) &= n\ h_o(v_2)\ f_1(z_1,t) \\ &\quad + n^2 \int dz_3\ [S^{(3)}(z_1,z_2,z_3,t) - S^{(2)}(z_1,z_3,t)]\ S^{(1)}(z_1,-t) \\ &\quad \times h_o(v_2)\ h_o(v_3)\ f_1(z_1,t) \\ &\quad + \ldots \end{aligned} \tag{3.13}$$

The term proportional to n^2 in equation (3.13) is zero unless particle o (which is at the point z_1 at time t) has interacted with both particles 2 and 3 (i.e. those particles at z_2 and z_3 at at time t) in the interval (o,t). In general the term associated with k-body collisions in this expansion will be non-zero only when the distinguished particle suffers k-1 collisions in the interval (o,t).

To evaluate the three-body term in (3.13), we note first that if particle o has not interacted or has collided only with particle 3 then

$$S^{(3)}(z_1,z_2,z_3,t) = S^{(2)}(z_1,z_3,t)\ S^{(1)}(z_2,t)$$

so that there is no contribution to the three-body term. If particle o suffers two collisions, it must first collide with particle 2 and then with particle 3. This is illustrated in Figure (3.1). We see that the integration over x_3 in the three-body term is restricted to values for which

$$(x_1 - x_3)\big(x_3 - v_3t - (x_2 - v_2t)\big) > o \tag{3.14}$$

Taking this into account we obtain

$$\begin{aligned} h_2(v_1,v_2,t) &= n\, h_o(v_2)h(v_1,t) \\ &\quad + n^2t \int dv_3\ \varepsilon[(v_1-v_2)(v_2-v_3)]\,|v_2-v_3| \\ &\quad \times h_o(v_1)\ [h_o(v_3)h(v_2,t) - h_o(v_2)h(v_3,t)] + \ldots \end{aligned} \tag{3.15}$$

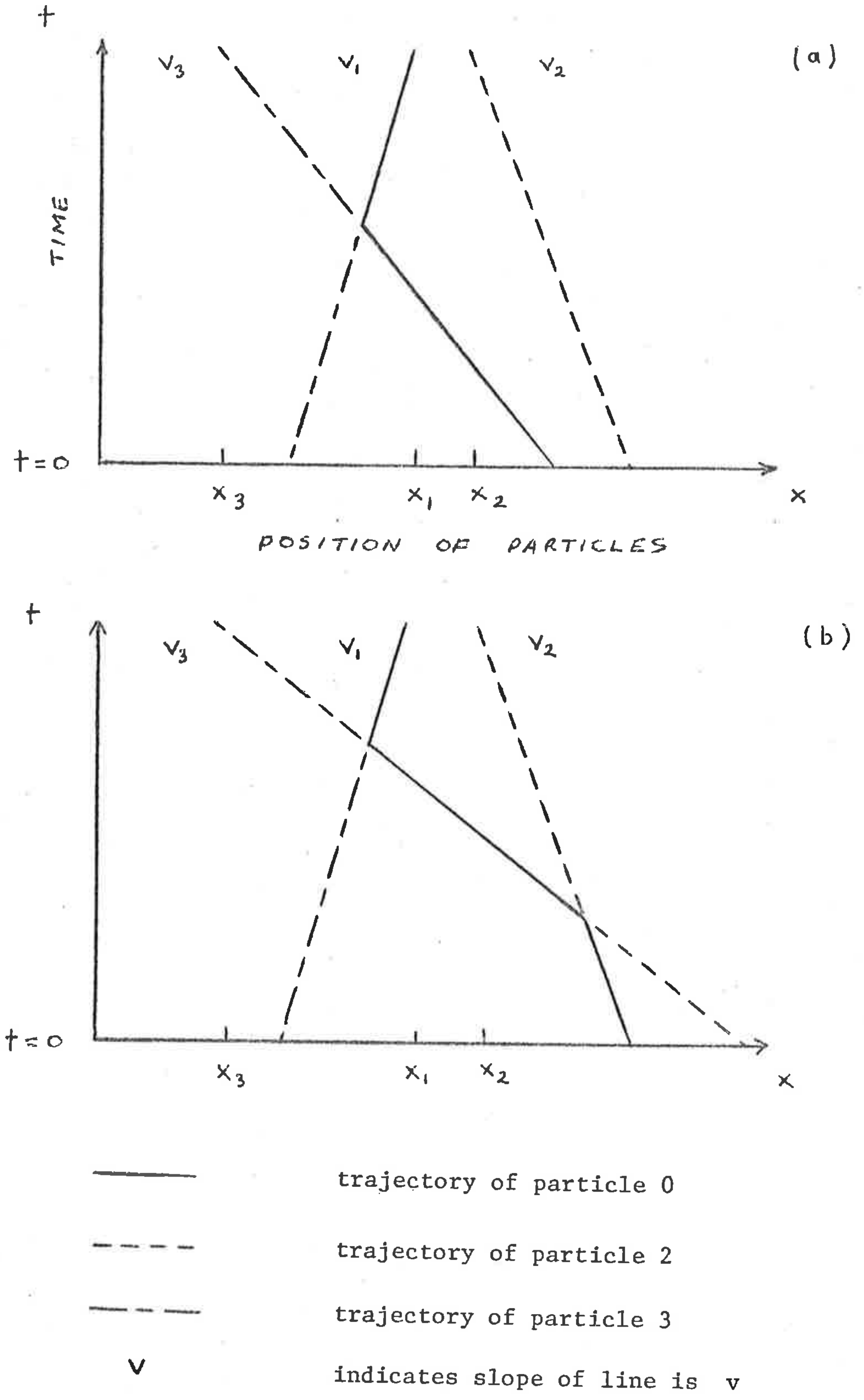

FIGURE 3.1

(a) A collision sequence which does not contribute to the operator $\left(S^{(3)}(z_1,z_2,z_3,t) - S^{(2)}(z_1,z_3,t)\right)$

(b) A collision sequence which does contribute.

The k-body term in this expansion contains the factor $n(nt)^{k-2}$. Hence the density expansion of the many-body collision operator exhibits the same type of divergent behaviour that is found in two and three dimensional systems. One cannot obtain in a straightforward manner a time-independent functional, relating h and h_2, by this approach. Nevertheless the diffusion coefficient can be calculated from the closed equation for h which results from substituting the first few terms of the expansion for h_2 into the hierarchy equation (2.27). If we retain just the two- and three-body terms of the expansion, the equation for h is of the form of (3.4). This can be written as

$$h(v,t) = e^{nBt}h(v,o) + \int_o^t dt' \, e^{nB(t-t')}t'C[h(t')] \tag{3.16}$$

and solved by iteration:

$$h(t) = e^{nBt}h(o) + \int_o^t dt' \, e^{nB(t-t')}t'Ce^{nBt'}h(o) + \ldots \tag{3.17}$$

It is shown in Appendix D that the eigenvalues of B are negative, except for the eigenvalue zero. Hence, on the understanding that h in (3.17) refers to the velocity distribution function minus its equilibrium value h_o, each term of the expansion (3.17) will approach zero for large times. This is not to say that the sum of all terms approaches zero. A more detailed analysis of equation (3.4), and in particular of the eigenvalues of the operator C, is needed to decide upon that point. However the numerical work which we have carried out indicates a rapid convergence of the sequence of partial sums obtained from (3.17).

To calculate the coefficient of self-diffusion from (3.17) we first derive an equation for ϕ defined by (3.6). From (3.17) we find that ϕ is given by

$$\phi(v) = -n^{-1}[1 + B^{-1}\,CB^{-1} + \ldots \qquad]B^{-1}[vh_o(v)] \qquad (3.18)$$

where B^{-1} is the inverse of Boltzmann's operator and is given by equations (D8) and (D9) of Appendix D. The functions $B^{-1}[g(v)]$ and $C[g(v)]$. Where g is some function, can be evaluated numerically. The contributions to the coefficient of self-diffusion from the first few terms of the expansion (3.18) are:

B^{-1}	0.328
$(B^{-1}CB^{-1})B^{-1}$	- 0.015
$(B^{-1}CB^{-1})^2B^{-1}$	0.002
$\left(2(B^{-1}C)^2B^{-2}\right)B^{-1}$	0.003
$(B^{-1}CB^{-1})^3B^{-1}$	0.000

Summing these contributions we obtain a value for D of $0.318\ n^{-1}$.

Finally we consider an alternative generalization to Boltzmann's equation which is based on the methods of Sections 3.4 and 3.5. We begin by writing the hierarchy equations for f_1 and f_2 as

$$\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial x} + n\alpha(v)\right) f_1 = J[f_2] + n\alpha(v)f_1 \qquad (3.19)$$

$$\left(\frac{\partial}{\partial t} + L^2 + n\alpha(v)\right) f_2 = J[f_3] + n\alpha(v)f_2 \qquad (3.20)$$

J is the collision operator which occurs in equation (2.16)

α is defined as

$$\alpha(v) = \int dw|v-w|h_o(w) \tag{3.21}$$

$n\alpha(v)$ is approximately the frequency of collisions experienced by a particle moving with velocity v. The factor $\exp(-n\alpha t)$ which appears in equations given below is, a contribution from dynamical events involving 1,2,3,... particles. It leads to modifications of terms arising from the dynamics of small numbers of particles so that divergences are avoided.

The following expressions are obtained from (3.19) and (3.20)

$$f_1(z,t) = e^{-\left(v\frac{\partial}{\partial x} + n\alpha(v)\right)t} f_1(z,o) + \int_o^t dt' \, e^{-\left(v\frac{\partial}{\partial x} + n\alpha(v)\right)(t-t')} \left(J[f_2(t')] + n\alpha(v)\, f_1(t')\right) \tag{3.22}$$

$$f_2(z,z_2,t) = e^{-\left(L^2 + n\alpha(v)\right)t} f_2(o) + \int_o^t dt' \, e^{-\left(L^2 + n\alpha(v)\right)(t-t')} \left(J[f_3(t')] + n\alpha(v)\, f_1(t')\right) \tag{3.23}$$

Now

$$J[f_2(t)] + n\alpha(v)\ f_1(t) = \int dv_3 |v-v_3|\ \{nh_o(v)\ f_1(x-v_3t, v_3, o) + O(n^2)\} \tag{3.24}$$

and for precollision values of z and z_2

$$\begin{aligned} &J[f_3(t)] + n\alpha(v)\ f_2(t) \\ &= \lim_{\varepsilon\to 0} \int dv_3\ |v-v_3|\ \{n^2 S(\bar{x}, v_3, z_2, z, t)\ h_o(v)\ h_o(v_3)\ f(\bar{x}, v_3, o) + o(n^3)\} \end{aligned} \tag{3.25}$$

and when (3.24) and (3.25) are substituted into (3.22) and (3.23) there results

$$\begin{aligned} f_2(t) &= nh_o(v_2)\ f_1(t) + n^2 \int_o^t dt'\ e^{-\left(L^2 + n\alpha(v)\right)(t-t')} \\ &\quad \times \lim_{\varepsilon\to 0} \int dv_3 |v-v_3| \left(S(\bar{x}, v_3, z_2, z, t') - S(\bar{x}, v_3, t')\right) \\ &\quad \times h_o(v)\ h_o(v_3)\ f(\bar{x}, v_3, o) \\ &\quad + \dots \end{aligned} \tag{3.26}$$

The second term in this expression vanishes unless particle 0, which collides with particle 3 at time t, has previously suffered a collision with particle 2. When the effect of the streaming operators in (3.26) is evaluated, we obtain

$$\begin{aligned} h_2(v, v_2, t) &= nh_o(v_2)\ h(v,t) \\ &+ n^2 \int_o^t dt' \int dv_3\ \varepsilon[v_1-v_2)(v_2-v_3)]\,|v_2-v_3|\ h_o(v_1) \\ &\times [h_o(v_3)\ h(v_2,o) - h_o(v_2)h(v_3,o)]\ \exp\,[-n\alpha(v_1)(t-t')|v_2-v_3|/|v_1-v_3|] \\ &+ \dots \end{aligned} \tag{3.27}$$

If we retain the first two terms of this expansion, and replace $h(v,o)$ by $h(v,t')$ in the second term, we obtain after substituting (3.27) into (2.27) an equation of the form

$$\frac{\partial h}{\partial t} = nB[h] + n^2 \int_0^t dt' \; A(t-t')h(t') \tag{3.28}$$

with A an operator.

If equation (3.28) is to correctly describe the development in time of h, then the three-body term in this equation must approach zero for long times. Since many-body dynamical effects are included in the operator A, (3.28) has the desired behaviour for long times. When the exponential damping terms in (3.27) and (3.28) are replaced by 1, this being the first term in their density expansion, we obtain from (3.28) an equation also derived by Lebowitz and Percus[45]. However, it does not have the property that $\partial h/\partial t \rightarrow 0$ for long times.

The coefficient of self-diffusion is obtained from (3.28) as follows: The function ϕ satisfies the integral equation

$$- \int dv' \; h_o(v') \; v' \; h(v,o)$$

$$= nB[\phi(v)] + n^2 \int_0^\infty dt \int_0^t dt' \int dv' v' h_o(v') \; A(t-t') \; h(v,t')$$

which can be simplified to

$$-vh_o(v) = nB[\phi(v)] + n^2 \int_0^\infty dt \; A(t) \; \phi(v) \tag{3.29}$$

Because of the exponential terms in A( ), the operator $\int_0^\infty dt \; A(t)$ is finite and is proportional to $1/n$. Hence on writing

$$\overline{A} = n \int_0^\infty dt \; A(t)$$

equation (3.29) can be written

$$-vh_o(v) = n(B + \overline{A}) \; \phi(v) \tag{3.30}$$

This integral equation can be solved iteratively:

$$\phi(v) = -n^{-1}(1 + B^{-1} \overline{A})^{-1} \; B^{-1}[vh_o(v)]$$

$$= -n^{-1}(1 - B^{-1} \overline{A} + B^{-1} \overline{A} \; B^{-1} \overline{A} + \ldots)B^{-1}[vh_o(v)] \tag{3.31}$$

$\phi(v)$ can be evaluated from this expression by numerical methods. The contribution of the first four terms of (3.31) to D is 0.280. Contributions from further terms appear to be negligible. Thus it seems that a very good approximation to the coefficient of self-diffusion can be obtained from a correction to Boltzmann's equation which takes into account three-body dynamics.

APPENDIX A. THE HIERARCHY EQUATIONS FOR A GAS OF RIGID SPHERES.

For a system of rigid spheres or discs, the hierarchy of equations satisfied by the velocity distribution functions can be written as

$$\left(\frac{\partial}{\partial t} + L_n\right) f_n(\underline{z}_1,\ldots,\underline{z}_n,t) = \sum_{i=1}^{n} J_{i,n+1}\left(f_{n+1}(\underline{z}_1,\ldots,\underline{z}_{n+1},t)\right) \tag{A1}$$

The operator $J_{i,k}$ is defined by equation (2.21) of Chapter 3.

We now show how (A1) can be derived from the usual form of the hierarchy equation i.e. equation (2.19) of Chapter 3. Our analysis is based on Green's approach to deriving Boltzmann's equation[7].

We begin the derivation of (A1) by considering the expression

$$\int d\underline{z}_{n+1} \left(\frac{\partial}{\partial \underline{x}_i} V_{i,n+1}\right)\cdot\frac{\partial}{\partial \underline{v}_i} f_{n+1}(\underline{z}_1;\ldots,\underline{z}_{n+1},t) \tag{A2}$$

which appears in the hierarchy equation for f_n. We consider the hard-sphere potential to be the limit of a sequence of continuous, short-ranged and repulsive potentials. The sequence $V_n(r)=(a/r)^n$, $n = 1,2\ldots$, is a suitable choice.

Only those configurations of particles i and $n+1$ in which the particles are within the range of their forces contribute to (A2). Let $(\underline{x}_i,\underline{v}_i)$ and $(\underline{x}_{n+1},\underline{v}_{n+1})$ be such a configuration at time t. We choose a time t_o prior to the time the particles begin interacting and such that $t-t_o$ is sufficiently short that we can neglect the possibility of a third particle interacting with i or $n+1$. $\underline{x}_i(t')$, $\underline{v}_i(t')$, $\underline{x}_{n+1}(t')$ and $\underline{v}_{n+2}(t')$ denote the positions and velocities of these particles at a time t' in the interval (t_o,t). Then

$$f_{n+1}\left(\underline{z}_1;\ldots,\underline{z}_i(t'),\ldots,\underline{z}_{n+1}(t'),t'\right) = f_{n+1}(\underline{z}_1;\ldots,\underline{z}_i,\ldots,\underline{z}_{n+1},t)$$

where $\underline{z}_i=\underline{z}_i(t)$ and $\underline{z}_{n+1} = \underline{z}_{n+1}(t)$

We now write

$$f_{n+1}(\underline{z}_1;\ldots,\underline{z}_{n+1},t) = f_{n+1}\left(\underline{z}_1;\ldots,\underline{x}_i,\underline{v}_i(t_o),\ldots,\underline{x}_{n+1},\underline{v}_{n+1}(t_o),t\right) + \Delta \tag{A3}$$

The term Δ depends on the differences $t_o - t$, $\underline{x}_i(t_o) - \underline{x}_i$ and $\underline{x}_{n+1}(t_o) - \underline{x}_{n+1}$. For a hard sphere potential Δ vanishes since these differences can be taken arbitrarily small.

$\underline{v}_i(t_o)$ and $\underline{v}_{n+1}(t_o)$ are functions of $\underline{v}_i(t)$, $\underline{v}_{n+1}(t)$ and $r(t) = \underline{x}_{n+1}(t) - \underline{x}_i(t)$. Alternatively they may be regarded as functions of $r(t_o)$ and the eight constants of the motion for two body encounters. These may be taken as the components of the total momentum vector, angular momentum, energy, and the angle between the direction of $\underline{v}_{n+1}(t_o) - \underline{v}_i(t_o)$ and some direction in the plane of the relative motion. The constants, which we denote by $I_\ell(\underline{v}_i, \underline{v}_{n+1}, \underline{r}), \ell = 1,..,8$, satisfy the differential equation

$$\left[(\underline{v}_{n+1} - \underline{v}_i) \cdot \frac{\partial}{\partial \underline{r}} + \frac{1}{m} \frac{\partial V}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{v}_i} - \frac{\partial}{\partial \underline{v}_{n+1}} \right) \right] I_\ell(\underline{v}_i, \underline{v}_{n+1}, \underline{r}) = 0 \qquad \text{(A4)}$$

As $\underline{v}_i(t_o)$ and $\underline{v}_{n+1}(t_o)$ are also functions of I_ℓ, they also satisfy (A4). Furthermore $f_{n+1}\left(\underline{z}_1; .., \underline{x}_i, \underline{v}_i(t_o), .., \underline{x}_{n+1}, \underline{v}_{n+1}(t_o), t\right)$ also satisfies that equation.

Using (A3) and neglecting Δ we write

$$\left(\frac{\partial}{\partial \underline{x}_i} V_{i,n+1} \right) \cdot \frac{\partial}{\partial \underline{v}_i} f_{n+1}(t) = - \frac{\partial V}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{v}_i} f_{n+1}\left(\underline{z}_1; .., \underline{x}_i, \underline{v}_i(t_o), .., \underline{x}_{n+1}, \underline{v}_{n+1}(t_o) t\right)$$

On using (A4), equation (A2) becomes

$$\int d\underline{z}_{n+1} \; (\underline{v}_{n+1} - \underline{v}_i) \cdot \frac{\partial}{\partial \underline{r}} f_{n+1}\left(\underline{z}_1; .., \underline{x}_i, \underline{v}_i(t_o), .., \underline{x}_{n+1}, \underline{v}_{n+1}(t_o), t\right) \qquad \text{(A5)}$$

In equation (A2) we may restrict the integration over $\underline{x}_{n+1}$ to a region in which $|\underline{x}_{n+1} - \underline{x}_i| < a + \varepsilon$, where $\varepsilon \ll 1$, provided the potential is sufficiently short-ranged. This corresponds to restricting the integration in (A5) to values of $\underline{r}$ for which $|\underline{r}| < a + \varepsilon$. Using Gauss's theorem and taking the limit as $\varepsilon \to 0$, which corresponds to taking a hard-sphere potential, (A5) becomes

$$\int d\underline{v}_{n+1} \int d\underline{a}.\ (\underline{v}_{n+1} - \underline{v}_i)\ f_{n+1}\big(\underline{z}_1; \ldots, \underline{x}_i, \underline{v}_i(t_o), \ldots, \underline{x}_i + \underline{a}, \underline{v}_{n+1}(t_o), t\big) \quad \text{(A6)}$$

where $d\underline{a}$ is an element of surface of a sphere of radius a. Now if $\underline{a}.(\underline{v}_{n+1} - \underline{v}_i) < 0$ the particles are approaching each other, and so $\underline{v}_i(t_o) = \underline{v}_i$ and $\underline{v}_{n+1}(t_o) = \underline{v}_{n+1}$, while if $\underline{a}.(\underline{v}_{n+1} - \underline{v}_i) > 0$ they are receeding and $\underline{v}_i(t_o) = \underline{v}_i'$ and $\underline{v}_{n+1}(t_o) = \underline{v}_{n+1}'$ are functions of $\underline{v}_i, \underline{v}_{n+1}$ and $\underline{a}$ which are given by equations (2.23) of Chapter 3.

Equation (A6) can then be written

$$\begin{aligned} &\int d\underline{v}_{n+1} \int d\underline{a}.\ (\underline{v}_{n+1} - \underline{v}_i)\ \varepsilon[\underline{a}.(\underline{v}_{n+1} - \underline{v}_i)] \\ &x\ [f_{n+1}(z_1; \ldots, \underline{x}_i, \underline{v}_i', \ldots, \underline{x}_i + a, \underline{v}_{n+1}', t) \\ &- f_{n+1}(\underline{z}_1; \ldots, \underline{x}_i, \underline{v}_i, \ldots, \underline{x}_i - \underline{a}, \underline{v}_{n+1}, t)] \qquad \text{(A7)} \end{aligned}$$

(A7) is one of the terms in equation (A1). The other terms can be obtained from the form (2.19) of the hierarchy in a similar fashion.

APPENDIX B. AN ALTERNATIVE CORRECTION TO BOLTZMANN's EQUATION

The equation for f which was derived in Section 3.5 resulted from a modification to the principle of molecular chaos in which the effects of three-body interactions were included. Since three particles can interact through a sequence of binary collisions for a long period of time, the effects of collisions with further particles were accounted for approximately. We now derive another closed equation for f which involves a three-body term. The possibility of interaction between three particles and other particles is allowed for by a damping term $\exp(-\lambda_k t)$ where

$$\lambda_k = -nB(\underline{v}_1) - \dots - nB(\underline{v}_k) \tag{B1}$$

The physical significance of this choice for λ_k is explained in Section 3.5.

The notation of this appendix is the same as for Chapter 3.

Because the operators L_k and λ_k as given by (B1) do not commute the effects of the operators $I(\underline{z}_1,\underline{z}_2,t)$ and $I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t)$ are somewhat more difficult to evaluate than when $\lambda_k = -n\alpha(\underline{v}_1)$.

The distribution functions f and f_2 were given as expansions in terms of the initial conditions by equations (4.7) and (4.8) of Chapter 3.

$$\begin{aligned} f(t) = I(\underline{z}_1,t)\ f(o) + n \int_o^t dt_1\ I(\underline{z}_1,t-t_1)\ J_{13}\big[\big(I(\underline{z}_1,\underline{z}_3,t_1) \\ - I(\underline{z}_1,t_1)\big)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)\big] \end{aligned} \tag{B2}$$

$$\begin{aligned} f_2(t) = {} & I(\underline{z}_1,\underline{z}_2,t)\ n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(\underline{z}_1,o) \\ & + n^2 \int_o^t dt_1\ I(\underline{z}_1,\underline{z}_2,t-t_1)\ (J_{13}+J_{23}) \\ & \times \big[\big(I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1) - I(z_1,z_2,t_1)\big)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)\big] \end{aligned} \tag{B3}$$

Now to obtain Enskog's form of Boltzmann's equation, we must express

f_2 as

$$f_2(t) = n_2(x_2;x_1)\ h_o(v_2)\ f(t) + \ldots$$

To achieve this we write

$$I(\underline{z}_1,\underline{z}_2,t) = S(\underline{z}_1,\underline{z}_2,t) + n \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)\ \left(B(\underline{v}_1) + B(\underline{v}_2)\right)$$

$$\times\ I(\underline{z}_1,\underline{z}_2,t_1) \qquad \text{(B4)}$$

which follows from an examination of the differential equation satisfied by $I(\underline{z}_1,\underline{z}_2,t)$. The streaming operator $S(t)$ was defined in Section 3.2.

Now, from the density expansion (2.30) of n_2, we find

$$S(\underline{z}_1,\underline{z}_2,t)\ n_2(\underline{x}_2;\underline{x}_1) = n_2(\underline{x}_2;\underline{x}_1) + n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\int d\underline{a}.\underline{v}_{12}\ (e^{-V(\underline{x}_{12} - \underline{a})} - 1) \qquad \text{(B5)}$$

where $\underline{x}_{12} = \underline{x}_1 - \underline{x}_2$.

Hence from (B3), (B4) and (B5), for precollision configurations of particles 1 and 2,

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ S(\underline{z}_1,t)\ f(o) + n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times \int d\underline{a}.\underline{v}_{12}\ (e^{-V(\underline{x}_{12}-\underline{a})} - 1)\ h_o(\underline{v}_2)\ S(\underline{z}_1,t)\ f(\underline{z}_1,o)$$

$$+ n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times\ (J_{13} + J_{23})[I(\underline{z}_1,\underline{z}_2,t_1)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)] + \ldots \qquad \text{(B6)}$$

From equation (B2)

$$f\ (t) = I(z\ ,t)\ f(\underline{z}_1,o) + \ldots$$

$$= S(\underline{z}_1,t)\ f(\underline{z}_1,o) + \int_o^t dt_1\ S(\underline{z}_1,t-t_1)\ J_{13}[I(\underline{z}_1,t)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)]$$

$$+ \ldots \qquad \text{(B7)}$$

Combining (B6) and (B7) leads to

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(t) + n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times \int d\underline{a}.\underline{v}_{12}\ (e^{-V(\underline{x}_{12}-\underline{a})} - 1)\ h_o(\underline{v}_2)\ f\big(\underline{x}_1-\underline{v}_1(t-t_1),\underline{v}_1,t_1\big)$$

$$+ n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times \{J_{13}[\big(I(\underline{z}_1,\underline{z}_2,t_1) - I(\underline{z}_1,t_1)\big)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)]$$

$$+ J_{23}\ I(\underline{z}_1,\underline{z}_2,t_1)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,o)]\} + \ldots \qquad \text{(B8)}$$

To express $I(\underline{z}_1,\underline{z}_2,t_1)\ h_o(\underline{v}_2)\ f(\underline{z}_1,o)$ in terms of $f(t)$, we observe that $I(\underline{z}_1,\underline{z}_2,t)$ satisfies

$$[\frac{\partial}{\partial t} + \underline{v}_1\cdot\frac{\partial}{\partial \underline{x}_1} + \underline{v}_2\cdot\frac{\partial}{\partial \underline{x}_2} - nB(\underline{v}_1) - nB(v_2)]\ I(\underline{z}_1,\underline{z}_2,t) = \theta_{12}\ I(\underline{z}_1,\underline{z}_2,t) \qquad \text{(B9)}$$

where

$$\theta_{ij} = \frac{1}{m}\frac{\partial V_{ij}}{\partial \underline{x}_i}\cdot\left(\frac{\partial}{\partial \underline{v}_i} - \frac{\partial}{\partial \underline{v}_j}\right) \qquad \text{(B10)}$$

Integrating (B9) and using (B4)

$$I(\underline{z}_1,\underline{z}_2,t) = I^o(\underline{z}_1,\underline{z}_2,t) + \int_o^t dt_1\ I^o(\underline{z}_1,\underline{z}_2,t-t_1)\ \theta_{12}\ \{S(\underline{z}_1,\underline{z}_2,t_1)$$

$$+ n\int_o^{t_1} dt_2\ S(\underline{z}_1,\underline{z}_2,t-t_1)\ \big(B(\underline{v}_1) + B(\underline{v}_2)\big)\ I(\underline{z}_1,\underline{z}_2,t_2)\} \qquad \text{(B11)}$$

where

$$I^o(\underline{z}_1,\ldots,\underline{z}_k,t) = \exp\ [-(\underline{v}_1\cdot\frac{\partial}{\partial \underline{x}_1} + \ldots + \underline{v}_k\cdot\frac{\partial}{\partial \underline{x}_k} - nB(\underline{v}_1) - \ldots - nB(\underline{v}_k))t] \qquad \text{(B12)}$$

Retaining the first two terms of the right hand side of (B11) and substituting into (B8), gives an expression for f_2 involving $S(\underline{z}_1,t_2)\ f(\underline{z}_1,o)$, which to a first approximation, equals $f(\underline{z}_1,t_2)$.

Hence

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(t) + n^2 \int_o^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times \int d\underline{a}.\underline{v}_{12}\ (e^{-V(\underline{x}_{12}-\underline{a})} - 1)\ h_o(\underline{v}_2)\ f\big(\underline{x}_1-\underline{v}_1(t-t_1),\underline{v}_1,t_1\big)$$

(cont.)

$$+ n^2 \int_0^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)\ (J_{13} + J_{23}) \int_0^{t_1} dt_2\ I^o(\underline{z}_1,\underline{z}_2,t_1-t_2)$$

$$\theta_{12}\ S(\underline{z}_1,\underline{z}_2,t_2)\ S(\underline{z}_1,-t_2)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,t_2) + \ldots \tag{B13}$$

There are additional terms in (B2) and (B3) which we have not yet considered. An analysis similar to that already carried out shows that the following term occurs in (B13).

$$n^2 \int_0^t dt_1\ I^o(\underline{z}_1,\underline{z}_2,t-t_1)\ J_{23}\Big[\int_0^{t_1} dt_2\ I^o(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1-t_2)\ \theta_{13}$$

$$\times\ S(\underline{z}_1,\underline{z}_3,t_2)\ S(\underline{z}_1,-t_2)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,t_2)$$

If we approximate $I^o(t-t_1)$ in this expression by $S(\underline{z}_1,\underline{z}_2,t-t_1)$, we obtain a relationship between f_2 and f which is similar to an expression derived by Dorfman[33] and others.

$$f_2(t) = n_2(\underline{x}_2;\underline{x}_1)\ h_o(\underline{v}_2)\ f(t) + n^2 \int_0^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)$$

$$\times \int d\underline{a}.\underline{v}_{12}(e^{-V(x_{12}-a)} - 1)\ h_o(\underline{v}_2)\ f\big(\underline{x}_1-\underline{v}_1(t-t_1),\underline{v}_1,t_1\big)$$

$$+ n^2 \int_0^t dt_1\ S(\underline{z}_1,\underline{z}_2,t-t_1)\ \big(J_{13}+ J_{23}\ (1 + P_{23})\big)$$

$$\times\ \Big[\int_0^t dt_2\ I^o(\underline{z}_1,\underline{z}_2,t_1-t_2)\ \theta_{12}$$

$$\times\ S(\underline{z}_1,\underline{z}_2,t_2)\ S(\underline{z}_1,-t_2)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,t_2)\Big] + \ldots \tag{B14}$$

P_{23} is an operator acting on functions of $\underline{z}_2$ and $\underline{z}_3$, defined by

$$P_{23}\ g(\underline{z}_2,\underline{z}_3) = g(\underline{z}_3,\underline{z}_2) \tag{B15}$$

Dorfman's expression differs from (B14) in that the operator $I^o(\underline{z}_1,\underline{z}_2,t_1-t_2)$, which appears in the third term of (B14) is replaced by

$$\exp\Big[-\Big(\underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}_1} + \underline{v}_2 \cdot \frac{\partial}{\partial \underline{x}_2} - nB(\underline{v}_1) - nB(\underline{v}_2) - nB'(\underline{v}_2)\Big)(t_1-t_2)\Big]$$

where $B'(\underline{v}_2)$ is defined on functions of $\underline{v}_2$ by

$$B'(\underline{v}_2)[g(\underline{v}_2)] = \int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{32}\ \varepsilon(\underline{a}\cdot\underline{v}_{32})\ [h_o(\underline{v}_2')\ g(\underline{v}_3') - h_o(\underline{v}_2)\ g(\underline{v}_3)] \qquad \text{(B16)}$$

When (B14) is substituted into the first hierarchy equation we obtain a closed equation for f which applies to gases in which three particle interactions are important.

APPENDIX C. SOLUTION OF THE HIERARCHY EQUATIONS FOR A GAS OF POINT PARTICLES.

In this appendix we solve the equations governing the distribution functions $f_j^{(n)}$ defined in Section 5.2 for a gas of point particles. From equation (2.16) and equations like (2.13) of Chapter 5, we have

$$\left(\frac{\partial}{\partial t} + L_j^n\right) f_j^{(n)}(z_1;..,z_n,t)$$

$$= \lim_{\varepsilon\to o} \int dv_{n+1}\, |v_{n+1} - v_1|\, [f_{(j)}^{(n+1)}(z_1;..,x_1^-,v_{n+1},t)$$

$$- f_j^{(n+1)}(z_1;..,x_1^-,v_{n+1},t)] \qquad \text{(C1)}$$

where

$$x_1^- = x_1 - \varepsilon \operatorname{sgn}(v_{n+1} - v_1)$$

and

$$(j) = j + \operatorname{sgn}(v_{n+1} - v_1)$$

We solve these equations when the initial conditions are

$$f_o^{(j)}(z,o) = \delta(x)\ \delta(v-v')$$

for $j > o$

$$f_j^{(1)}(z,o) = \frac{n(nx)^{j-1}}{(n-1)!} e^{-nx} h_o(v) \qquad o \leq x < L$$

$$= 0 \qquad \text{otherwise}$$

for $j < o$

$$f_j^{(1)}(z,o) = f_{-j}^{(1)}(-x,v,o) \qquad \text{(C2)}$$

We show that $f_j^{(n+1)}$ can be expressed in terms of $f_k^{(n)}$ $(k = j-1,j,j+1)$ and thus it is possible to break the chain of equations (C1) and effect their solution.

We introduce the function, defined for $n \geq 2$,

$$g_j^{(n)}(z_1,..,z_n t) = f_j^{(n)}(z_1;..,z_n,t)$$

$$- f_{j*}^{(n-1)}(z_1;..,z_{n-1},t)\ h(z_n,t) \qquad \text{(C3)}$$

where

$$\begin{aligned} j^* &= j - 1 && 0 < x_n - v_n t < x_1 - v_1 t \\ &= j + 1 && x_1 - v_1 t < x_n - v_n t < 0 \\ &= j && \text{otherwise} \end{aligned}$$

and

$$\begin{aligned} h(x,v,t) &= n\ h_o(v) + \delta(x-v't)\ \delta(v-v') \\ &\qquad \text{if } - L < x-vt < L \\ &= 0 \quad \text{otherwise} \end{aligned}$$

We now confine our attention to configurations of an n-particle system for which particle j has suffered no collision in its past history under the n-particle motion, although there may have been collisions involving other particles. For such cases, the Liouville operator L_j^n becomes

$$v_1 \frac{\partial}{\partial x_1} + \ldots + v_n \frac{\partial}{\partial x_n}$$

Using the fact that

$$\left(\frac{\partial}{\partial t} + v \frac{\partial}{\partial x}\right) h(x,v,t) = 0$$

we have from (C.1) that for the configurations under consideration

$$\left(\frac{\partial}{\partial t} + v_1 \frac{\partial}{\partial x_1} + \ldots + v_n \frac{\partial}{\partial x_n}\right) g_j^{(n)}(z_1;..,z_n,t)$$

$$= \lim_{\varepsilon \to o} \int dv_{n+1}\ |v_{n+1} - v_1|\ [g_{(j)}^{(n+1)}(z_1;..,z_n,x_1^-,v_{n+1},t)$$

$$- g_j^{(n+1)}(z_1;..,z_n,x_1^-,v_{n+1},t)] \qquad \text{(C4)}$$

The functions $g_j^{(n)}$, $g_j^{(n+1)}$ and $g_{(j)}^{(n+1)}$ appearing in this equation are evaluated only for configurations in which particle j, or particle (j), has suffered no collision.

Now $g_j^{(n)} = 0$ at $t = 0$, as can be seen from a consideration of the initial conditions (C2). Hence equation (C4) implies $g_j^{(n)} = 0$ for all subsequent times and so

$$f_j^{(n)}(z_1;\ldots,z_n,t) = f_{j*}^{(n-1)}(z_1;\ldots,z_{n-1},t)\; h(z_n,t) \tag{C5}$$

for regions of phase space being considered.

It is this relationship which enables the hierarchy equations to be solved for $f_j^{(1)}$.

Since (C1) for $n = 1$ involves $f_j^{(2)}$ only for precollision configurations of two particles, equation (C5) can be applied to this equation and we obtain

$$\begin{aligned}\left(\frac{\partial}{\partial t} + v\,\frac{\partial}{\partial x}\right) f_j(z,t) &= \gamma_o[f_{j-1}(z,t) - f_j(z,t)] \\ &\quad + \beta_o[f_{j+1}(z,t) - f_j(z,t)] \\ &\quad + \lim_{\zeta\to o} \delta(x^- - v't) \begin{bmatrix} \varepsilon(x-vt)\;(v'-v)\;[f_{j+1}(z,t) - f_j(z,t)] \\ + \varepsilon(vt-x)\;(v-v')\;[f_{j-1}(z,t) - f_j(z,t)] \end{bmatrix}\end{aligned} \tag{C6}$$

where $x^- = x - \zeta\,\mathrm{sgn}(v'-v)$ and $\varepsilon(x)$ is the unit step function,

$$\beta_o = n\int_{x/t}^{(x+L)/t} dw(w - v)\; h_o(w)$$

$$\gamma_o = n\int_{(x-L)/t}^{x/t} dw(v - w)\; h_o(w)$$

Because of the δ-function term on the right hand side of this equation, f_j is discontinuous at $x = v't$ and consequently $\lim_{\zeta\to o} \delta(x^- - v't)$ cannot be replaced simply by $\delta(x-vt)$. In the immediate neighbourhood of the discontinuity, (C6) can be simplified to

$$(v-v')\,\frac{\partial}{\partial(x-v't)}\, f_j$$

$$= \lim_{\zeta\to o} \delta(x^- - v't) \begin{bmatrix} \varepsilon(x-vt)\;(v'-v)\;[f_{j+1} - f_j] \\ + \\ \varepsilon(vt-x)\;(v-v')\;[f_{j-1} - f_j] \end{bmatrix}$$

Integrating this equation across the discontinuity yields the following relation between the values of f_j on either side of the discontinuity:

$$\lim_{\zeta\to o} f_j(v't - \zeta, v, t) = \lim_{\zeta\to o} f_{j+1}(v't + \zeta, v, t) \tag{C7}$$

Using these relations and those of equation (C2) as boundary conditions, we can solve the equation

$$\begin{aligned}\left(\frac{\partial}{\partial t} + v\,\frac{\partial}{\partial x}\right) f_j(z,t) &= \gamma_o[f_{j-1}(z,t) - f_j(z,t)] \\ &\quad + \beta_o[f_{j+1}(z,t) - f_j(z,t)]\end{aligned} \tag{C8}$$

which is valid everywhere except at the previously mentioned point of discontinuity. To solve this equation, we define the transform function $\eta(\theta)$ by

$$\eta(\theta) = \sum_{j=-\infty}^{\infty} e^{i\theta j}\, f_j \tag{C9}$$

which has the inverse transform

$$f_j = \frac{1}{2\pi}\int_o^{2\pi} d\theta\; e^{-i\theta j}\, \eta(\theta) \tag{C10}$$

From (C8) and (C9) we find that $\eta(\theta)$ satisfies the equation

$$\left(\frac{\partial}{\partial t} + v\,\frac{\partial}{\partial x}\right) \ln \eta(\theta) = \gamma_o(e^{i\theta}-1) + \beta_o(e^{-i\theta}-1) \tag{C11}$$

which can be integrated immediately to obtain

$$\begin{aligned}&\eta(\theta,x,v,t) \\ &= \eta\left(\theta, x-v(t-t_o^{+}), v, t_o^{+}\right) \exp\left(\int_{t_o^{+}}^{t} dt' \,[\gamma_o(e^{i\theta} - 1) + \beta_o(e^{-i\theta} - 1)]\right) \\ &\qquad\qquad\qquad\qquad t > t_o > 0 \\ &= \eta(\theta, x-vt, v, o) \exp\left(\int_o^t dt' \,[\gamma_o(e^{i\theta} - 1) + \beta_o(e^{-i\theta} - 1)]\right. \\ &\qquad\qquad\qquad\qquad \text{otherwise}\end{aligned} \tag{C12}$$

where

$$t_o = (x-vt)/(v'-v)$$

and t_o^{+} is infinitesimally larger than t_o. These results follow from integrating (C11) down to the point of discontinuity at $t' = t_o$ or to $t' = o$ if t_o does not lie between o and t.

It can be shown that

$$n^{-1} \int_T^t dt' \, \beta_o = \int_{x/t}^{(x+L)/t} dw(wt - x) \, h_o(w) - \int_{X/T}^{(X+L)/T} dw(wT - X) \, h_o(w) - L \int_{(X+L)/T}^{(x+L)/t} dw \, h_o(w) \tag{C13}$$

and

$$n^{-1} \int_T^t dt' \, \gamma_o = \int_{(x-L)/t}^{x/t} dw(x - wt) \, h_o(w) - \int_{(X-L)/T}^{X/T} dw(X - wT) \, h_o(w) - L \int_{(x-L)/t}^{(X-L)/T} dw \, h_o(w) \tag{C14}$$

where T is arbitrary and $X = x-vt + vT$. It can also be shown from (C2) and (C9) that

$$\begin{aligned} \eta(\theta,x-vt,v,o) &= \delta(x-vt) \, \delta(v-v') \\ &+ e^{i\theta} n \, h_o(v) \, \varepsilon(x-vt) \, \varepsilon(L-x+vt) \exp [n(x-vt) \, (e^{i\theta} - 1)] \\ &+ e^{-i\theta} n \, h_o(v) \, \varepsilon(vt-x) \, \varepsilon(L+x-vt) \exp [n(vt-x) \, (e^{-i\theta} - 1)] \end{aligned} \tag{C15}$$

and from (C7) that

$$\begin{aligned} &\eta(\theta,x-v(t-t_o^+),v,t_o^+) \\ &\quad = \exp [i\theta \operatorname{sgn}(v-v')] \, \eta\left(\theta,x-v(t-t_o^-),v,t_o^-\right) \end{aligned} \tag{C16}$$

where t_o^- is infinitesimally less than t_o.

Finally from (C10), (C12) - (C16) we have that

$$\begin{aligned} f_j(z,t) = \frac{1}{2\Pi} \int_o^{2\Pi} d\theta \, e^{-i\theta j} \Big\{ & \delta(x-vt) \, \delta(v-v') \\ & + n \, h_o(v) \, \varepsilon(t_o) \, \varepsilon(t-t_o) \, \varepsilon(L - x + vt) \, \varepsilon(L + x - vt) \\ & + n \, h_o(v) \, [1 - \varepsilon(t-t_o) \, \varepsilon(t_o)][e^{i\theta} \varepsilon(L - x + vt) \, \varepsilon(x -vt) \\ & + e^{-i\theta} \varepsilon(L + x - vt) \, \varepsilon(vt - x)]\Big\} \\ & \times \exp [(e^{i\theta} - 1) \, \nu(t) + (e^{-i\theta} - 1) \, \mu(t)] \end{aligned} \tag{C17}$$

where

$$\mu(t) = n\int_{x/t}^{(x+L)/t} dw\ (wt - x)\ h_o(w) + nL \int_{(x+L)/t}^{\infty} dw\ h_o(w)$$

and

$$\nu(t) = n\int_{(x-L)/t}^{x/t} dw\ (x - wt)\ h_o(w) + nL \int_{-\infty}^{(x-L)/t} dw\ h_o(w) \tag{C18}$$

In the limit $L\to\infty$ and for $j=o$, equation (C17) reduces to the results obtained by Jepsen[44] and Lebowitz and Percus[45].

The important feature of the model we have been considering which makes it possible to solve the hierarchy equations, is that the order along the line of the particles is maintained for all times. However, it is possible to extend the results obtained above to more complicated one-dimensional systems by using perturbation techniques. As an example consider the case of point particles which have a velocity independent probability R of being reflected upon collision. The hierarchy equations in this case are

$$\left(\frac{\partial}{\partial t} + L_j^n\right) f_j^{(n)} = R\int dw\ |w-v|\ \left(Pf_j^{(n+1)} - f_j^{(n+1)}\right)$$

$$= R\int dw\ |w-v|\ \left(f_{(j)}^{(n+1)} - f_j^{(n+1)}\right) + \xi R\int dw\ |v-w|\ \left(Pf_j^{(n+1)} - f_{(j)}^{(n+1)}\right) \tag{C19}$$

Here P is an operator which permutes the coordinates of the jth particle (i.e. x,v) with those of the unlabelled particles with which it is about to collide (i.e. x^-,w). The quantity $\xi = 1$ is a marking parameter which indicates that the term it multiplies is presumed to be small. This term vanishes in both the $R=0$ and $R=1$ limits. We assume a solution to (C19) of the form

$$f_j^{(n)} = \sum_k \xi^k \left(f_j^{(n)}\right)_k \tag{C20}$$

The ξ^o equation is

$$\left(\frac{\partial}{\partial t} + L_j^n\right) \left(f_j^{(n)}\right)_o = R \int dw\ |w-v|\ \left[\left(f_{(j)}^{(n+1)}\right)_o - \left(f_j^{(n+1)}\right)_o\right] \tag{C21}$$

which can be solved for $n \geqslant 2$ in precollision regions as before to obtain

$$\left(f_j^{(n)}\right)_o = \left(f_{j*}^{(n-1)}\right)_o h \tag{C22}$$

where it is assumed that at $t=o$ $\left(f_j^{(n)}\right)_o = f_j^{(n)}$. A closed equation for $\left(f_j^{(1)}\right)_o$ can be obtained by substituting (C22) for $n=2$ into (C21) for $n=1$. This equation can be solved in exactly the manner previously discussed to obtain

$$\left(f_j^{(1)}\right)_o = \frac{1}{2\Pi}\int_o^{2\Pi} d\theta \; e^{-ij\theta} \eta(\theta,x,v,t) \tag{C23}$$

where

$$\begin{aligned}
&\eta(\theta,x,v,t)\\
&\quad = \left\{\delta(x-vt)\delta(v-v') + e^{i\theta} nh_o(v)\;\varepsilon(x-vt)\;\exp[n|x-vt|\;(e^{i\theta}-1)\;(1-R)]\right.\\
&\quad \left. + e^{-i\theta} nh_o(v)\;\varepsilon(vt-x)\;\exp[n|vt-x|\;(e^{-i\theta}-1)\;(1-R)]\right\}\\
&\quad \times \left\{1 + \varepsilon(t-t_o)\;\varepsilon(t_o)\;(R-1)\;\exp[i\theta \operatorname{sgn}(v-v')]\right\}\\
&\quad \times \exp[(e^{-i\theta}-1)\;Rt\gamma(x/t) + (e^{i\theta}-1)\;Rt\beta(x/t)]
\end{aligned} \tag{C24}$$

Here

$$\beta(v) = n\int_v^{\infty} dw\;(w-v)\;h_o(w)$$

$$\gamma(v) = n\int_{-\infty}^{v} dw\;(v-w)\;h_o(w)$$

(C24) is derived by assuming that the initial distribution of particles is over an infinite interval.

Equation (C24) provides a correct expression for $f_j^{(1)}$ in the cases $R=0$ (a perfect gas) and $R=1$ (impenetrable particles). For $R\neq 1$, the factors

$$\exp[n\;|x-vt|\;(e^{\pm i\theta}-1)(1-R)]$$

which appear in (C24) assure that $(f_j^{(1)})_o$ is exponentially damped and so higher order perturbation terms of (C20), which from (C19) obey equations of the form:

$$\left(\frac{\partial}{\partial t} + L_j^n\right) \left(f_j^{(n)}\right)_k = R\int dw \; |w-v| \; \left[\left(f_{(j)}^{(n+1)}\right)_k - \left(f_j^{(n+1)}\right)_k\right]$$

$$+ R\int dw \; |w-v| \; \left[P\left(f_j^{(n+1)}\right)_{k-1} - \left(f_{(j)}^{(n+1)}\right)_{k-1}\right]$$

will not exhibit secular behaviour.

APPENDIX D. THE SOLUTION OF BOLTZMANN'S EQUATION IN ONE DIMENSION

The purpose of the appendix is to solve the one dimensional form of Boltzmann's equation

$$\frac{\partial}{\partial t} h(v,t) = \rho \int dw|v - w|\,[h_o(v)h(w,t) - h_o(w)h(v,t)] \tag{D1}$$

Define

$$g(v,t) = \int dv' \, v' \, h_o(v')h(v,t). \tag{D2}$$

It should be recalled that $h(v,t)$ is also a function of v'. In fact $h(v,0) = \delta(v - v')$ so that $g(v,0) = vh_o(v)$ is an odd function of v.

Let

$$\tilde{g}(v,s) = \int_o^\infty dt \, e^{-st} \, g(v,t) \tag{D3}$$

be the Laplace transform of $g(v,t)$. $\tilde{g}(v,s)$ then satisfies

$$s\tilde{g}(v,s) - g(v,0) = \rho \int d\omega|v - \omega|\,[h_o(v)\tilde{g}(\omega,s) - h_o(\omega)\tilde{g}(v,s)] \tag{D4}$$

Since $g(v,0)$ is an odd function of v, the linear equation (D4) implies that $\tilde{g}(v,s)$ is also odd.

Introducing the auxiliary function

$$G(v,s) = \int d\omega|v - \omega| \, \tilde{g}(\omega,s) \tag{D5}$$

we can write equation D4 as

$$s\frac{\partial^2}{\partial v^2}G(v,s) - 2g(v,0) = \rho\frac{\partial}{\partial v}\left\{G(v,s)\frac{d\alpha}{dv} - \alpha(v)\frac{\partial G}{\partial v}\right\} \tag{D6}$$

where $\alpha(v)$ is defined as

$$\alpha(v) = \int d\omega|v - \omega| \, h_o(\omega) \tag{D7}$$

Integrating equation (D6) and using the boundary conditions

$$G(0,s) = 0 \, , \; \frac{\partial G}{\partial v}\bigg|_{v=0} = -2\int_o^\infty d\omega \, \tilde{g}(\omega,s)$$

we obtain

$$G(v,s) = \{s + \rho\alpha(v)\} \int_o^v d\omega \, f(\omega)\{s + \rho\alpha(\omega)\}^{-2} \tag{D8}$$

where

$$f(v) = 2\int_0^v d\omega\ g(\omega,0) - 2\left[s + \rho\alpha(0)\right]\int_0^\infty d\omega\ \tilde{g}(\omega,s)$$

and hence

$$\tilde{g}(v,s) = \tfrac{1}{2}\frac{\partial^2}{\partial v^2}G(v,s) = \rho h_o(v)\int_0^v d\omega\ f(\omega)\left[s + \rho\alpha(\omega)\right]^{-2} + g(v,0)\left[s + \rho\alpha(v)\right]^{-1} \tag{D9}$$

$\int_0^\infty d\omega\ \tilde{g}(\omega,s)$ an unknown quantity in equation (D9), can be obtained by integrating equation (D10) to obtain

$$\left[1 + 2\left(s + \rho\alpha(0)\right)\int_0^\infty dv\int_0^v d\omega\ h_o(v)\left(s + \rho\alpha(\omega)\right)^{-2}\right]\int_0^\infty dv\ \tilde{g}(v,s)$$
$$= 2\rho\int_0^\infty dv\ h_o(v)\int_0^v d\omega\ \left(s + \rho\alpha(\omega)\right)^{-2}\int_0^\infty du\ g(u,0)$$
$$+ \int_0^\infty dv\ g(v,0)\left(s + \rho\alpha(v)\right)^{-1} \tag{D10}$$

The quantity $\phi(v)$ defined in equation (3.6) of Section 5.3 is given by equations (D9) and (D10) with $s = 0$.

Let us consider the eigenvalue equation

$$\lambda b(v) = B[b(v)] \tag{D11}$$

One solution is $b(v) = h_o(v)$ with $\lambda = 0$. To find other solutions we note that the eigenvalue equation is of the form of equation (D4) with $g(v,0) = 0$ and $s/\rho = \lambda$. Hence the solution is given by equation (D9) and (D10). In particular the right hand side of (D10) is zero. By considering the left hand side we see that $\lambda < -\alpha(0)$.

APPENDIX E COMPARISON WITH THE WORK OF SENGERS.

It is the purpose of this appendix to show that the integral equation

$$-\underline{v}\; h_o(\underline{v}) = \left(n_2 B + \int_o^\infty dt\; A_3(t)\right) \underline{\phi}(\underline{v}) \tag{E1}$$

which results from equation (2.21) of Chapter 4 reduces to an integral equation derived by Sengers et al.[75] when the exponential terms in the operator A_3 are replaced by 1 i.e. when only three-body contributions to A_3 are considered. Sengers' equations result from an analysis of the Choh-Uhlenbeck equation. A_3 is given by equation (2.22) of Chapter 4. If $\tilde{A}_3$ is the result of neglecting many-body contributions to A_3 we write

$$\int_o^\infty dt\; \tilde{A}_3(t) = n^2 \overline{A}_3$$

and show that $\overline{A}_3$ is related to the operator I_3 considered by Sengers[75].

From (2.22) of Chapter 4, we find

$$\begin{aligned}
\overline{A}_3(\underline{v}_1)\; \underline{\phi}(\underline{v}_1) \quad = \quad & \int d\underline{x}_3\; f_{13}\; f_{23}\; J_{12}\; \{h_o(\underline{v}_2)\; \underline{\phi}(\underline{v}_1)\} \\
& + J_{12}\; \{G_o(\underline{z}_1,\underline{z}_2) \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{12}\; \left(1-e^{-V(\underline{x}_{12}-\underline{a})}\right) \\
& x\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; \underline{\phi}(\underline{v}_1)\} \\
& + J_{12}\{G_o(\underline{z}_1,\underline{z}_2)\; J_{13}\; [f_{23}\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; \underline{\phi}(\underline{v}_1)]\} \\
& + J_{12}\{G_o(\underline{z}_1,\underline{z}_2)\; J_{23}\; [f_{13}\; h_o(\underline{v}_2)\; h_o(\underline{v}_3)\; \underline{\phi}(\underline{v}_1)]\} \\
& + J_{12}\; G_o(\underline{z}_1,\underline{z}_2) \int d\underline{v}_3 \int d\underline{a}.\underline{v}_{31}\; \varepsilon(\underline{a}.\underline{v}_{31}) \int d\underline{h}(\underline{v}_2-\underline{v}_1')\,\varepsilon[\underline{b}.(\underline{v}_2-\underline{v}_1')] \\
& x\; G_o(\underline{x}_1,\underline{v}_1',\underline{x}_2,\underline{v}_2)\; \delta(\underline{x}_{21}-\underline{b})\; h_o(\underline{v}_3')[h_o(\underline{v}_2')\phi(\underline{v}_1'') \\
& -\; h_o(\underline{v}_2)\;\; \underline{\phi}(\underline{v}_1')]\}
\end{aligned}$$

$$+ J_{12}\ \{G_o(\underline{z}_1,\underline{z}_2) \int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{32}\ \varepsilon(\underline{a}\cdot\underline{v}_{32}) \int d\underline{b}\cdot(\underline{v}_2'-\underline{v}_1)\varepsilon[\underline{b}\cdot(\underline{v}_2'-\underline{v}_1)]$$

$$\times\ G_o(\underline{x}_1,\underline{v}_1,\underline{x}_2,\underline{v}_2')\ \delta(\underline{x}_{21}-\underline{b})\ h_o(\underline{v}_3')[h_o(\underline{v}_2'')\ \underline{\phi}(\underline{v}_1')-h_o(\underline{v}_2')\underline{\phi}(\underline{v}_1)]\}$$

$$+ J_{12}\{G_o(\underline{z}_1,\underline{z}_2) \int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{32}\ \varepsilon(\underline{a}\cdot\underline{v}_{32}) \int d\underline{b}\cdot(\underline{v}_3'-\underline{v}_1)\varepsilon[\underline{b}\cdot(\underline{v}_3'-\underline{v}_1)]$$

$$\times\ G_o(\underline{x}_1,\underline{v}_2,\underline{x}_2+\underline{a},\underline{v}_3')\ \delta(\underline{x}_{21}+\underline{a}-\underline{b})\ h_o(\underline{v}_2')[h_o(\underline{v}_3'')\underline{\phi}(\underline{v}_1')\}$$

$$- h_o(\underline{v}_3')\underline{\phi}(\underline{v}_1)]$$

$$- J_{12}\ \{G_o(\underline{z}_1,\underline{z}_2) \int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{32}\ \varepsilon(\underline{a}\cdot\underline{v}_{32}) \int d\underline{b}\cdot\underline{v}_{31}\ \varepsilon(\underline{b}\cdot\underline{v}_{31})$$

$$\times\ G_o(\underline{x}_1,\underline{v}_1,\underline{x}_2-\underline{a},\underline{v}_3)\ \delta(\underline{x}_{21}-\underline{a}-\underline{b})\ h_o(\underline{v}_2)[h_o(\underline{v}_3')\underline{\phi}(\underline{v}_1')$$

$$- h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)]\} \tag{E2}$$

We have introduced the symbols

$$f_{jk} = e^{-V_{jk}} -1 \tag{E3}$$

and

$$G_o(\underline{z}_1,\underline{z}_2) = \int_0^\infty dt\ \exp[-(\underline{v}_1\cdot\frac{\partial}{\partial\underline{x}_1} + \underline{v}_2\cdot\frac{\partial}{\partial\underline{x}_2}\ )t] \tag{E4}$$

which is equal to the term $\lim_{\varepsilon\to\infty} G_o$ defined by Sengers[75].

The fourth term of the expression (E2) can be seen to arise from the fact that the term

$$J_{23}\ [I(\underline{z}_1,\underline{z}_2,\underline{z}_3,t_1)\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ f(\underline{z}_1,0)]$$

of equation (5.11) is zero for configurations in which

$$|\underline{x}_1 - \underline{x}_3| < a.$$

Consider the second term of the right hand side of (E2). We write

$$\int d\underline{v}_3 \int d\underline{a}\cdot\underline{v}_{12}\ (1-e^{-V(\underline{x}_{12}-\underline{a})}\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)$$

$$= \int d\underline{z}_3 \int d\underline{a}\cdot\underline{v}_{13}\ (-f_{23})\ \delta(\underline{x}_{13}-\underline{a})\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)$$

$$+ \int d\underline{z}_3 \int d\underline{a}\cdot\underline{v}_{23}\ f_{13}\ \delta(\underline{x}_{23}+\underline{a})\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)$$

$$= \int d\underline{z}_3 \int d\underline{a}.\underline{v}_{31}\ \varepsilon(\underline{a}.\underline{v}_{31})\ f_{23}\ [\delta(\underline{x}_{13}-\underline{a}) - \delta(\underline{x}_{13}+\underline{a})]h_o(\underline{v}_2)h_o(\underline{v}_3)\underline{\phi}(\underline{v}_1)$$

$$+ \int d\underline{z}_3 \int d\underline{a}.\underline{v}_{32}\ \varepsilon(\underline{a}.\underline{v}_{32})\ f_{13}\ [\delta(\underline{x}_{23}-\underline{a}) - \delta(\underline{x}_{23}+\underline{a})]h_o(\underline{v}_2)h_o(\underline{v}_3)\underline{\phi}(\underline{v}_1) \tag{E5}$$

We now introduce the operators T^i_{jk}, T^n_{jk} and $\overline{T}^n_{jk}$ defined by

$$T^i_{jk}\ g(\underline{z}_j,\underline{z}_k) = \int d\underline{a}.\underline{v}_{jk}\ \varepsilon(\underline{a}.\underline{v}_{jk})\ \delta(\underline{x}_{jk}-\underline{a})\ g(\underline{x}_j,\underline{v}_j',\underline{x}_k,\underline{v}_k') \tag{E6}$$

where

$$\underline{v}_j' = \underline{v}_j - (\underline{v}_{kj}.\underline{a})\ \underline{a}/a^2$$

$$\underline{v}_k' = \underline{v}_k + (\underline{v}_{kj}\underline{a})\ \underline{a}/a^2 \tag{E7}$$

$$T^n_{jk} = - \int d\underline{a}.\underline{v}_{jk}\ \varepsilon(\underline{a}.\underline{v}_{jk})\ \delta(\underline{x}_{jk}-\underline{a}) \tag{E8}$$

$$\overline{T}^n_{jk} = - \int d\underline{a}.\underline{v}_{kj}\ \varepsilon(\underline{a}.\underline{v}_{kj})\ \delta(\underline{x}_{jk}-\underline{a}) \tag{E9}$$

These are just the operators used by Sengers[10]. The operator J_{jk} is given by

$$J_{jk} = \int d\underline{x}_k \int d\underline{v}_k\ \left(T^i_{jk} + \overline{T}^n_{jk}\right) \tag{E10}$$

Using (E5), we can write (E2) as follows:

$$\overline{A}_3(\underline{v}_1)\ \underline{\phi}(\underline{v}_1) = \int d\underline{z}_2 \int d\underline{z}_3\ f_{13}\ f_{23}\ \overline{T}_{12}\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \ \underline{\phi}(\underline{v}_1)$$

$$+ \int d\underline{z}_2 \int d\underline{z}_3\ \overline{T}_{12}\ G_o[\left(T^n_{13} - \overline{T}^n_{13}\right)f_{23} + \left(T^n_{23} - \overline{T}^n_{23}\right)f_{13}$$

$$+ \overline{T}_{13}\ f_{23} + \overline{T}_{23}\ f_{13}]\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1)$$

$$+ \int d\underline{z}_2 \int d\underline{z}_3\ \overline{T}_{12}\ G_o[T^i_{13}\ G_o\ T_{12} + T^i_{23}\ G_o\ T_{12} + \overline{T}_{23}\ G_o\ T_{13}]$$

$$\times\ h_o(\underline{v}_2)\ h_o(\underline{v}_3)\ \underline{\phi}(\underline{v}_1) \tag{E11}$$

where we have written

$$G_o = \int_o^\infty dt\ \exp[-(\underline{v}_1\cdot\frac{\partial}{\partial\underline{x}_1} + \underline{v}_2\cdot\frac{\partial}{\partial\underline{x}_2} + \underline{v}_3\cdot\frac{\partial}{\partial\underline{x}_3})t] \tag{E12}$$

Equation (E11) is equivalent to an expression derived by Sengers et al.[75] if sequences of four collisions between three particles are neglected. Indeed from equation (4.9) of reference 75 we have

$$I_3(\underline{v}_1)\ \underline{\phi}(\underline{v}_1) = \int d\underline{z}_2 \int d\underline{z}_3\ \{f_{13}\ f_{23}\ \overline{T}_{12} + f_{13}\ \overline{T}_{12}\ G_o\ f_{23}$$

$$+ f_{23}\ \overline{T}_{12}\ G_o\ f_{13} + \overline{T}_{12}\ G_o\ \left(T^1_{13} + T^1_{23}\right)\ G_o\ T_{12}$$

$$+ \overline{T}_{12}\ G_o\ T_{23}\ G_o\ T_{13} + \overline{T}_{12}\ G_o\ T_{13}\ G_o\ T_{23}\}h_o(\underline{v}_2)h_o(\underline{v}_3)\underline{\phi}(\underline{v}_1)$$

The final term of this expression vanishes since

$$T_{23}\ \ h_o(\underline{v}_2)\ h_o(\underline{v}_3) = 0$$

If we use the properties (see properties I.3 and I.4 of ref. 75)

$$f_\alpha\ \overline{T}_\beta = \overline{T}_\beta\ f_\alpha$$

and

$$f_\alpha\ G_o = G_o\ f_\alpha + G_o\left(\overline{T}^n_\alpha - T^n_\alpha\right)\ G_o$$

where α,β stand for the pairs 12, 13 or 23, we see that I_3, and $\overline{A}_3$, are equal.

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