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THEORETICAL CHEMISTRY INSTITUTE
THE UNIVERSITY OF WISCONSIN

UNPUBLISHED PRELIMINARY DATA

THE DENSITY EXPANSIONS OF THE TRANSPORT COEFFICIENTS

by

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WIS-TCI-48

15 May 1964

MADISON, WISCONSIN

REPORTS CONTROL No. 9

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ABSTRACT

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The theory of transport phenomena in a gas is considered from a statistical mechanical viewpoint. The theory is based on the Liouville equation for the time evolution of an ensemble of systems and the B.B.G.K.Y. equations which are integrals of the Liouville equation. The B.B.G.K.Y. hierarchy is truncated by a factorization principle which is a generalization of the molecular chaos assumption. For purely repulsive potentials, the set of equations obtained by truncating at $f^{(3)}$ is shown to give rise to the three body interaction term obtained by Hollinger and Curtiss and by a different argument by Bogolubov.

The two coupled equations obtained by truncating the B.B.G.K.Y. hierarchy at $f^{(3)}$ are considered in detail. An approximation to these equations leads to a Boltzmann equation which is a soft potential generalization of the Enskog dense gas equation for rigid spheres. This Boltzmann equation includes both collisional transfer and three body collision effects. The equation is solved and expressions for the transport coefficients based on this solution are obtained.

* This research was carried out in part under Grant NsG-275-62(4180) from the National Aeronautics and Space Administration and in part under a grant from the National Science Foundation.

Numerical calculations of the three body collision corrections to the transport coefficients are made for a Lennard-Jones gas. These calculations, along with the collisional corrections obtained in a previous paper by Curtiss, McElroy and Hoffman, give in approximation, the contribution of the non-bound states to the full first density corrections. The calculations are compared with experimental values.

ACKNOWLEDGEMENTS

The author would like to express his appreciation to the following people:

Dr. C. F. Curtiss, who suggested the problem and supervised the research. The author feels privileged to have worked under his direction.

Dr. J. O. Hirschfelder, whose efforts have made the Theoretical Chemistry Institute a stimulating environment for theoretical research.

Dr. W. Byers-Brown and William Meath who made some helpful suggestions concerning the solution of the integral equations.

John Mueller and Herbert Wood with whom the author held many useful discussions.

Grace Rahjes, Marion Taylor and Dr. Michael McElroy who did the CDC 1604 programming.

Bowen Liu, Raymond Beshinske and John Huntington who helped with other aspects of the computing.

Beth Slocum, who provided editorial assistance; Gary Schroeder, who drew the figures; Mary Wilson, who did the typing and reproduction; and Karen Rick, who helped with the reproduction.

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CHAPTER I

INTRODUCTION

In this study we consider one of the classic problems of statistical mechanics, the determination of the transport coefficients of a gas. Early research on this subject was carried on by some of the truly great theoreticians such as Maxwell, Boltzmann and Hilbert and culminated in the now classic book The Mathematical Theory of Non-uniform Gases by Chapman and Cowling¹. The problem has received continued attention to the present day and still presents many unanswered questions and avenues for further research.

The methods of both continuum mechanics and particle mechanics have been used extensively in the theoretical study of gases. The two approaches give complimentary descriptions. The continuum approach yields relations (such as the relation between the temperature gradient and the energy flux vector) which link macroscopically observed properties. However, to complete the description of any particular gas certain parameters characteristic of that gas (for example, the thermal conductivity) must be specified. In the continuum approach, these characteristic parameters can only be determined empirically. However, by the methods of statistical mechanics, they can be calculated, at least in principle, in terms of the intermolecular potential.

From the continuum view, a non-equilibrium state of a gas composed of a single chemical component is specified by the density, temperature and stream velocity as functions of position. The

macroscopic state determined by these quantities evolves in time according to the equation of continuity, the equation of motion, and the equation of energy balance. These equations, which are known as the equations of change, involve explicitly the flux of momentum or pressure tensor, $\underline{p}$, and the flux of energy, $\underline{q}$. Under conditions not too far removed from equilibrium, these fluxes depend linearly on the gradients within the system. The coefficients relating the fluxes and gradients are known as the transport coefficients. It is the role of kinetic theory to express these coefficients in terms of the intermolecular potential.

At a point $\underline{r}$ in the gas, the dependence of the fluxes on the gradients of the temperature, T , and the streamvelocity, $\underline{u}$, can be written in the general tensor forms

$$\underline{p} = p_0 - \underline{H} : \frac{\partial \underline{u}}{\partial \underline{r}} \quad (1 - 1)$$

and

$$\underline{q} = - \underline{\Lambda} \cdot \frac{\partial T}{\partial \underline{r}} \quad (1 - 2)$$

where p_0 , $\underline{H}$ and $\underline{\Lambda}$ are isotropic tensors which depend only on the density and temperature. By an isotropic tensor we mean a tensor that is invariant under any rotation or inversion of the coordinate system. The pressure tensor, $\underline{p}$, does not depend on the gradient $\frac{\partial T}{\partial \underline{r}}$ because there are no odd order isotropic tensors. Similarly, $\underline{q}$ does not depend on $\frac{\partial \underline{u}}{\partial \underline{r}}$.

All isotropic tensors of second order are scalar multiples of

the unit tensor, $\underline{\underline{U}}$, defined by

$$\underline{\underline{U}}_{ij} = \delta_{ij} \quad (1 - 3)$$

Hence, we have

$$\underline{\underline{p}}_0 = p \underline{\underline{U}} \quad (1 - 4)$$

and

$$\underline{\underline{\Delta}} = \lambda \underline{\underline{U}} \quad (1 - 5)$$

The coefficient p is the hydrostatic pressure and λ is the coefficient of thermal conductivity.

Every fourth order isotropic tensor is a linear combination of the tensors $\underline{\underline{\Psi}}$, $\underline{\underline{\Psi}}$ and $\underline{\underline{U}}\underline{\underline{U}}$ which are defined by

$$\underline{\underline{\Psi}}_{ijkl} = \delta_{il} \delta_{jk} \quad (1 - 6)$$

$$\underline{\underline{\Psi}}_{ijkl} = \delta_{ik} \delta_{jl} \quad (1 - 7)$$

and

$$(\underline{\underline{U}}\underline{\underline{U}})_{ijkl} = \delta_{ij} \delta_{kl} \quad (1 - 8)$$

The tensor $\underline{\underline{H}}$ can therefore be written

$$\underline{\underline{H}} = 2\eta \left[\frac{1}{2} (\underline{\underline{\Psi}} + \underline{\underline{\Psi}}) - \frac{1}{3} \underline{\underline{U}}\underline{\underline{U}} \right] + \kappa \underline{\underline{U}}\underline{\underline{U}} + \nu [\underline{\underline{\Psi}} - \underline{\underline{\Psi}}] \quad (1 - 9)$$

This particular grouping of the isotropic fourth order tensors is convenient because the tensors $\left[\frac{1}{2} (\underline{\underline{\psi}} + \underline{\underline{\psi}}) - \frac{1}{3} \underline{\underline{U}} \underline{\underline{U}} \right]$, $(\underline{\underline{\psi}} - \underline{\underline{\psi}})$ and $\underline{\underline{U}} \underline{\underline{U}}$ divide the gradient $\frac{\partial \underline{\underline{u}}}{\partial \underline{\underline{x}}}$, in equation (1 - 1), into its traceless symmetric, antisymmetric and trace parts. For spherically symmetric intermolecular potentials, it can be shown that the pressure tensor is symmetric; and hence

$$\underline{\underline{v}} = 0 \quad (1 - 10)$$

We restrict our attention to this case. The quantity η is the coefficient of shear viscosity and μ is the coefficient of bulk viscosity.

If we write equations (1 - 1) and (1 - 2) in terms of the hydrostatic pressure and the transport coefficients, we have

$$\underline{\underline{p}} = p \underline{\underline{U}} - 2 \eta \underline{\underline{S}} - \mu \left(\frac{\partial}{\partial \underline{\underline{x}}} \cdot \underline{\underline{u}} \right) \underline{\underline{U}} \quad (1 - 11)$$

and

$$\underline{\underline{q}} = - \lambda \frac{\partial T}{\partial \underline{\underline{x}}} \quad (1 - 12)$$

where

$$\underline{\underline{S}} = \frac{1}{2} \left[\frac{\partial \underline{\underline{u}}}{\partial \underline{\underline{x}}} + \left(\frac{\partial \underline{\underline{u}}}{\partial \underline{\underline{x}}} \right)^{\dagger} \right] - \frac{1}{3} \left(\frac{\partial}{\partial \underline{\underline{x}}} \cdot \underline{\underline{u}} \right) \underline{\underline{U}} \quad (1 - 13)$$

The symbol $\dagger$ indicates a transposed tensor. The tensor $\underline{\underline{S}}$ is known as the rate of shear tensor.

The hydrostatic pressure is essentially an equilibrium property since it is the only contribution to the pressure tensor at

equilibrium, i.e., when there are no gradients within the system. In 1908 Ornstein² developed an expression for the second coefficient in the virial expansion of p . This and the subsequent development of similar expressions for the higher virial coefficients were early triumphs of the statistical mechanical method.

The transport coefficients λ , η and κ depend on the one and two particle non-equilibrium distribution functions. A fundamental problem of kinetic theory has been to derive equations which govern the time evolution of these distribution functions. In 1872 Boltzmann³ obtained his now famous equation for the one particle distribution function. This equation is valid for dilute gases composed of molecules which undergo only binary collisions by interacting, according to classical mechanics, through a spherically symmetric potential. Some forty years after the original derivation, Chapman⁴ and Enskog⁵, proceeding independently, obtained identical solutions of the Boltzmann equation. From this solution they developed low density expressions for the transport coefficients.

In 1922 Enskog⁶ proposed a modified Boltzmann equation which is applicable to a dense gas of rigid spheres. His modification takes into account two separate effects which ultimately contribute to all but the constant terms in the density expansions of the transport coefficients. First, since rigid spheres are of finite size, molecular collisions result in an instantaneous transfer of momentum and energy between molecular centers. Second, since the molecules in a real gas are not restricted to binary collisions, higher order collisions affect the time evolution of the one particle

distribution function. Enskog allowed for the second effect in only an approximate manner.

Subsequent efforts have been made to generalize the effects Enskog considered to soft potentials. Green⁷ has developed collisional contributions to the Boltzmann equation. Bogolubov^{8,9} and Hollinger and Curtiss¹⁰ have separately developed corrections to the Boltzmann equation in series expansions. These, in principle, are exact expansions; but they are valid only for purely repulsive potentials. The results of Bogolubov and those of Hollinger and Curtiss are in agreement. In the lowest order they are identical to the results of Green. Snider and Curtiss¹¹ have solved the Boltzmann equation with collisional corrections (as obtained by Green), and from their solution have developed expressions for the transport coefficients. Due to the complexity of multibody collision terms in the series expansions of the Boltzmann equation, no attempt has yet been made to develop higher order collisional corrections to the transport coefficients on the basis of these expansions. The restriction to purely repulsive potentials eliminates the contribution of bound states to the transport coefficients. Bound states have not yet been treated in a satisfactory theoretical manner, although approximate treatments have been given¹².

The study of the origin and generalization of the Boltzmann equation is international. This is indicated by the men for which a particular hierarchy of equations, known as the B.B.G.K.Y. equations, is named. This hierarchy, which we discuss in detail later, is named for Bogolubov of Russia, Born and Green¹³ who worked in

England, Kirkwood¹⁴ of the United States, and Yvon¹⁵ of France. The works of these authors share as a common starting point the Liouville equation for the ensemble distribution function, but vary considerably in concept and methodology. Choh and Uhlenbeck^{16,17} have considered the Bogolubov development in detail. A somewhat similar development has been given by M. S. Green^{18,19}. The rigid sphere gas has been discussed by a number of authors from a variety of approaches - particularly by Rice, Kirkwood, Ross and Zwanzig²⁰; Rice²¹; Dahler and O'Toole^{22,23}; and Livingston and Curtiss²⁴.

In the present work we develop equations which are formally equivalent to the series expansions of the Boltzmann equation mentioned above. We consider specifically the effect of three body interactions and show that these effects, when considered in approximation, lead to a soft potential generalization of the Enskog equation. This generalized equation is solved; and expressions for the transport coefficients are derived from the solution. Finally, we reduce our expressions for the transport coefficients to a computational form, and obtain some numerical results for a particular intermolecular potential.

Our approach is not essentially restricted to non-bound states; but the bound state problem is not considered in detail.

CHAPTER II

GENERALIZED BOLTZMANN EQUATIONS

In this chapter we develop a system of equations which govern the time evolution of the lower order distribution functions. We consider in detail the equations for the first two distribution functions and an approximation to these equations which gives rise to a generalization of the Enskog rigid sphere treatment to soft potentials.

Section 1. Distribution Functions

The molecular description of fluids is a statistical problem and is thus conveniently formulated in terms of distribution functions. Let us consider a system containing a large number, N , of identical molecules (N is typically of the order 10^{23}). Further, let us suppose the forces between molecules in the system to be limited to purely repulsive two body forces arising from a potential of interaction which is spherically symmetric. The system is completely specified by $3N$ position and $3N$ velocity coordinates or, equivalently, by a point in a $6N$ dimensional position-velocity space. The probabilistic behavior of this system is described by an ensemble of dynamically similar systems.

Let us define the function $f^{(N)}$ on the N particle position-velocity space equal to $N!$ times the probability density of finding one system in the ensemble at a specified point in the $6N$ dimensional space. The factor $N!$ in the definition of $f^{(N)}$ is the number of permutations of N molecules which give rise to the same mechanical state of the system except for molecule interchange.

This normalization of $f^{(N)}$ is such that integration of $f^{(N)}$ over the entire position-velocity space gives $N!$. The ensemble is so chosen that $f^{(N)}$ is initially symmetric in all the molecules. This does not result in a loss of generality because properties which distinguish one molecule from another are not of interest. Since the equations of motion of any system in the ensemble are symmetric with respect to molecule interchange, $f^{(N)}$ remains symmetric in its time evolution.

Because of the symmetry of $f^{(N)}$, lower order distribution functions can be defined without ambiguity by the set of relations

$$f^{(h)} = \frac{1}{(N-h)!} \int f^{(N)} \prod_{i=(h+1)}^N \{d\underline{r}_i d\underline{v}_i\} \quad (2.1 - 1)$$

where $h = 1$ to $N-1$ and $\underline{r}_i$ and $\underline{v}_i$ are respectively the position and velocity of the i^{th} molecule. The integration is understood to be over the entire range of the variables. The h^{th} order distribution function is proportional to the probability density of finding h molecules with positions and velocities corresponding to a point in the h particle position-velocity space, without regard to the situation of the other $N-h$ molecules. The h^{th} order distribution function is normalized to the factor $[N!/(N-h)!]$ which is the number of permutations of h molecules chosen from N .

Section 2.2 The Liouville Equation and the B.B.G.K.Y. Equations

The time evolution of $f^{(N)}$ is governed by the Liouville equation:

$$\frac{\partial f^{(N)}}{\partial t} + [f^{(N)}, H^{(N)}]^{(N)} = 0 \quad (2.2 - 1)$$

Here $H^{(N)}$ is the Hamiltonian and $[,]^{(N)}$ is the Poisson bracket of an N particle system. The Hamiltonian and the Poisson bracket are defined by the relations

$$H^{(N)} = \frac{1}{2m} \sum_{i=1}^N (m \underline{v}_i)^2 + \frac{1}{2} \sum_{i,j=1}^N \phi^{(i,j)} \quad (2.2 - 2)$$

and

$$[p, \xi]^{(N)} = \sum_{i=1}^N \left\{ \frac{\partial p}{\partial \underline{x}_i} \cdot \frac{\partial \xi}{\partial (m \underline{v}_i)} - \frac{\partial \xi}{\partial \underline{x}_i} \cdot \frac{\partial p}{\partial (m \underline{v}_i)} \right\} \quad (2.2 - 3)$$

where m is the particle mass, $m \underline{v}_i$ is the momentum of the i th particle, $\phi^{(i,j)}$ is the potential of interaction between molecules i and j , and p and ξ are arbitrary functions of the position and momentum of the particles. The Liouville equation is the continuity equation for points in position-velocity space.

Equations for the time evolution of the lower order distribution functions are obtained by integration of the Liouville equation:

$$\frac{\partial f^{(h)}}{\partial t} + [f^{(h)}, H^{(h)}]^{(h)} = \frac{1}{m} \int \sum_{i=1}^h \frac{\partial \phi^{(i,h+1)}}{\partial \underline{x}_i} \cdot \frac{\partial f^{(h+1)}}{\partial \underline{v}_i} d\underline{x}_{h+1} d\underline{v}_{h+1} \quad (2.2 - 4)$$

In the derivation of these equations, $f^{(N)}$ is assumed to approach zero rapidly as either $\underline{x}_i$ or $\underline{v}_i$ approaches infinity. This set of equations form an interrelated hierarchy known as the

B.B.G.K.Y. equations. To solve any one equation exactly would require a solution to the original Liouville equation.

We wish to determine the lower order distribution functions of the system uniquely in terms of the macroscopic state. In kinetic theory the number density, stream velocity and temperature, which, when specified throughout space determine the macroscopic state, are statistical averages over $f^{(1)}$. However, as we have seen, the reduced distribution functions which are solutions to the B.B.G.K.Y. equations depend ultimately on $f^{(N)}$. There are many choices of the ensemble which give rise to the same macroscopic state. Hence the solution we wish seems to be underdetermined. This is a paradox which ultimately must be resolved in the statistics of systems which are composed of extremely large numbers of molecules. The resolution of this paradox has not been carried out completely satisfactorily on a theoretical basis. Operationally the problem can be solved by terminating the B.B.G.K.Y. hierarchy and solving the resulting equations on the basis of physically reasonable assumptions about the nature of the lower order distribution functions. The effect of this procedure is to limit solutions for the lower order distribution functions to a set of functions determined by the macroscopic state.

Section 2.3 Molecular Chaos and the Boltzmann Equation

We now discuss a derivation of the Boltzmann equation from the $f^{(1)}$ B.B.G.K.Y. equation. The derivation involves terminating the B.B.G.K.Y. hierarchy by the so-called molecular chaos assumption. This assumption is that $f^{(2)}$ factors into a product of $f^{(1)}$'s

in those regions of the two particle position-velocity space which correspond to pre-collision positions and velocities of two particles. The rationale for this assumption is that in a realistic gas there can be little correlation between two molecules prior to their collision. That is, they have very little influence on each other's history prior to collisions. They, of course, have great influence on each other's history after collision. The effect of this differentiation between pre-collision and post-collision portions of the position-velocity space is to introduce irreversibility into the equations.

It remains to express $f^{(2)}$ everywhere in the two particle position-velocity space in terms of $f^{(2)}$ in pre-collision portions of the position-velocity space. This can be done by a method used by Hollinger and Curtiss¹⁰ based on formal solutions of the B.B.G.K.Y. equations. The h^{th} order B.B.G.K.Y. equation is

$$\frac{\partial f^{(h)}}{\partial t} + [f^{(h)}, H^{(h)}] = \frac{1}{m} \int \sum_{i=1}^h \frac{\partial f^{(i, h+1)}}{\partial x_i} \cdot \frac{\partial}{\partial v_i} f^{(h+1)} dx_{h+1} dv_{h+1} \quad (2.3 - 1)$$

which can be written

$$\frac{D^{(h)}}{D^{(h)}_t} (f^{(h)}) = \beta J^{(h)}(f^{(h+1)}) \quad (2.3 - 2)$$

Here $\frac{D^{(h)}}{D^{(h)}_t}$ is the total time derivative considering position and velocity coordinates to be implicit functions of time along an h^{th} order collision trajectory. The quantity $J^{(h)}(f^{(h+1)})$ is a notation for the right side of equation (2.3 - 1) and β is an

ordering parameter which will ultimately be set equal to one.

We define an operator $T^{(A)}(\tau)$ by the relations

$$T^{(A)}(\tau) = e^{\tau [, H^{(A)}]^{(A)}} \quad (2.3 - 3)$$

and

$$T^{(A)-1}(\tau) = e^{-\tau [, H^{(A)}]^{(A)}} \quad (2.3 - 4)$$

The effect of $T^{(A)}(\tau)$ on a function is to transform the position and velocity variables of the function to their value a time τ later on the A particle trajectory. We can then integrate equation (2.3 - 2) and write the result in terms of $T^{(A)}(\tau)$.

$$f^{(A)}(t) - T^{(A)-1}(t-t_0) [f^{(A)}(t_0)] = \rho \int_{t_0}^t T^{(A)-1}(t-t') [J^{(A)}(f^{(A)}(t'))] dt' \quad (2.3 - 5)$$

For clarity, we have indicated the explicit time dependence of the operators and distribution functions in equation (2.3 - 5).

We now make use of the fact that the force between any two molecules is purely repulsive and hence there are no bound molecular pairs. Then if $t - t_0$ is positive and sufficiently large we can use the molecular chaos assumption to write

$$T^{(2)-1}(t-t_0) [f^{(2)}(t_0)] = T^{(2)-1}(t-t_0) [f_1^{(1)}(t_0) f_2^{(1)}(t_0)] \quad (2.3 - 6)$$

where the subscripts on the $f^{(i)}$'s denote the particle to which the functional variables refer. From equations (2.3 - 5) and

(2.3 - 6) we have

$$f^{(2)}(t) = T^{(2)-1}(t-t_0) [f_1^{(1)}(t_0) f_2^{(1)}(t_0)] \\ + \beta \int_{t_0}^t T^{(2)-1}(t-t') [J^{(2)}(f^{(3)}(t'))] dt' \quad (2.3 - 7)$$

Equation (2.3 - 5) can similarly be used to express $f^{(1)}(t_0)$ in terms of $f^{(1)}(t)$.

$$f^{(1)}(t_0) = T^{(1)-1}(t-t_0) [f^{(1)}(t)] - \beta \int_{t_0}^t T^{(1)-1}(t-t') [J^{(1)}(f^{(2)}(t'))] dt' \quad (2.3 - 8)$$

From equations (2.3 - 7) and (2.3 - 8) we have

$$f^{(2)}(t) = T^{(2)-1}(t-t_0) T_1^{(1)-1}(t-t_0) T_2^{(1)-1}(t-t_0) [f_1^{(1)}(t) f_2^{(1)}(t)] \quad (2.3 - 9) \\ + \beta \left\{ \int_{t_0}^t T^{(2)-1}(t-t') [J^{(2)}(f^{(3)}(t'))] dt' - T_1^{(1)-1}(t-t_0) [f_1^{(1)}(t)] \int_{t_0}^t T_2^{(1)-1}(t-t') [J_2^{(1)}(f^{(2)}(t'))] dt' \right. \\ \left. - T_2^{(1)-1}(t-t_0) [f_2^{(1)}(t)] \int_{t_0}^t T_1^{(1)-1}(t-t') [J_1^{(1)}(f^{(2)}(t'))] dt' \right. \\ \left. + \beta^2 \left\{ \int_{t_0}^t T_2^{(1)-1}(t-t') [J_2^{(1)}(f^{(2)}(t'))] dt' \int_{t_0}^t T_1^{(1)-1}(t-t') [J_1^{(1)}(f^{(2)}(t'))] dt' \right\} \right\}$$

Equation (2.3 - 9) can be expanded in an infinite power series in β if we assume that all distribution functions factor into a product of $f^{(i)}$'s in pre-collision regions of their respective position-velocity spaces. We can use equation (2.3 - 5) to carry out the

factorizations and transform the time dependence of the $f^{(2)}$ in a manner similar to what we have done above.

We will be concerned with only the β^0 term of the expansion of $f^{(2)}$. All other terms contain complex time integrations which are extremely difficult to deal with. If the intermolecular forces are short range, the operator $T^{(2)-1}(t-t_0) T_1^{(1)}(t-t_0) T_2^{(1)}(t-t_0)$ has a limit as $t_0 \rightarrow -\infty$ which will be denoted by $S^{(2)}$. We can replace $f^{(2)}$ in the $f^{(1)}$ B.B.G.K.Y. equation by the β^0 term of equation (2.3 - 9). Then in terms of $S^{(2)}$ we have

$$\frac{\partial f^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial f^{(1)}}{\partial \underline{r}_1} = \frac{1}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{v}_1} S^{(2)} [f_1^{(1)} f_2^{(1)}] d\underline{r}_2 d\underline{v}_2 \quad (2.3 - 10)$$

By straightforward manipulation equation (2.3 - 10) can be transformed into the ordinary Boltzmann equation plus the collisional transfer corrections due to Green⁷.

Equation (2.3 - 10) suffers from two disadvantages as a theoretical description of gases. First it takes into account only binary collisions in the sense that it considers only the β^0 term of the series expansion for $f^{(2)}$. Higher terms in the expansion require explicitly taking into account the dynamics of higher order collisions. Second, since equation (2.3 - 10) is based on the molecular chaos assumption, it tacitly ignores bound molecular pairs. Theoretically this difficulty is overcome by considering purely repulsive molecular forces. This, however, is not realistic. We will now develop a formalism which overcomes the first disadvantage of equation (2.3 - 10). The general formalism may also be adequate

to treat bound molecular states. However, we will limit our considerations to purely repulsive molecular forces.

Section 2.4 The Factorization Principle

Let us consider the first h B.B.G.K.Y. equations as a set to be solved simultaneously for the first h distribution functions. We will terminate the hierarchy by approximating $f^{(h+1)}$ in terms of the first h distribution functions. In order to truncate the hierarchy and also to obtain boundary conditions on the solutions to the truncated set of B.B.G.K.Y. equations, we introduce a factorization principle. This principle, in the case of purely repulsive forces, is sufficient to uniquely determine the $h+1$ higher order distribution functions in terms of $f^{(h)}$. Let us consider regions of the S particle position-velocity space ($2 \leq S \leq h+1$) where the S particles can be divided into two groups which have not interacted in their past history as determined by the S particle trajectory. The factorization principle states that in such regions $f^{(S)}$ is given by

$$f^{(S)} = f^{(q)} f^{(S-q)} \quad (2.4 - 1)$$

where q and $S-q$ are the numbers of particles in the two groups. This principle is introduced as a physically reasonable postulate.

In order to provide a satisfactory boundary condition on the distribution functions, the factorization principle must be consistent with the B.B.G.K.Y. equations governing the distribution

functions. This consistency can be shown by considering the equation for $f^{(s)}$:

$$\frac{\partial f^{(s)}}{\partial t} + [f^{(s)}, H^{(s)}]^{(s)} = \frac{1}{m} \int \sum_{i=1}^s \frac{\partial \phi^{(i,s+1)}}{\partial \underline{r}_i} \cdot \frac{\partial f^{(s+1)}}{\partial \underline{v}_i} d\underline{r}_{s+1} d\underline{v}_{s+1} \quad (2.4 - 2)$$

From equations (2.2 - 2) and (2.2 - 3) it follows that, when the groups of g and $s-g$ molecules are far enough separated so that the potential of interaction between any molecule of one group with any molecule of the other is zero, then

$$[, H^{(s)}]^{(s)} = [, H^{(g)}]^{(g)} + [, H^{(s-g)}]^{(s-g)} \quad (2.4 - 3)$$

If equation (2.4 - 3) is substituted into equation (2.4 - 2) and the factored expressions for $f^{(s)}$ and $f^{(s+1)}$ are also introduced, then equation (2.4 - 2) is

$$\begin{aligned} & f^{(g)} \left\{ \frac{\partial f^{(s-g)}}{\partial t} + [f^{(s-g)}, H^{(s-g)}]^{(s-g)} \right\} + f^{(s-g)} \left\{ \frac{\partial f^{(g)}}{\partial t} + [f^{(g)}, H^{(g)}]^{(g)} \right\} \\ &= f^{(g)} \left\{ \frac{1}{m} \int \sum_{i=g+1}^s \frac{\partial \phi^{(i,s+1)}}{\partial \underline{r}_i} \cdot \frac{\partial f^{(s+1-g)}}{\partial \underline{v}_i} d\underline{r}_{s+1} d\underline{v}_{s+1} \right\} + f^{(s-g)} \left\{ \frac{1}{m} \int \sum_{i=1}^g \frac{\partial \phi^{(i,s+1)}}{\partial \underline{r}_i} \cdot \frac{\partial f^{(g+1)}}{\partial \underline{v}_i} d\underline{r}_{s+1} d\underline{v}_{s+1} \right\} \end{aligned} \quad (2.4 - 4)$$

Equation (2.4 - 4) is the sum of the equations governing $f^{(g)}$ and $f^{(s-g)}$. Hence the factorization principle is consistent with the B.B.G.K.Y. equations.

In order to use the factorization principle to terminate the B.B.G.K.Y. hierarchy, it is necessary to obtain a form for $f^{(s)}$

which is applicable in any factorization region. For example, $f^{(s)}$ in any factorization region can be written

$$f^{(3)} = \frac{f_{1,2}^{(2)} f_{1,3}^{(2)} f_{2,3}^{(2)}}{f_1^{(1)} f_2^{(1)} f_3^{(1)}} \quad (2.4 - 5)$$

In the regions where molecule 3 is separated from molecules 1 and 2, equation (2.4 - 5) is

$$f^{(3)} = \frac{f_{1,2}^{(2)} (f_1^{(1)} f_3^{(1)}) (f_2^{(1)} f_3^{(1)})}{f_1^{(1)} f_2^{(1)} f_3^{(1)}} = f_{1,2}^{(2)} f_3^{(1)} \quad (2.4 - 6)$$

The expression for $f^{(3)}$ reduces in a similar way in any factorization region. A general expression of this type for $f^{(s)}$ is

$$f^{(s)} = \frac{\rho_{s-1}^{(s)} (f^{(s-1)}) \rho_{s-3}^{(s)} (f^{(s-3)}) \rho_{s-5}^{(s)} (f^{(s-5)}) \dots}{\rho_{s-2}^{(s)} (f^{(s-2)}) \rho_{s-4}^{(s)} (f^{(s-4)}) \rho_{s-6}^{(s)} (f^{(s-6)}) \dots} \quad (2.4 - 7)$$

where the notation $\rho_{\alpha'}^{(s)}$ means the product of all combinations of functions of the s molecules taken α' at a time. For $s=3$, this equation is equation (2.4 - 5). Two other examples are:

$$f^{(2)} = f_1^{(1)} f_2^{(1)} \quad (2.4 - 8)$$

and

$$f^{(4)} = \frac{f_{1,2,3}^{(3)} f_{1,2,4}^{(3)} f_{1,3,4}^{(3)} f_{2,3,4}^{(3)} f_1^{(1)} f_2^{(1)} f_3^{(1)} f_4^{(1)}}{f_{1,2}^{(2)} f_{1,3}^{(2)} f_{1,4}^{(2)} f_{2,3}^{(2)} f_{2,4}^{(2)} f_{3,4}^{(2)}} \quad (2.4 - 9)$$

We note that equation (2.4 - 8) is the molecular chaos assumption discussed previously. In Appendix A we prove the validity of the

general equation (2.4 - 7).

Equation (2.4 - 7) provides us with a general expression for $f^{(h+1)}$ in all factorization regions. We can relate $f^{(h+1)}$ in the entire $h+1$ position-velocity space to $f^{(h+1)}$ in factorization regions by a series expansion similar to that developed in Section 2.3. If we restrict ourselves to the lowest order term in this expansion, we find

$$f^{(h+1)} = T^{(h+1)-1} \left[\frac{\rho_h^{(h+1)}(T^{(h)} f^{(h)}) \rho_{h-2}^{(h+1)}(T^{(h-2)} f^{(h-2)}) \dots}{\rho_{h-1}^{(h+1)}(T^{(h-1)} f^{(h-1)}) \rho_{h-3}^{(h+1)}(T^{(h-3)} f^{(h-3)}) \dots} \right] \quad (2.4 - 10)$$

This expression for $f^{(h+1)}$ in terms of the h lower order distribution function terminates the B.B.G.K.Y. hierarchy. The resulting closed set of coupled equations are to be solved simultaneously for the h distribution functions. The factorization principle provides boundary conditions on these solutions. In the next section we compare the factorization principle with other methods of terminating the B.B.G.K.Y. hierarchy; and we also show that, for purely repulsive forces, $f^{(2)}$, $f^{(3)}$, etc. are uniquely determined in terms of $f^{(1)}$ by the factorization boundary conditions.

Section 2.5 The Factorization Principle and other Termination Procedures of the B.B.G.K.Y. Hierarchy

Let us consider the set of equations obtained by terminating the B.B.G.K.Y. hierarchy with the factorization approximation for $f^{(3)}$. These equations are:

$$\frac{\partial}{\partial t} f^{(1)} + [f^{(1)}, H^{(1)}]^{(1)} = \left(\frac{1}{m} \right) \int \frac{\partial \phi^{(1,2)}}{\partial \underline{x}_1} \cdot \frac{\partial}{\partial \underline{v}_1} f^{(2)} d\underline{x}_2 d\underline{v}_2 \quad (2.5 - 1)$$

and

$$\frac{\partial f^{(2)}}{\partial t} + [f^{(2)}, H^{(2)}]^{(2)} \quad (2.5 - 2)$$

$$= \frac{1}{m} \int \left\{ \frac{\partial \phi^{(1,2)}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} + \frac{\partial \phi^{(2,3)}}{\partial \underline{r}_2} \cdot \frac{\partial}{\partial \underline{p}_2} \right\} T^{(3)-1} \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)})(T_{1,3}^{(2)} f_{1,3}^{(2)})(T_{2,3}^{(2)} f_{2,3}^{(2)})}{(T_1^{(1)} f_1^{(1)})(T_2^{(1)} f_2^{(1)})(T_3^{(1)} f_3^{(1)})} d\underline{r}_3 d\underline{p}_3$$

$$= \int^{(2)} \left(T^{(3)-1} \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)})(T_{1,3}^{(2)} f_{1,3}^{(2)})(T_{2,3}^{(2)} f_{2,3}^{(2)})}{(T_1^{(1)} f_1^{(1)})(T_2^{(1)} f_2^{(1)})(T_3^{(1)} f_3^{(1)})} \right)$$

If we consider purely repulsive forces, there are no bound molecular states, and hence every trajectory has a pre-collision portion. The factorization principle can thus be applied on a portion of every trajectory. This allows us to formally integrate equation (2.5 - 2) in a manner analogous to the procedure in Sec. 2.3. In terms of the ordering parameter β , introduced in Sec. 2.3, the result of the integration is

$$f^{(2)}(t) = T^{(2)-1}(t-t_0) T_1^{(1)}(t-t_0) T_2^{(1)}(t-t_0) [f_1^{(1)}(t) f_2^{(1)}(t)] \quad (2.5 - 3)$$

$$+ \beta \left\{ \int_{t_0}^t T^{(2)-1}(t-t') \left[J^{(2)}(T^{(3)-1}) \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)}(t')) (T_{1,3}^{(2)} f_{1,3}^{(2)}(t')) (T_{2,3}^{(2)} f_{2,3}^{(2)}(t'))}{(T_1^{(1)} f_1^{(1)}(t')) (T_2^{(1)} f_2^{(1)}(t')) (T_3^{(1)} f_3^{(1)}(t'))} \right] dt' \right. \\ + \\ - T_1^{(1)}(t-t_0) [f_1^{(1)}(t)] \int_{t_0}^t T_2^{(1)-1}(t_0-t') [J_2^{(1)}(f^{(2)}(t'))] dt' \\ + \\ \left. - T_2^{(1)}(t-t_0) [f_2^{(1)}(t)] \int_{t_0}^t T_1^{(1)-1}(t_0-t') [J_1^{(1)}(f^{(2)}(t'))] dt' \right\} \\ + \beta^2 \left\{ \int_{t_0}^t T_2^{(1)-1}(t_0-t') [J_2^{(1)}(f^{(2)}(t'))] dt' \int_{t_0}^t T_1^{(1)-1}(t_0-t') [J_1^{(1)}(f^{(2)}(t'))] dt' \right\}$$

By substituting equation (2.5 - 3) back on itself, we obtain $f^{(2)}$ as an expansion in terms of $f^{(1)}$ and powers of β . The time dependences of the singlet distribution functions can be transformed to time t by the integrated $f^{(1)}$ equation. This equation has the form of equation (2.3 - 8). In this way, $f^{(2)}$ is uniquely given in terms of $f^{(1)}$. This procedure can easily be generalized to a set of B.B.G.K.Y. equations truncated at any order.

The Hollinger and Curtiss series expansion for $f^{(2)}$ was discussed in Sec. 2.3. The lowest order term in this expansion,

as can be seen from equation (2.3 - 9), is

$$T^{(2)-1} [T_1^{(1)} T_2^{(1)} (f_1^{(1)} f_2^{(1)})]$$

The next order term depends on the lowest order approximation to $f^{(3)}$. Hollinger and Curtiss have taken $f^{(3)}$ in this approximation to be

$$f^{(3)} = T^{(3)-1} [T_1^{(1)} T_2^{(1)} T_3^{(1)} (f_1^{(1)} f_2^{(1)} f_3^{(1)})] \quad (2.5 - 4)$$

By comparing equation (2.5 - 3) with equation (2.3 - 9), we see that to lowest order, our expansion of $f^{(2)}$ is identical to that of Hollinger and Curtiss. In order to show the equivalence in the next term of the expansion, we must demonstrate that our approximate expression for $f^{(3)}$ which is

$$f^{(3)} = T^{(3)-1} \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)}) (T_{1,3}^{(2)} f_{1,3}^{(2)}) (T_{2,3}^{(2)} f_{2,3}^{(2)})}{(T_1^{(1)} f_1^{(1)}) (T_2^{(1)} f_2^{(1)}) (T_3^{(1)} f_3^{(1)})} \quad (2.5 - 5)$$

reduces in the lowest approximation to equation (2.5 - 4). If we substitute equation (2.5 - 3) into equation (2.5 - 5) and retain only the β^0 term, we find

$$f^{(3)} = \frac{1}{(T_1^{(1)} f_1^{(1)}) (T_2^{(1)} f_2^{(1)}) (T_3^{(1)} f_3^{(1)})} X \quad (2.5 - 6)$$

$$T^{(3)-1} \left\{ [T_{1,2}^{(2)} (T_{1,2}^{(2)-1} T_1^{(1)} T_2^{(1)} f_1^{(1)} f_2^{(1)})] [T_{1,3}^{(2)} (T_{1,3}^{(2)-1} T_1^{(1)} T_3^{(1)} f_1^{(1)} f_3^{(1)})] \right. \\ \left. [T_{2,3}^{(2)} (T_{2,3}^{(2)-1} T_2^{(1)} T_3^{(1)} f_2^{(1)} f_3^{(1)})] \right\}$$

That is,

$$f^{(3)}(t) = [T^{(3)-1} T_1^{(1)} T_2^{(1)} T_3^{(1)} f_1^{(1)}(t) f_2^{(1)}(t) f_3^{(1)}(t)] \quad (2.5 - 7)$$

Thus, if we terminate the B.B.G.K.Y. hierarchy by an approximation for $f^{(3)}$ we formally have the same expansion as obtained by Hollinger and Curtiss, through the second term in their expansion. Hollinger and Curtiss have shown that the Boltzmann equation obtained by Bogolubov^{8,9} is identical to second order to the Boltzmann equation they derive from the $f^{(1)}$ equation and their expansion of $f^{(2)}$.

The second order term in the Boltzmann equation derived by Hollinger and Curtiss contains very complex time integrations involving the dynamics of binary collisions. To date, no practical calculations have been made on the basis of this term. Our approach, however, is somewhat different in that we do not formally solve the $f^{(2)}$ equation in terms of $f^{(1)}$. Instead, we solve the $f^{(1)}$ and $f^{(2)}$ equations simultaneously. This can be done approximately and gives rise to a soft potential generalization of the Enskog dense gas treatment for rigid spheres⁶. That is, in the limit of rigid spheres, the Enskog treatment and the approximate simultaneous solution of the $f^{(1)}$ and $f^{(2)}$ equations are identical. Thus, our treatment provides a tie-in between two quite different approaches to the problem of three body collision modifications of the Boltzmann equation.

Section 2.6 The Dynamics of Binary Collisions

In the present discussion we consider some general properties of the dynamics of binary collisions between elastic, spherically symmetric molecules. Again, we restrict our attention to molecules which interact through purely repulsive forces. The detailed dynamics of such collisions depend on an intermolecular potential which is a function of the magnitude of $\underline{r}$. The quantity $\underline{r}$ is the radial separation vector. By formulating the problem in the center of mass coordinates, the interaction can be viewed as that of a particle with mass $m/2$ being scattered by a symmetric force center. The non-trivial part of the dynamics is the description of the time evolution of the three scalar quantities r , $\underline{g}$ and $\underline{r} \cdot \underline{g}$. Here $\underline{g}$ is the velocity of the particle relative to the scatterer. The dependence on $\underline{r} \cdot \underline{g}$ in the Hamiltonian occurs only in the rotational kinetic energy. By making use of the conservation of angular momentum, we can express the rotational kinetic energy as a function of r only. Thus, for a given angular momentum, we can conveniently reformulate the problem as a one dimensional problem. In the reformulation, a particle moves in one dimension under the influence of a pseudo-potential which is the sum of the true potential and the rotational kinetic energy written as a function of r . Since the rotational kinetic energy and the intermolecular potential are both monotonically decreasing functions of r , the pseudo-potential decreases monotonically. This precludes the possibility of bound states.

A typical collision is illustrated in Fig. 1.

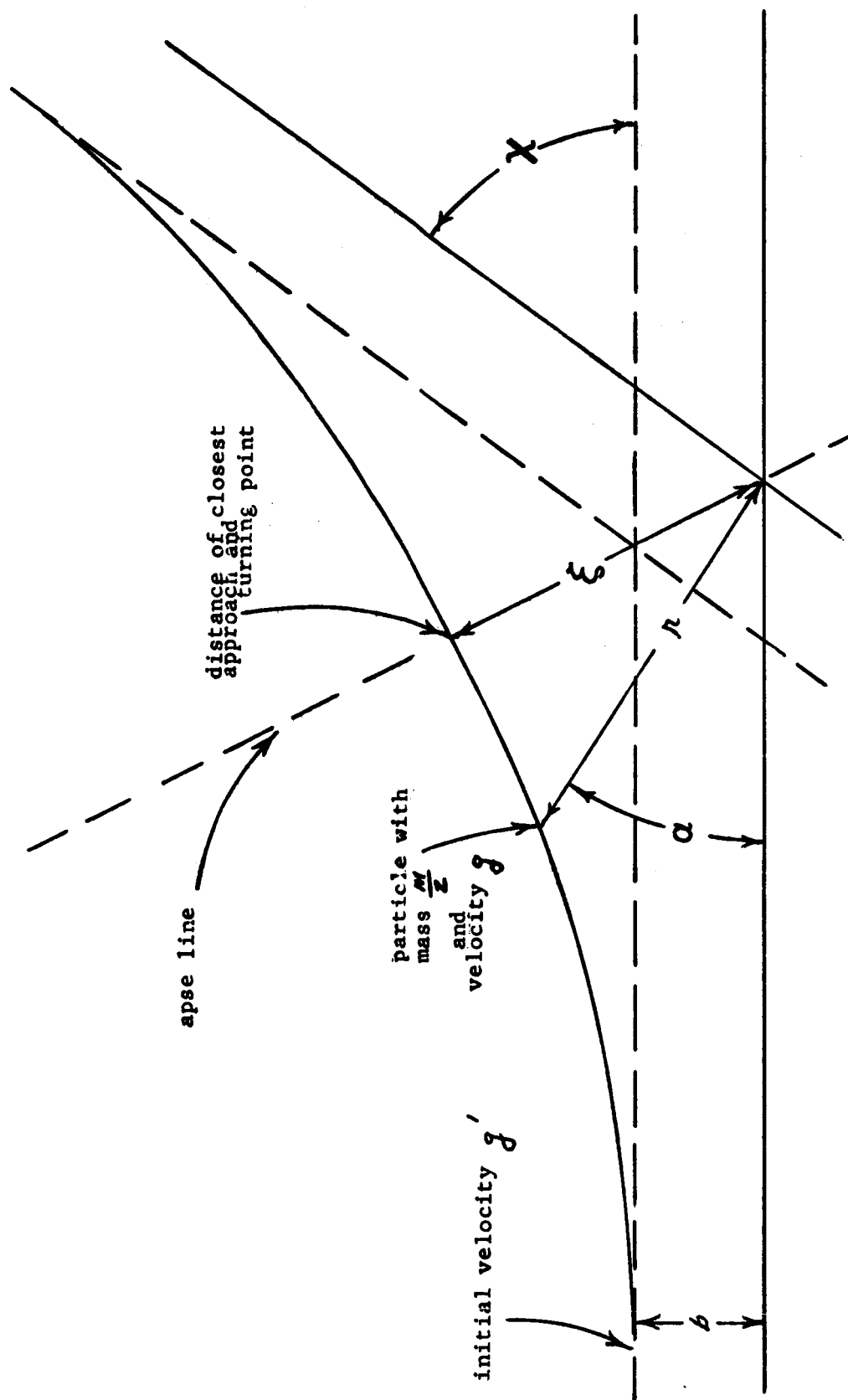


Fig. 1
Dynamics of a Molecular Collision

A particle with initial velocity g' approaches the scatterer with an impact parameter (or miss distance) b . It eventually passes through a radial separation distance, r , which is the distance of closest approach or turning point. Finally it leaves the field of force having been scattered through an angle χ . We note that the collision trajectory is symmetric about the apse line which is a line through the force center and the point of closest approach. This symmetry makes it necessary to examine only the incoming portion of the collision trajectory in detail. The angle α between $-g'$ and $\hat{r}$ on the incoming portion of the collision trajectory conveniently describes the trajectory. It follows from the differential equations which govern the collision that²⁵

$$\alpha = \int_r^\infty \frac{\left(\frac{b}{r^2}\right) dr}{\sqrt{1 - \left(\frac{\phi(r)}{m(g')^2}\right) - \frac{b^2}{r^2}}} \quad (2.6 - 1)$$

The quantity α_m is the largest value of α and occurs when $r = r_s$.

In order to perform certain numerical computations discussed in Chapter V, we need expressions for the scalar products $\hat{g}' \cdot \hat{r}$ and $\hat{g}' \cdot \hat{g}$ where the symbol $\hat{}$ indicates a unit vector. These scalar products are conveniently determined in terms of the quantities α , b , χ , g , g' and ϖ which is the angle between $\hat{r}$ and $-g$. These quantities can be written in terms of the independent variables g' , r_s and r . The variables g' and r_s determine a trajectory and r determines a point on either the incoming or outgoing portion of this trajectory. From the

conservation of energy we find that g is given by

$$g = \left[(g')^2 - \left(\frac{4}{m}\right) \phi(r) \right]^{1/2} \quad (2.6 - 2)$$

and from the conservation of angular momentum that

$$b = \frac{5}{g'} \left[(g')^2 - \frac{4}{m} \phi(5) \right] \quad (2.6 - 3)$$

$$\sin \vartheta = \frac{g' b}{g r} \quad (2.6 - 4)$$

and (for ϑ on the incoming portion of the trajectory)

$$\cos \vartheta = \sqrt{1 - \left(\frac{g' b}{g r}\right)^2} \quad (2.6 - 5)$$

The angle of deflection, χ , is given by

$$\chi = \pi - 2\alpha_m \quad (2.6 - 6)$$

where α_m is obtained from equation (2.6 - 1) by replacing the integration limit r by 5 .

On the incoming portion of the trajectory it follows from the definition of α that

$$\hat{g}' \cdot \hat{r} = -\cos \alpha \quad (2.6 - 7)$$

The quantity $\hat{g}' \cdot \hat{g}$ can be determined from geometry and a knowledge of α and ϑ by summing the appropriate angles. The fixed

sign of the angular momentum makes this summing unique. We find

$$\hat{g}' \cdot \hat{g} = \cos \alpha \cos \vartheta + \sin \alpha \sin \vartheta \quad (2.6 - 8)$$

The two scalar products on the outgoing portion of the trajectory can be written in terms of α for the corresponding point on the incoming portion of the trajectory and χ . This can be done because of the symmetry of the trajectory about the apse line.

We find

$$\hat{g}' \cdot \hat{h} = \cos(\alpha + \chi) \quad (2.6 - 9)$$

and

$$\hat{g}' \cdot \hat{g} = \cos(\alpha + \chi) \cos \vartheta + \sin(\alpha + \chi) \sin \vartheta \quad (2.6 - 10)$$

It is convenient to define a variable $\underline{h}'$ by the relation

$$\underline{h}' = \int^{(2)}(\underline{h}) = T_{1,2}^{(2)-1} T_1^{(1)} T_2^{(1)}(\underline{h}) \quad (2.6 - 11)$$

In words, $\underline{h}'$, is obtained from $\underline{h}$ and $\underline{g}$ by first transforming $\underline{h}$ back along the two particle trajectory until the two particles are not interacting and then transforming an equal length of time forward along single particle trajectories. We also note that the initial velocity $\underline{g}'$ satisfies the relation

$$\underline{g}' = \int^{(2)}(\underline{g}) \quad (2.6 - 12)$$

The coordinate and momentum transformation $(\underline{r}, \frac{m}{2} \underline{g}) \rightarrow (\underline{r}', \frac{m}{2} \underline{g}')$ is canonical²⁶ since $\underline{r}'$ and $\frac{m}{2} \underline{g}'$ obey Hamilton's equations for the Hamiltonian

$$H' = \frac{1}{m} \left(\frac{m}{2} \underline{g}' \right)^2 \quad (2.6 - 13)$$

That is,

$$\frac{d\underline{r}'}{dt} = \underline{g}' = \frac{\partial H'}{\partial (\frac{m}{2} \underline{g}')} \quad (2.6 - 14)$$

and

$$\frac{d}{dt} \left(\frac{m}{2} \underline{g}' \right) = 0 = - \frac{\partial H'}{\partial \underline{r}'} \quad (2.6 - 15)$$

Physically, the transformation can be seen to be canonical since it is the result of two successive canonical transformations.

These are the backward and forward transformations along the trajectories mentioned above.

An important property of a canonical transformation is that its Jacobian is unity. Integrations over the entire position-velocity space can therefore be carried out equally well by integrating over the entire domain of $\underline{r}$ and $\underline{g}$ or the entire domain of $\underline{r}'$ and $\underline{g}'$. The coordinates $\underline{r}'$ and $\underline{g}'$ form a particularly convenient set of integration variables because they allow us to integrate over trajectories. The velocity $\underline{g}'$ (as discussed above) is the initial velocity and is a constant of the motion. The angles of $\underline{g}'$ fix the plane of collision. If we write $d\underline{r}'$ in

cylindrical coordinates with the $\underline{z}$ -axis in the direction of $\underline{g}'$, then

$$d\underline{z}' = b \, db \, d\underline{z} \, d\epsilon \quad (2.6 - 16)$$

The angle ϵ determines the orientation of the collision plane.

The impact parameter, b , which is a constant of the motion along with $\underline{g}'$, determines a trajectory in the collision plane. The variable $\underline{z}$ specifies the position on the trajectory and is simply related to the time by

$$d\underline{z} = \underline{g}' \, dt \quad (2.6 - 17)$$

The Poisson bracket is invariant in form under a canonical transformation. If we consider in particular the Poisson bracket $[\quad , H]$ expressed in the systems $(\underline{z}, \frac{m}{2} \underline{g})$ and $(\underline{z}', \frac{m}{2} \underline{g}')$ we obtain the differential relation

$$[\quad , H] = \underline{g} \cdot \left(\frac{\partial}{\partial \underline{z}} \right)_{\underline{g}} - \frac{2}{m} \frac{\partial \phi}{\partial \underline{z}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{z}} = \underline{g}' \cdot \left(\frac{\partial}{\partial \underline{z}'} \right)_{\underline{g}'} \quad (2.6 - 18)$$

If $\underline{z}'$ is expressed in the cylindrical coordinate system mentioned above, and if $\underline{g}'$ is expressed in polar coordinates, then

$$\underline{g}' \cdot \left(\frac{\partial}{\partial \underline{z}'} \right)_{\underline{g}'} = \underline{g}' \cdot \left(\frac{\partial}{\partial \underline{z}} \right)_{\underline{g}', b, \epsilon} = \left(\frac{\partial}{\partial t} \right)_{\text{constant trajectory}} \quad (2.6 - 19)$$

Equations (2.6 - 18) and (2.6 - 19) show this well-known relation: that the operator $[\quad , H]$ gives the implicit time derivative of a function of $\underline{z}$ and $\underline{g}$.

For the computations discussed in Chapter V, we need expressions for the scalar products $\underline{r}' \cdot \hat{n}$ and $\underline{r}' \cdot \hat{g}$. Let us define a quantity ω_f/g' as the absolute value of the time required for a particle to travel from the turning point, f , to the point r on the trajectory. Let us also define $\frac{\Delta\omega}{g'}$ as the difference in the time required for a particle to travel from some pre-collision point on the trajectory to the distance of closest approach, and the time required to reach the distance of closest approach if no collision occurs. The quantity $\frac{\Delta\omega}{g'}$ is related to the energy derivative of the quantum mechanical phase shift. Further, let us define $\underline{b}$ as the vector from the scatterer to the distance of closest approach on the non-collision trajectory. Then, $\underline{r}'$ on the incoming portion of the trajectory can be written

$$\underline{r}' = (\Delta\omega - \omega_f) \hat{g}' + \underline{b} \quad (2.6 - 20)$$

and thus,

$$\underline{r}' \cdot \hat{n} = (\Delta\omega - \omega_f)(\hat{g}' \cdot \hat{n}) + \underline{b} \cdot \hat{n} \quad (2.6 - 21)$$

and

$$\underline{r}' \cdot \hat{g} = (\Delta\omega - \omega_f)(\hat{g}' \cdot \hat{g}) + \underline{b} \cdot \hat{g} \quad (2.6 - 22)$$

On the outgoing portion of the trajectory we have

$$\underline{r}' = (\Delta\omega + \omega_f) \hat{g}' + \underline{b} \quad (2.6 - 23)$$

$$\underline{r}' \cdot \hat{r} = (\Delta\omega + \omega_F)(\hat{g}' \cdot \hat{r}) + (\underline{b} \cdot \hat{r}) \quad (2.6 - 24)$$

and

$$\underline{r}' \cdot \hat{g} = (\Delta\omega + \omega_F)(\hat{g}' \cdot \hat{g}) + (\underline{b} \cdot \hat{g}) \quad (2.6 - 25)$$

The scalar products $\hat{g}' \cdot \hat{r}$ and $\hat{g}' \cdot \hat{g}$ are given by equations (2.6 - 7), (2.6 - 8), (2.6 - 9) and (2.6 - 10). We now give analytic forms for ω_F , $\Delta\omega$, $\underline{b} \cdot \hat{r}$ and $\underline{b} \cdot \hat{g}$. The time, $t_{r \rightarrow \tilde{r}}$ required for a particle to go from r to $\tilde{r}$ on the incoming portion of the trajectory is²⁷

$$t_{r \rightarrow \tilde{r}} = \frac{1}{g'} \int_{\tilde{r}}^r \frac{d\rho}{\sqrt{1 - \frac{4\phi(\rho)}{m(g')^2} - \frac{b^2}{\rho^2}}} \quad (2.6 - 26)$$

Hence,

$$\omega_F = \int_F^r \frac{d\rho}{\sqrt{1 - \frac{4\phi(\rho)}{m(g')^2} - \frac{b^2}{\rho^2}}} \quad (2.6 - 27)$$

and

$$\Delta\omega = \int_F^R \frac{d\rho}{\sqrt{1 - \frac{4\phi(\rho)}{m(g')^2} - \frac{b^2}{\rho^2}}} - (R^2 - b^2)^{1/2} \quad (2.6 - 28)$$

where R is a pre-collision separation distance. We can write

$$\Delta\omega = \int_F^R \left[\frac{1}{\sqrt{1 - \frac{4\phi(\rho)}{m(g')^2} - \frac{b^2}{\rho^2}}} - 1 \right] d\rho + [R - (R^2 - b^2)^{1/2}] - F \quad (2.6 - 29)$$

On passing to the limit $R \rightarrow \infty$, we have

$$\Delta \omega = \int_{\mathcal{F}} \left[\frac{1}{\sqrt{1 - \frac{q^2(\rho)}{m(q')^2} - \frac{b^2}{\rho^2}}} - 1 \right] d\rho \quad (2.6 - 30)$$

We can find the scalar products $\underline{b} \cdot \hat{n}$ and $\underline{b} \cdot \hat{g}$ in a manner analogous to that used to find $\hat{g}' \cdot \hat{n}$ and $\hat{g}' \cdot \hat{g}$. On the incoming portion of the trajectory

$$\underline{b} \cdot \hat{n} = b \sin \alpha \quad (2.6 - 31)$$

and

$$\underline{b} \cdot \hat{g} = b [\cos(\alpha) \sin(\vartheta) - \sin(\alpha) \cos(\vartheta)] \quad (2.6 - 32)$$

On the outgoing portion of the trajectory

$$\underline{b} \cdot \hat{n} = b \sin(\alpha + \chi) \quad (2.6 - 33)$$

and

$$\underline{b} \cdot \hat{g} = b [-\cos(\alpha + \chi) \sin(\vartheta) + \sin(\alpha + \chi) \cos(\vartheta)] \quad (2.6 - 34)$$

These relations determine the scalar products $\hat{n}' \cdot \hat{n}$ and $\hat{n}' \cdot \hat{g}$ on both the incoming and outgoing portions of the trajectory.

Section 2.7 The Truncation of the B.B.G.K.Y. Equations - The First Order Approximation

The development in Sec. 2.4 provides a formalism for finding the lower order distribution functions by solving a truncated set of

B.B.G.K.Y. equations. In principle this procedure is very general and should lead to expressions for the lower order distribution functions to any desired accuracy. In practice, however, mathematical and computational considerations limit this generality. We must content ourselves with very simple applications of the formalism.

The simplest application is to obtain an equation for $f^{(1)}$ by approximating $f^{(2)}$ in the first B.B.G.K.Y. equation. From equation (2.4 - 7) we see that $f^{(2)}$ is approximated by

$$f^{(2)} = T_{1,2}^{(2)} T_1^{(1)} T_2^{(1)} (f_1^{(1)} f_2^{(1)}) = \int^{(2)} (f_1^{(1)} f_2^{(1)}) \quad (2.7 - 1)$$

This is the same approximation for $f^{(2)}$ which we obtained in Sec. 2.3 by assuming molecular chaos. Equation (2.7 - 1) leads to the $f^{(1)}$ equation

$$\frac{\partial f_1^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial f_1^{(1)}}{\partial \underline{r}_1} = \frac{1}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{v}_1} \int^{(2)} [f_1^{(1)} f_2^{(1)}] d\underline{r}_2 d\underline{v}_2 \quad (2.7 - 2)$$

From the identity

$$\frac{2}{m} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{G}} = \frac{1}{m} \left\{ \frac{\partial \phi^{(1,2)}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{v}_1} + \frac{\partial \phi^{(1,2)}}{\partial \underline{r}_2} \cdot \frac{\partial}{\partial \underline{v}_2} \right\} \quad (2.7 - 3)$$

where $\underline{G} = \frac{1}{2}(\underline{v}_1 + \underline{v}_2)$, it follows that equation (2.7 - 2) can be written

$$\frac{\partial f_1^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial f_1^{(1)}}{\partial \underline{r}_1} = \frac{2}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{G}} \int^{(2)} [f_1^{(1)} f_2^{(1)}] d\underline{r} d\underline{g} \quad (2.7 - 4)$$

It is convenient to introduce the notation

$$h'(\underline{r}_1, \underline{r}_2, \underline{v}_1, \underline{v}_2) = \int^{(2)} h(\underline{r}_1, \underline{r}_2, \underline{v}_1, \underline{v}_2) \quad (2.7 - 5)$$

where h is an arbitrary function of the variables $\underline{r}_1$, $\underline{r}_2$, $\underline{v}_1$ and $\underline{v}_2$. We note that special cases of this definition are

$$\underline{r}' = \int^{(2)}(\underline{r}) \quad (2.7 - 6)$$

and

$$\underline{g}' = \int^{(2)}(\underline{g}) \quad (2.7 - 7)$$

which is consistent with the notation of Sec. 2.6. Thus equation (2.7 - 4) can be written

$$\frac{\partial f^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial f^{(1)}}{\partial \underline{r}_1} = \frac{2}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} f_1^{(1)} f_2^{(1)} d\underline{r} d\underline{g} \quad (2.7 - 8)$$

We assume that $f^{(1)}$ at any point in the position-velocity space is uniquely determined by specifying n , $\underline{u}$ and $\mathcal{T}$ everywhere in the system. That is $f^{(1)}$ is determined by the macroscopic state. It then follows that $f^{(1)}$ depends on space and time only through the macroscopic state. If n , $\underline{u}$ and $\mathcal{T}$ are assumed to be analytic functions of space, then a knowledge of the macroscopic state is equivalent to a knowledge of n , $\underline{u}$ and $\mathcal{T}$ and their space gradients at a point. At equilibrium n , $\underline{u}$ and $\mathcal{T}$ are constant throughout space. Thus, from equation (2.7 - 8), the equilibrium equation for $f^{(1)}$ is

$$0 = \frac{2}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} f_1^{(1)} f_2^{(1)} d\underline{h} d\underline{g} \quad (2.7 - 9)$$

The solution to equation (2.7 - 9) is

$$f_1^{(1)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} \underline{V}_1^2} \quad (2.7 - 10)$$

where $\underline{V}_1 = \underline{v}_1 - \underline{u}$. The quantity $\underline{V}_1$ is known as the peculiar velocity.

As was discussed in the Introduction, the transport coefficients arise from a linear approximation for the dependences of the energy and momentum fluxes on gradients within the system. The linear approximation is valid only when gradients in the system are not too large, or, equivalently, when the system is close to equilibrium. This suggests that equation (2.7 - 8) should be solved in a perturbation expansion of some sort about the equilibrium solution. The particular method of expansion we consider is due to Enskog⁵. On the one hand, it is based on physical intuition; and on the other, on the satisfaction of certain mathematical requirements. The expansion is convenient because it linearizes equation (2.7 - 8) and thus makes it more tractable.

Let us assume that $f^{(1)}$ is given by the expansion

$$f^{(1)} = \sum_{k=0}^{\infty} \epsilon^k f_{[k]}^{(1)} \quad (2.7 - 11)$$

where ϵ is an expansion parameter which marks the order of

perturbation. In the final expression for $f^{(1)}$ as given by equation (2.7 - 11), ϵ will be set equal to one. The equilibrium state is characterized by a lack of spatial gradients. Hence, it seems reasonable that deviation from equilibrium should be marked by the order of spatial gradients in the system. Therefore, we expand the right side of equation (2.7 - 8) in a Taylor series about $\underline{r}$, and write successive orders in the gradient $\frac{\partial}{\partial \underline{r}}$, proportional to the corresponding power of ϵ . This expansion of (2.7 - 8) yields

$$\epsilon \left\{ \frac{\partial f^{(1)}}{\partial t} + \underline{v} \cdot \frac{\partial f^{(1)}}{\partial \underline{r}} \right\} \quad (2.7 - 12)$$

$$= \frac{2}{m} \int d\underline{r} d\underline{g} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left[\begin{aligned} & \bar{f}_1^{(1)'} \bar{f}_2^{(1)'} + \\ & \epsilon \left\{ (\underline{r}_1' - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_1^{(1)'} \right) \bar{f}_2^{(1)'} \right. \\ & \quad \left. + (\underline{r}_2' - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_2^{(1)'} \right) \bar{f}_1^{(1)'} \right\} \\ & + \epsilon^2 (\quad) + \epsilon^3 (\quad) + \dots \end{aligned} \right]$$

The bar over the functions $\bar{f}_1^{(1)'}$ and $\bar{f}_2^{(1)'}$ indicates that the space variable at which they are evaluated is $\underline{r}$. The left side of equation (2.7 - 12) is written proportional to ϵ because the operator $\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \frac{\partial}{\partial \underline{r}} \right\}$ is first order in the gradient $\frac{\partial}{\partial \underline{r}}$. That this is true for $\frac{\partial}{\partial t}$, follows from the fact that $f^{(1)}$ depends on time only through n , μ and T and their spatial gradients. From the equations of change, the time derivative of these quantities is proportional to $\frac{\partial}{\partial \underline{r}}$.

If equation (2.7 - 11) is substituted into equation (2.7 - 12)

we can write the result as a series of integral equations which are the coefficients of the various powers of ϵ . The ϵ^0 equation is

$$0 = \frac{2}{m} \int \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left\{ \bar{f}_{1[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} \right\} d\underline{r} d\underline{g} \quad (2.7 - 13)$$

As is to be expected (since our method of solution is a perturbation expansion about the equilibrium solution) equation (2.7 - 13) is identical to equation (2.7 - 9) and has the solution

$$\bar{f}_{1[0]}^{(1)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} v_1^2} \quad (2.7 - 14)$$

This equation states that to lowest order in the perturbation the velocity distribution is Maxwellian. The quantities n , $\underline{u}$ and T are considered here to be local properties and are defined in terms of $f^{(1)}$ by the relations

$$\int f_1^{(1)} d\underline{v}_1 = n \quad (2.7 - 15)$$

$$\int f_1^{(1)} \underline{v}_1 d\underline{v}_1 = \underline{u} \quad (2.7 - 16)$$

and

$$\int f_1^{(1)} v_1^2 d\underline{v}_1 = \frac{3n kT}{m} \quad (2.7 - 17)$$

Since the equilibrium form of $f_1^{(1)}$ must also obey equations (2.7 - 15), (2.7 - 16) and (2.7 - 17), these equations are satisfied if we replace $f^{(1)}$ by $f_{1[0]}^{(1)}$. Hence, we require as additional conditions on the perturbation expansion of equation (2.7 - 11) that

$$\sum_{k=1}^{\infty} \int f_{,[k]}^{(1)} d\underline{v}_1 = 0 \quad (2.7 - 18)$$

$$\sum_{k=1}^{\infty} \int f_{,[k]}^{(1)} \underline{v}_1 d\underline{v}_1 = 0 \quad (2.7 - 19)$$

and

$$\sum_{k=1}^{\infty} \int f_{,[k]}^{(1)} v_1^2 d\underline{v}_1 = 0 \quad (2.7 - 20)$$

It is possible, however, to require the stronger conditions that

$$\int f_{,[k]}^{(1)} d\underline{v}_1 = 0 \quad (2.7 - 21)$$

$$\int f_{,[k]}^{(1)} \underline{v}_1 d\underline{v}_1 = 0 \quad (2.7 - 22)$$

and

$$\int f_{,[k]}^{(1)} v_1^2 d\underline{v}_1 = 0 \quad (2.7 - 23)$$

These conditions uniquely determine the perturbations in terms of n , $\underline{u}$ and $\mathcal{T}$ and also insure that equations (2.7 - 15), (2.7 - 16) and (2.7 - 17) are satisfied by $f^{(1)}$ to any order of approximation.

The remaining equations corresponding to ϵ' , ϵ^2 , etc. are linear, inhomogeneous equations. The ϵ' equation is

$$\begin{aligned}
 & \frac{\partial}{\partial t} f_{1[0]}^{(1)} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{h}_1} f_{1[0]}^{(1)} \\
 &= \frac{2}{m} \int d\underline{h} d\underline{g} \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_G \left[\left\{ \bar{f}_{1[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} + \bar{f}_{1[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} \right\} \right. \\
 & \quad + \\
 & \quad \left. (\underline{h}_1' - \underline{h}_1) \cdot \frac{\partial}{\partial \underline{h}_1} [\bar{f}_{1[0]}^{(1)'}] \bar{f}_{2[0]}^{(1)'} \right. \\
 & \quad + \\
 & \quad \left. (\underline{h}_2' - \underline{h}_1) \cdot \frac{\partial}{\partial \underline{h}_1} [\bar{f}_{2[0]}^{(1)'}] \bar{f}_{1[0]}^{(1)'} \right]
 \end{aligned} \tag{2.7 - 24}$$

It can be shown from the theory of integral equations²⁸ that a necessary and sufficient condition for the solubility of equation (2.7 - 24) is that the inhomogeneity, J , defined by

$$\begin{aligned}
 J &= \frac{\partial}{\partial t} f_{1[0]}^{(1)} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{h}_1} f_{1[0]}^{(1)} \\
 &= \frac{2}{m} \int d\underline{h} d\underline{g} \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_G \left[(\underline{h}_1' - \underline{h}_1) \cdot \left(\frac{\partial}{\partial \underline{h}_1} \bar{f}_{1[0]}^{(1)'} \right) \bar{f}_{2[0]}^{(1)'} + (\underline{h}_2' - \underline{h}_1) \cdot \left(\frac{\partial}{\partial \underline{h}_1} \bar{f}_{2[0]}^{(1)'} \right) \bar{f}_{1[0]}^{(1)'} \right]
 \end{aligned} \tag{2.7 - 25}$$

be orthogonal to the solutions of the homogeneous equation. These solutions are the summational invariants $\psi_i^{(1)}$,

$$\psi_1^{(1)} = 1 \tag{2.7 - 26}$$

$$\psi_2^{(1)} = \underline{V}_1 \tag{2.7 - 27}$$

and

$$\psi_i^{(3)} = V_i^2 \quad (2.7 - 28)$$

The orthogonality conditions are

$$\int J \psi_i^{(2)} d\underline{v}_i = 0 \quad (2.7 - 29)$$

and have been verified by Snider and Curtiss¹¹. Corresponding to each solution of the homogeneous equation, there is an arbitrary constant in the inhomogeneous equation solution. The conditions of equations (2.7 - 21), (2.7 - 22) and (2.7 - 23) are sufficient to uniquely determine these constants.

Snider and Curtiss have solved equation (2.7 - 24) and have developed expressions for the transport coefficients in terms of their solutions. In the subsequent sections we refer extensively to their work.

Section 2.8. The Truncation of the B.B.G.K.Y. Equations - The Second Order Approximation

We now wish to examine the next application of the formalism of Sec. 2.4. In this case we truncate the B.B.G.K.Y. hierarchy by approximating $f^{(3)}$, which appears in the $f^{(2)}$ equation, in terms of $f^{(1)}$ and $f^{(2)}$. This procedure is discussed in Sec. 2.5, and results in the pair of equations (2.5 - 1) and (2.5 - 2). We can write the Poisson brackets explicitly to obtain

$$\left\{ \frac{\partial}{\partial t} + \underline{v}_i \cdot \frac{\partial}{\partial \underline{v}_i} \right\} f^{(1)} = \frac{2}{m} \int d\underline{v}_j d\underline{q} \frac{\partial \phi^{(1,2)}}{\partial \underline{v}_i} \left(\frac{\partial}{\partial \underline{q}} \right)_{\underline{q}} f_{i,2}^{(2)} \quad (2.8 - 1)$$

and

$$\left\{ \frac{\partial}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{r}_1} + \underline{g} \cdot \frac{\partial}{\partial \underline{r}} - \frac{2}{m} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \right\} f_{1,2}^{(2)} \quad (2.8 - 2)$$

$$= \frac{1}{m} \int d\underline{r}_3 d\underline{v}_3 \left\{ \frac{\partial \phi^{(1,3)}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{v}_1} + \frac{\partial \phi^{(2,3)}}{\partial \underline{r}_2} \cdot \frac{\partial}{\partial \underline{v}_2} \right\} T^{(3)-1} \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)})(T_{1,3}^{(2)} f_{1,3}^{(2)})(T_{2,3}^{(2)} f_{2,3}^{(2)})}{(T_1^{(1)} f_1^{(1)})(T_2^{(1)} f_2^{(1)})(T_3^{(1)} f_3^{(1)})}$$

In Equations (2.8 - 1) and (2.8 - 2), $\underline{v}_1$ and $\underline{r}_1$ are the gross velocity and position coordinates; whereas $\underline{g}$ and $\underline{r}$ are coordinates relative to $\underline{v}_1$ and $\underline{r}_1$. Since the macroscopic state uniquely determines $f^{(2)}$, it follows that the dependence of $f^{(2)}$ on the gross position and time only can be through the macroscopic state.

This result is more general than is stated above. It applies to a distribution function of any order and is not dependent on how the gross position coordinate is chosen. To see this, let us consider an N particle system and the two general transformations

$$\underline{r}_i' = \underline{X} + \underline{x}_i' = \underline{Y} + \underline{y}_i' \quad (2.8 - 3)$$

where $i' = 1$ to N . Here $\underline{X}$ and $\underline{Y}$ are the gross position coordinates in the two systems and the sets $\{\underline{x}_i'\}$ and $\{\underline{y}_i'\}$ are sets of relative coordinates. The coordinates $\underline{x}_1$ and $\underline{y}_1$ are taken as the linearly dependent pair and it is assumed that $\underline{x}_1$ is not a function of $\underline{X}$ nor $\underline{y}_1$ of $\underline{Y}$. If the total system undergoes a translation, only the gross position coordinates $\underline{X}$ and $\underline{Y}$ are changed. That is, the coordinate sets $\{\underline{x}_i'\}$ and $\{\underline{y}_i'\}$

remain unchanged. Thus, in the transformation equations any relative coordinate $\underline{x}_j$ must be a function solely of the set of relative coordinates $\{\underline{y}_i\}$ and vice versa. From this it follows that if the h particle distribution function depends on the gross position in one coordinate system only through the macroscopic state, this also must be true in the other system.

Let us consider the operator

$$\left[\frac{1}{2m} \left(\sum_{i=1}^h (m \underline{v}_i)^2 \right) \right]^{(h)} = \sum_{i=1}^h \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i} \quad (2.8 - 4)$$

which appears on the left side of the h^{th} order B.B.G.K.Y. equation. It is straightforward to show that this operator is invariant in form under any linear transformation. In particular, if we consider one of the transformations of equation (2.8 - 3), we have

$$\sum_{i=1}^h \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i} = \dot{\underline{X}} \cdot \frac{\partial}{\partial \underline{X}} + \sum_{i=2}^h \dot{\underline{x}}_i \cdot \frac{\partial}{\partial \underline{x}_i} \quad (2.8 - 5)$$

where the dot above a position vector denotes the corresponding velocity. Since the potential of interaction is a function of only the relative coordinates $\{\underline{x}_i\}$, it follows that the operator $\left[\frac{1}{2m} \left(\sum_{i=1}^h (m \underline{v}_i)^2 \right) \right]^{(h)}$ which appears on the left side of the h^{th} order B.B.G.K.Y. equation depends on the gross position and velocity only through the operator $\dot{\underline{X}} \cdot \frac{\partial}{\partial \underline{X}}$. At equilibrium n , $\underline{u}$ and T are constant throughout space. Thus the equilibrium equations for the distribution functions are written by omitting the operator

from the left side of the B.B.G.K.Y. equations.

The equilibrium forms of equations (2.8 - 1) and (2.8 - 2) then are

$$0 = \frac{2}{m} \int d\underline{h} \, d\underline{g} \, \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} f_{1,2}^{(2)} \quad (2.8 - 6)$$

and

$$\left\{ \underline{g} \cdot \frac{\partial}{\partial \underline{h}} - \frac{2}{m} \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \right\} f_{1,2}^{(2)} \quad (2.8 - 7)$$

$$= \frac{1}{m} \int d\underline{h}_3 \, d\underline{u}_3 \left\{ \frac{\partial \phi^{(1,3)}}{\partial \underline{h}_1} \cdot \frac{\partial}{\partial \underline{u}_1} + \frac{\partial \phi^{(2,3)}}{\partial \underline{h}_2} \cdot \frac{\partial}{\partial \underline{u}_2} \right\} T^{(3)-1} \frac{(T_{1,2}^{(2)} f_{1,2}^{(2)}) (T_{1,3}^{(2)} f_{1,3}^{(2)}) (T_{2,3}^{(2)} f_{2,3}^{(2)})}{(T_1^{(1)} f_1^{(1)}) (T_2^{(1)} f_2^{(1)}) (T_3^{(1)} f_3^{(1)})}$$

These coupled equations have the solutions

$$f^{(1)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} V^2} \quad (2.8 - 8)$$

and

$$f^{(2)} = y f_1^{(1)} f_2^{(1)} \quad (2.8 - 9)$$

where through first order in the density y is given by

$$y(x) = e^{-\frac{\phi^{(1,2)}}{kT}} \left[1 + n \int d\underline{h}_3 \left(e^{-\frac{\phi^{(1,3)}}{kT}} - 1 \right) \left(e^{-\frac{\phi^{(2,3)}}{kT}} - 1 \right) \right] \quad (2.8 - 10)$$

We note that $f^{(1)}$ at equilibrium maintains the same Maxwellian form as in equation (2.7 - 10). The function y depends only on the magnitude of the radial separation distance. As defined in equation (2.8 - 9), y is the radial distribution function. Equation (2.8 - 7), however, is only an approximate equation for y . This approximate equation yields the exact radial distribution function to order n in the density (as given in equation (2.8 - 10)). Livingston and Curtiss²⁴ have examined higher terms in the solution of the approximate equation for rigid spheres.

It is convenient to write $f^{(2)}$ in terms of a function y defined by

$$f^{(2)} = y f_1^{(1)} f_2^{(1)} \quad (2.8 - 11)$$

From equations (2.8 - 8) and (2.3 - 9) we find that $y_{r \rightarrow 0}$, the equilibrium limit of y , is

$$y_{r \rightarrow 0} = e^{\frac{\phi}{kT}} y = 1 + n \int d\mathbf{r}_3 \left(e^{-\frac{\phi}{kT}} - 1 \right) \left(e^{-\frac{\phi}{kT}} - 1 \right) \quad (2.8 - 12)$$

Equations (2.8 - 1) and (2.8 - 2) are difficult to solve simultaneously, because in general the factor y as well as $f^{(1)}$ in equation (2.8 - 11) is perturbed from its equilibrium value when the system is not at equilibrium. However, it is possible to solve equation (2.8 - 1) approximately for $f^{(1)}$ by assuming

$$y = y_{r \rightarrow 0}(\underline{R}, n)$$

Here the coordinate $\underline{R}$ is the center of mass coordinate and is defined by

$$\underline{R} = \frac{\underline{r}_1 + \underline{r}_2}{2} \quad (2.8 - 13)$$

In our equilibrium approximation for the function ψ , the quantities n and τ in equation (2.8 - 12) are functions of this gross position coordinate. The gross dependence is chosen in this way in order that equation (2.8 - 11) retain its symmetry in particles 1 and 2. We note that the lead term in the density of ψ_{101} is one. This lead term when substituted into equation (2.8 - 11) gives rise to the molecular chaos expression for $f^{(2)}$.

Setting $\psi = \psi_{101}(\underline{R}, \underline{r})$ can be thought of as the first step in an iterative solution of equations (2.8 - 1) and (2.8 - 2). First under this approximation, equation (2.8 - 1) is solved for $f^{(1)}$. Then, this approximate expression for $f^{(1)}$ is substituted into equation (2.8 - 2) which in turn is solved for ψ . This solution is then substituted into equation (2.8 - 1) and the iterative procedure is repeated. It should be pointed out, however, that it is difficult to decide if such a procedure is convergent.

Section 2.9 The Rigid Sphere Limit and the Enskog Dense Gas Equation

Let us consider the approximation $\psi = \psi_{101}(\underline{R}, \underline{r})$ for the special case of rigid spheres. We now show that in this approximation and to the order in the density which ψ is given by equation (2.8 - 12), equation (2.8 - 1) reduces to the Enskog equation for dense gases⁶. Thus our treatment can be thought of as

a soft potential generalization of the Enskog treatment.

If $\psi = \psi_{[0]}(\underline{R}, \underline{r})$, then equation (2.8 - 1) is

$$\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \frac{\partial}{\partial \underline{r}} \right\} f_i^{(1)} = \frac{2}{m} \int d\underline{r} d\underline{g} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left[\psi_{[0]}(\underline{R}, \underline{r}) f_i^{(1)} f_z^{(2)} \right] \quad (2.9 - 1)$$

In Sec. 2.6 the operator identity

$$\frac{2}{m} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} = \underline{g} \cdot \frac{\partial}{\partial \underline{r}} - \underline{g}' \cdot \left(\frac{\partial}{\partial \underline{r}'} \right)_{\underline{g}} \quad (2.9 - 2)$$

was introduced. If equation (2.9 - 2) is substituted into equation (2.9 - 1), then

$$\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \frac{\partial}{\partial \underline{r}} \right\} f_i^{(1)} = \int d\underline{r} d\underline{g} \left\{ \underline{g} \cdot \frac{\partial}{\partial \underline{r}} - \underline{g}' \cdot \left(\frac{\partial}{\partial \underline{r}'} \right)_{\underline{g}} \right\} \left[\psi_{[0]} f_i^{(1)} f_z^{(2)} \right] \quad (2.9 - 3)$$

In the case of rigid spheres of diameter σ , it is seen from equation (2.9 - 1) that there is no contribution to the integral for $\underline{r} > \sigma$ since then $\phi^{(1,2)}(\underline{r}) = 0$. On the other hand, for $\underline{r} < \sigma$ the integrand is also zero since this corresponds to penetration of the spheres. This is impossible for rigid spheres and hence $f_{1,2}^{(2)} = 0$. There is, however, a δ -function contribution to the integral on the surface Σ defined by $\underline{r} = \sigma$. This contribution arises from the gradient of $\underline{g}'$ which changes discontinuously across the surface Σ . The gradient $\frac{\partial}{\partial \underline{r}}$ in equation (2.9 - 3) is taken holding $\underline{g}'$ fixed. Hence, only $\frac{\partial}{\partial \underline{r}}$ gives rise to the δ -function behavior. Making use of these conclusions, we can rewrite equation (2.9 - 3) in the form

$$\left\{ \frac{\partial}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{z}_1} \right\} f_1^{(1)} = \int_{\underline{z} \in \sigma} d\underline{z} d\underline{g} \left\{ \underline{g} \cdot \frac{\partial}{\partial \underline{z}} \left[\chi_{[\sigma]} f_1^{(1)} f_2^{(1)} \right] \right\} \quad (2.9 - 4)$$

which by Gauss' theorem is

$$\left\{ \frac{\partial}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{z}_1} \right\} f_1^{(1)} = \int_{\Sigma} d\underline{g} d\underline{z} \cdot \underline{g} \left[\chi_{[\sigma]}(\underline{z}, \sigma) f_1^{(1)} f_2^{(1)} \right] \quad (2.9 - 5)$$

On the surface Σ the vector $\underline{z}'$ is equal to $\underline{z}$ because the collision is instantaneous. Therefore, we have on the surface

$$\underline{z} = \underline{z}' = \sigma \hat{k} \quad (2.9 - 6)$$

and

$$\underline{R} = \underline{z}_1 + \left(\frac{1}{2}\right) \sigma \hat{k} \quad (2.9 - 7)$$

where $\hat{k}$ is a unit vector in the direction of $\underline{z}$. By restricting the collision integral in equation (2.9 - 5) to an integral over the surface $\Sigma \cdot \underline{g} > 0$, we can write equation (2.9 - 5) in the form

$$\begin{aligned} & \left\{ \frac{\partial}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{z}_1} \right\} f_1^{(1)} \\ &= \int_{\Sigma \cdot \underline{g} > 0} d\underline{g} d\underline{z} \cdot \underline{g} \left[\chi_{[\sigma]}(\underline{z}_1 + \frac{1}{2} \sigma \hat{k}, \sigma) f^{(1)}(\underline{z}_1, \underline{v}_1) f^{(1)}(\underline{z}_1 + \sigma \hat{k}, \underline{v}_2') \right. \\ & \quad \left. + \right. \\ & \quad \left. \left[-\chi_{[\sigma]}(\underline{z}_1 - \frac{1}{2} \sigma \hat{k}, \sigma) f^{(1)}(\underline{z}_1, \underline{v}_1) f^{(1)}(\underline{z}_1 - \sigma \hat{k}, \underline{v}_2) \right] \right] \end{aligned} \quad (2.9 - 8)$$

In equation (2.9 - 8) the explicit gross variable dependence of the functions in the integrand is given as obtained from equations (2.9 - 6) and (2.9 - 7).

The factor $\gamma_{[0]}^{(R, \sigma)}$ through first order in the density is

$$\gamma_{[0]}^{(R, \sigma)} = 1 + n(\underline{R}) \left(\frac{C}{B} \right) \quad (2.9 - 9)$$

where B and C are respectively the second and third rigid sphere virial coefficients. Equation (2.9 - 8) is the Enskog dense gas equation to the order in the density of $\gamma_{[0]}$ given in equation (2.9 - 9).

CHAPTER III

SOLUTION OF THE TRUNCATED B.B.G.K.Y. EQUATIONS

In Sec. 2.8 we discussed an approximate method of solution of the pair of equations which result from truncating the B.B.G.K.Y. hierarchy at $f^{(3)}$. We now solve the $f^{(1)}$ equation in this approximation.

Section 3.1 Linearization of the $f^{(1)}$ Equation

If we approximate $f^{(2)}$ by

$$f^{(2)} = \psi_{[0]}^{(2)} f_1^{(1)'} f_2^{(1)'} \quad (3.1 - 1)$$

then equation (2.8 - 1) becomes

$$\left\{ \frac{\partial}{\partial t} + v_1 \cdot \frac{\partial}{\partial \mathbf{r}_1} \right\} f_1^{(1)} = \frac{2}{m} \int d\mathbf{r}_2 d\mathbf{g} \frac{\partial \psi^{(1,2)}}{\partial \mathbf{r}_1} \cdot \left(\frac{\partial}{\partial \mathbf{g}} \right) \left[\psi_{[0]} f_1^{(1)'} f_2^{(1)'} \right] \quad (3.1 - 2)$$

In analogy with the procedure in Sec. 2.8 we can expand equation (3.1 - 2) about the equilibrium equation. This procedure linearizes equation (3.1 - 2) and thus simplifies the problem of solution. We again arrive at a series of integral equations. The lowest order equation

$$0 = \frac{2}{m} \int d\mathbf{r}_2 d\mathbf{g} \frac{\partial \psi^{(1,2)}}{\partial \mathbf{r}_1} \cdot \left(\frac{\partial}{\partial \mathbf{g}} \right) \left[\bar{\psi}_{[0]} \bar{f}_{[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} \right] \quad (3.1 - 3)$$

corresponds, of course, to the equilibrium equation (2.8 - 6). The bar over a function indicates that the gross position variable of that function is $\mathbf{r}_1$. The function $\bar{f}_{[0]}^{(1)}$ has the form

$$\bar{f}_{[0]}^{(1)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{m}{2kT} v^2} \quad (3.1 - 4)$$

That is, to lowest order, the velocity distribution is Maxwellian.

The remaining equations in the expansion about equilibrium of equation (3.1 - 2) are all linear, inhomogeneous integral equations.

The lowest order of the remaining equations is

$$\left\{ \frac{\partial}{\partial t} + \underline{v} \cdot \frac{\partial}{\partial \underline{r}} \right\} \bar{f}_{[0]}^{(1)} \quad (3.1 - 5)$$

$$= \frac{2}{m} \int d\underline{r} d\underline{g} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left[\bar{y}_{[0]} \left\{ \bar{f}_{[1]}^{(1)'} \bar{f}_{[2]}^{(1)'} + \bar{f}_{[1]}^{(1)'} \bar{f}_{[2]}^{(1)'} \right\} \right. \\ \left. + (\underline{r} - \underline{r}') \cdot \left(\frac{\partial}{\partial \underline{r}}, \bar{y}_{[0]} \right) \bar{f}_{[1]}^{(1)'} \bar{f}_{[2]}^{(1)'} \right. \\ \left. + \bar{y}_{[0]} \left\{ (\underline{r}' - \underline{r}) \cdot \left(\frac{\partial}{\partial \underline{r}}, \bar{f}_{[1]}^{(1)'} \right) \bar{f}_{[2]}^{(1)'} + (\underline{r}' - \underline{r}) \cdot \left(\frac{\partial}{\partial \underline{r}}, \bar{f}_{[2]}^{(1)'} \right) \bar{f}_{[1]}^{(1)'} \right\} \right]$$

This equation is to be solved for the function $\bar{f}_{[1]}^{(1)}$. If we assume that $\bar{f}_{[1]}^{(1)}$ can be written in a density expansion, then we can write equation (3.1 - 5) in the general form

$$0 = \alpha n + \beta n^2 + \delta n^3 + \dots \quad (3.1 - 6)$$

where α , β , δ etc. are density independent functions of $\underline{v}$, $\underline{u}$ and T . Since n is an arbitrary parameter of the problem, we can replace equation (3.1 - 6) by the series of equations

$$\alpha = 0 ; \quad \beta = 0 ; \quad \delta = 0 \quad \dots \quad (3.1 - 7)$$

In order that the equation $\alpha = 0$ be satisfied, we see from equation (3.1 - 5) that the leading term in the expansion of $\bar{f}_{I,J}^{(n)}$ must be constant in the density. Further, we see from equation (3.1 - 5) that $\beta = 0$ is an equation for the term of order n of $\bar{f}_{I,J}^{(n)}$ and depends on the solution of the equation $\alpha = 0$. A similar statement can be made for each of the equations of (3.1 - 7). If we limit our attention to the constant and first order terms in the density expansion of $\bar{f}_{I,J}^{(n)}$ (and consequently to the equations $\alpha = 0$ and $\beta = 0$) equation (3.1 - 5) can be simplified to

$$\left\{ \frac{\partial}{\partial t} + \underline{u} \cdot \frac{\partial}{\partial \underline{x}} \right\} \bar{f}_{I,J}^{(n)} \quad (3.1 - 8)$$

$$= \frac{2}{\pi} \int d\underline{x} \int d\underline{y} \frac{\partial^{(1,2)}}{\partial \underline{x} \partial \underline{y}} \cdot \left(\frac{\partial}{\partial \underline{y}} \right) \underline{q} \left[\bar{y}_{I,J} \left\{ \bar{f}_{I,I}^{(n')} \bar{f}_{2,I}^{(n')} + \bar{f}_{I,I}^{(n')} \bar{f}_{2,I}^{(n')} \right\} \right. \\ \left. + (x'_1 - x_1) \cdot \left(\frac{\partial}{\partial x_1} \bar{f}_{I,I}^{(n')} \right) \bar{f}_{2,I}^{(n')} + (x'_2 - x_1) \cdot \left(\frac{\partial}{\partial x_1} \bar{f}_{2,I}^{(n')} \right) \bar{f}_{I,I}^{(n')} \right]$$

If we compare equation (3.1 - 8) with equation (2.7 - 24), we see that $\alpha = 0$ and the corresponding equation in the density expansion of equation (2.7 - 24) are identical. Hence the constant term in the density of $\bar{f}_{I,J}^{(n)}$, as given by the two equations is the same. However, the equation $\beta = 0$ and the corresponding equation from the expansion of equation (2.7 - 4) are not the same due to the first order term in the density of $\bar{y}_{I,J}$. Hence the first order terms for $\bar{f}_{I,J}^{(n)}$ given by the two equations are different.

The inhomogeneity, $\bar{J}$, in equations (2.7 - 4) and (3.1 - 8) is

$$J = \frac{\partial f_{[0]}^{(1)}}{\partial t} + \underline{v}_i \cdot \frac{\partial f_{[0]}^{(1)}}{\partial \underline{r}_i} \quad (3.1 - 9)$$

$$- \frac{2}{m} \int d\underline{r} d\underline{q} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{q}} \right)_{\underline{q}} \left[(\underline{r}'_1 - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_{[0]}^{(1)'} \right) \bar{f}_{2[0]}^{(1)'} \right. \\ \left. + (\underline{r}'_2 - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_{2[0]}^{(1)'} \right) \bar{f}_{[0]}^{(1)'} \right]$$

Snider and Curtiss have shown that part of J can be written¹¹

$$\frac{2}{m} \int d\underline{r} d\underline{q} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{q}} \right)_{\underline{q}} \left\{ (\underline{r}'_1 - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_{[0]}^{(1)'} \right) \bar{f}_{2[0]}^{(1)'} + (\underline{r}'_2 - \underline{r}_1) \cdot \left(\frac{\partial}{\partial \underline{r}_1} \bar{f}_{2[0]}^{(1)'} \right) \bar{f}_{[0]}^{(1)'} \right\} \quad (3.1 - 10)$$

$$= - \frac{\partial}{\partial \underline{r}_1} \cdot (n B \underline{v}_i f_{[0]}^{(1)}) + \frac{m n^2}{2 k T} \left\{ \frac{\partial \underline{u}}{\partial \underline{r}_1} - \left(\frac{k T}{2 m} \right) \left(\frac{\partial \underline{m T}}{\partial \underline{r}_1} \right) \frac{\partial}{\partial \underline{v}_i} \right\} : \underline{\underline{I}}$$

Here B is the second virial coefficient given by

$$B = - \frac{1}{2} \int [e^{-\frac{\phi^{(1,2)}}{k T}} - 1] d\underline{r} \quad (3.1 - 11)$$

and the tensor $\underline{\underline{I}}$ is defined by

$$\underline{\underline{I}} = \frac{2}{n^2 m} \int d\underline{r} d\underline{q} \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \right) \cdot \left(\frac{\partial}{\partial \underline{q}} \right)_{\underline{q}} \left\{ \underline{q}'_1 \cdot \bar{f}_{[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} e^{-\frac{\phi^{(1,2)}}{k T}} \right\} \quad (3.1 - 12)$$

The time derivatives of n , $\underline{u}$ and T which appear in J can be eliminated by the equations of change. Since $f_{[0]}^{(1)}$ is the equilibrium form $f_{[0]}^{(1)}$, it follows that the pressure tensor and energy flux vector which appear in the equations of change have their equilibrium forms. Thus, through terms of order n^2 in the density,

$$\underline{p} = nkT(1+nB)\underline{U} = \underline{p}\underline{U} \quad (3.1 - 13)$$

and

$$\underline{q} = 0 \quad (3.1 - 14)$$

Using these forms for the fluxes, Snider and Curtiss have shown that

$$\frac{\partial f_{i,0}^{(1)}}{\partial t} + \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i} f_{i,0}^{(1)} \quad (3.1 - 15)$$

$$= f_{i,0}^{(1)} \left[\begin{aligned} & \left\{ 2 \underline{w}_i \underline{w}_i : \left(\underline{\underline{\Psi}} - \frac{1}{3} \underline{\underline{U}} \underline{\underline{U}} \right) \right. \\ & \quad + \left. \left[\frac{1}{n c_v} \left(\frac{\partial \underline{p}}{\partial T} \right)_v - \frac{2}{3} \right] \left(\frac{5}{2} - w_i^2 \right) \underline{\underline{U}} \right\} : \left(\frac{\partial \underline{u}}{\partial \underline{x}_i} \right) \\ & \quad + \\ & \quad \left. - \left(\frac{5}{2} - w_i^2 \right) \underline{v}_i \cdot \frac{\partial \underline{z}_i T}{\partial \underline{x}_i} - \frac{1}{n k T} \underline{v}_i \cdot \frac{\partial}{\partial \underline{x}_i} (p - n k T) \right] \end{aligned} \right]$$

Here $\underline{w}_i = \left(\frac{m}{2 k T} \right)^{1/2} \underline{v}_i$ and c_v is the heat capacity. The fourth order tensors $\underline{\underline{\Psi}}$ and $\underline{\underline{U}}$ are discussed in the Introduction. From equations (3.1 - 10) and (3.1 - 15) we can write $\underline{J}$ (as given by equation 3.1 - 9) in the form

$$\underline{J} = f_{i,0}^{(1)} \left[\begin{aligned} & (1+nB) \left(w_i^2 - \frac{5}{2} \right) \underline{v}_i \cdot \frac{\partial \underline{z}_i T}{\partial \underline{x}_i} \\ & \quad + \\ & \quad 2(1+nB) \underline{w}_i \underline{w}_i : \left\{ \frac{\partial \underline{u}}{\partial \underline{x}_i} - \frac{1}{3} \left(\frac{\partial \underline{u}}{\partial \underline{x}_i} : \underline{\underline{U}} \right) \underline{\underline{U}} \right\} \\ & \quad + \\ & \quad \left(w_i^2 - \frac{5}{2} \right) \left\{ (1+nB) \left(\frac{2}{3} - \frac{k}{c_v} \right) - \frac{n k T}{c_v} \frac{dB}{dT} \right\} \frac{\partial \underline{u}}{\partial \underline{x}_i} \\ & \quad + \\ & \quad - \frac{m n^2}{2 k T} \left\{ \frac{\partial \underline{u}}{\partial \underline{x}_i} - \left(\frac{k T}{2 m} \right) \left(\frac{\partial \underline{z}_i T}{\partial \underline{x}_i} \right) \left(\frac{\partial \underline{v}_i}{\partial \underline{x}_i} \right) \right\} : \underline{\underline{I}} \end{aligned} \right] \quad (3.1 - 16)$$

Let us define the tensors $\underline{K}$, $\underline{L}$ and $\underline{M}$ by the relation

$$\underline{J} = -\underline{K} \cdot \frac{\partial \underline{Z}}{\partial \underline{\lambda}} - \underline{L} : \frac{\partial \underline{u}}{\partial \underline{\lambda}} - \underline{M} \frac{\partial \underline{u}}{\partial \underline{\lambda}} \quad (3.1 - 17)$$

and the condition that $\underline{L}$ is traceless. It then follows from equation (3.1 - 16) that

$$\underline{K} = f_{[0]}^{(1)} (1 + nB) \left(\frac{\underline{Z}}{2} - w_i^2 \right) \underline{V}_i - \frac{n^2}{4} \frac{\partial}{\partial \underline{V}_i} \underline{I} \quad (3.1 - 18)$$

$$\underline{L} = \left[-2(1 + nB) f_{[0]}^{(1)} \underline{w}_i \underline{w}_i + \frac{m n^2}{2 k T} \underline{I} \right] : \left(\underline{\Psi} - \frac{1}{3} \underline{U} \underline{U} \right) \quad (3.1 - 19)$$

and

$$\underline{M} = f_{[0]}^{(1)} \left(\frac{\underline{Z}}{2} - w_i^2 \right) \left\{ (1 + nB) \left(\frac{\underline{Z}}{3} - \frac{\underline{h}}{c v} \right) - \frac{n k T}{c v} \frac{d B}{d \underline{v}} \right\} + \frac{m n^2}{6 k T} \underline{I} : \underline{U} \quad (3.1 - 20)$$

In the following sections, the use of tensor properties results in considerable simplification of the integral equation to be solved.

Section 3.2 The Integral Equations for the Perturbation

Let us define a perturbation function ϕ by

$$\bar{f}_{[1]}^{(1)} = \bar{f}_{[0]}^{(1)} \phi \quad (3.2 - 1)$$

In terms of ϕ equation (3.1 - 8) is

$$\underline{J} = \frac{2}{m} \int d\underline{\lambda} \frac{d\underline{g}}{d\underline{\lambda}} \frac{\partial \phi^{(1,2)}}{\partial \underline{\lambda}} \left(\frac{\underline{g}}{d\underline{g}} \right) \left\{ \bar{y}_{[0]} \bar{f}_{[0]}^{(1)} \bar{f}_{[1]}^{(1)} (\phi'_1 + \phi'_2) \right\} \quad (3.2 - 2)$$

Let us also define the linear operator Δ which acts on any function $\xi_i = \xi(\underline{u})$ by the relation

$$\Delta(\xi_i) = \frac{2}{m} \int d\Delta \, d\bar{g} \left(\frac{\partial \phi}{\partial \Delta} \right)^{(1,2)} \cdot \left(\frac{\partial}{\partial \bar{g}} \right)_g \left\{ \bar{u}_{10\alpha} \bar{f}_{10\alpha}^{\mu\nu} \bar{f}_{20\alpha}^{\mu\nu} (\xi'_1 + \xi'_2) \right\} \quad (3.2 - 3)$$

Equation (3.2 - 2) can then be written

$$J = \Delta(\phi_i) \quad (3.2 - 4)$$

The inhomogeneity, J , given by equation (3.1 - 17) is a linear function of

$$\frac{\partial \mathcal{L}_T}{\partial \Delta_i}, \quad \frac{\partial}{\partial \Delta_i} \underline{u} \quad \text{and} \quad \frac{\partial}{\partial \Delta_i} \cdot \underline{u}$$

It follows then that ϕ must also be a linear function of these quantities. Thus we can write

$$\phi = -\underline{A} \cdot \frac{\partial \mathcal{L}_T}{\partial \Delta_i} - \underline{B} : \frac{\partial}{\partial \Delta_i} \underline{u} - \underline{C} \frac{\partial}{\partial \Delta_i} \cdot \underline{u} \quad (3.2 - 5)$$

where $\underline{B}$ is traceless. Equation (3.2 - 4) is equivalent to the set of equations

$$\underline{K} = \Delta(\underline{A}_i) \quad (3.2 - 6)$$

$$\underline{L} = \Delta(\underline{B}_i) \quad (3.2 - 7)$$

and

$$M = \Delta(\underline{C}_i) \quad (3.2 - 8)$$

We now show that the summational invariants introduced in equations (2.7 - 26), (2.7 - 27) and (2.7 - 28) are solutions to the homogeneous equation

$$\Delta(\xi_i) = 0 \quad (3.2 - 9)$$

Let us consider the equation

$$\Delta(\psi_i^{(1)}) = \frac{2}{m} \int d^3p \int d^3q \frac{\partial \phi^{(1,2)}}{\partial \lambda} \left(\frac{\partial}{\partial q} \right) \left\{ \bar{y}_{[0]} \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(2)'} (\psi_1^{(1)'} + \psi_2^{(2)'}) \right\} \quad (3.2 - 10)$$

The quantities $\phi^{(1,2)}$, $\bar{y}_{[0]}$ and $\bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(2)'} = \bar{f}_{[0]}^{(1)} \bar{f}_{[0]}^{(2)} e^{-\frac{\phi^{(1,2)}}{\hbar r}}$ are functions of only the scalar λ and so are unchanged by the transformation $\lambda \rightarrow -\lambda$. It follows from the conservation equations of a two particle system that the summational invariants obey the relation

$$\psi_1^{(1)'} + \psi_2^{(2)'} = \psi_1^{(1)} + \psi_2^{(2)} + \chi^{(1)} \quad (3.2 - 11)$$

where

$$\chi^{(1)} = 0 \quad (3.2 - 12)$$

$$\chi^{(2)} = 0 \quad (3.2 - 13)$$

and

$$\chi^{(3)} = \frac{2}{m} \phi^{(1,2)} \quad (3.2 - 14)$$

Hence the quantity $(\psi_1^{(i)})' + \psi_2^{(i)'})$ is also unchanged under the transformation $\underline{A} \rightarrow -\underline{A}$. The integrand in equation (3.2 - 10) therefore switches sign under the transformation $\underline{A} \rightarrow -\underline{A}$ because the gradient $\frac{\partial}{\partial \underline{A}}$ switches sign. Thus, if we integrate over the angles of $\underline{A}$ in equation (3.2 - 10), we arrive at the desired result:

$$\Delta(\psi_1^{(i)}) = 0 \quad (3.2 - 15)$$

The transposed operator Δ^+ can be defined by the relation

$$\int \xi_i \Delta(\rho_i) d\underline{v}_i = \int \rho_i \Delta^+(\xi_i) d\underline{v}_i \quad (3.2 - 16)$$

which holds for arbitrary $\xi_i = \xi(\underline{v}_i)$ and $\rho_i = \rho(\underline{v}_i)$

We now show that the summational invariants are also solutions to the transposed homogeneous equation

$$\Delta^+(\xi_i) = 0 \quad (3.2 - 17)$$

To do this we must establish that for arbitrary ρ_i

$$\int \rho_i \Delta^+(\psi_1^{(i)}) d\underline{v}_i = \int \psi_1^{(i)} \Delta(\rho_i) d\underline{v}_i = 0 \quad (3.2 - 18)$$

From equation (3.2 - 3) and the identity of equation (2.6 - 18)

we have

$$\begin{aligned} \int \rho_i \Delta^+(\psi_1^{(i)}) d\underline{v}_i &= \int d\underline{A} d\underline{g} d\underline{G} g \cdot \frac{\partial}{\partial \underline{A}} \left\{ \psi_1^{(i)} \bar{y}_{107} \bar{f}_{1107}^{(i)'} \bar{f}_{2107}^{(i)'} (\rho_1' + \rho_2') \right\} \\ &- \int d\underline{A} d\underline{g} d\underline{G} \psi_1^{(i)} g \cdot \frac{\partial}{\partial \underline{A}} \left\{ \bar{y}_{107} \bar{f}_{1107}^{(i)'} \bar{f}_{2107}^{(i)'} (\rho_1' + \rho_2') \right\} \end{aligned} \quad (3.2 - 19)$$

where $\underline{G} = \underline{v}_1 + \frac{1}{2} \underline{g}$ is the velocity of the center of mass. The first integral in equation (3.2 - 19) can be transformed to a surface integral on a sphere of sufficient radius such that $\bar{y}_{[0]} = 1$ on the surface. This integral is of a type which is shown to be zero in the theory of the ordinary Boltzmann equation²⁹. Equation (3.2 - 9) can then be written

$$\int \rho_i \Delta^+(\psi_i^{(i)}) d\underline{v}_i \quad (3.2 - 20)$$

$$= - \int d\underline{r} d\underline{g} d\underline{G} \psi_i^{(i)} \frac{\partial}{\partial \underline{r}_i} \left\{ \bar{y}_{[0]} \left[\bar{f}_{[0]}^{(i')} \bar{f}_{[0]}^{(i')} (\underline{r}_i' + \underline{r}_2') \right] \right\}$$

We can write equation (3.2 - 20) in the symmetric form

$$\int \rho_i \Delta^+(\psi_i^{(i)}) d\underline{v}_i \quad (3.2 - 21)$$

$$= - \frac{1}{2} \int d\underline{r} d\underline{g} d\underline{G} (\psi_i^{(i)} + \psi_2^{(i)}) \frac{\partial}{\partial \underline{r}_i} \left\{ \bar{y}_{[0]} \left[\bar{f}_{[0]}^{(i')} \bar{f}_{[0]}^{(i')} (\underline{r}_i' + \underline{r}_2') \right] \right\}$$

If we make the variable transformation $(\underline{r}, \underline{g}) \rightarrow (\underline{r}', \underline{g}')$ as discussed in Sec. 2.6, and write $\underline{r}'$ and $\underline{g}'$ in the particular coordinate systems given there, then we have

$$\int \rho_i \Delta^+(\psi_i^{(i)}) d\underline{v}_i \quad (3.2 - 22)$$

$$= - \frac{1}{2} \int d\underline{r} d\underline{z} d\underline{b} d\underline{g}' d\underline{G} b (\psi_i^{(i)} + \psi_2^{(i)}) \frac{\partial}{\partial \underline{r}} \left\{ \bar{y}_{[0]} \left[\bar{f}_{[0]}^{(i')} \bar{f}_{[0]}^{(i')} (\underline{r}_i' + \underline{r}_2') \right] \right\}$$

The integration over $\underline{z}$ is an integration over a particular trajectory determined by $\underline{g}'$ and $\underline{b}$. The quantities $(\psi_i^{(i)} + \psi_2^{(i)})$ and $\bar{y}_{[0]}$ are the only functions of $\underline{z}$ in the integrand. From equation (3.2 - 11), we see that the integrand is a function of only through the dependent variable $\underline{r}$. If we choose $\underline{z} = 0$

as the center of symmetry of the trajectory, then

$$\lambda(z) = \lambda(-z) \quad (3.2 - 23)$$

The integrand of the integral in equation (3.2 - 22) then switches sign under the transformation $z \rightarrow -z$ by virtue of the derivative $\frac{\partial}{\partial z}$. Hence, if we integrate over z we obtain the desired result:

$$\int_C \Delta^+(\psi,^{(1)}) d\underline{u}_i = 0 \quad (3.2 - 24)$$

or, since ϕ_i is an arbitrary function,

$$\Delta^+(\psi,^{(1)}) = 0 \quad (3.2 - 25)$$

Since from equation (3.2 - 24) we have

$$\int \psi,^{(1)} \Delta(\phi_i) d\underline{u}_i = 0 \quad (3.2 - 26)$$

it follows that if equation (3.2 - 4) is consistent, then

$$\int \psi,^{(1)} J d\underline{u}_i = 0 \quad (3.2 - 27)$$

From equation (3.1 - 17) we can write the equivalent statements:

$$\int \psi,^{(1)} \underline{K} d\underline{u}_i = 0 \quad (3.2 - 28)$$

$$\int \psi,^{(1)} \underline{L} d\underline{u}_i = 0 \quad (3.2 - 29)$$

and

$$\int \psi_{,i}^{(1)} M d\underline{v}_i = 0 \quad (3.2 - 30)$$

We note from equations (3.1 - 18), (3.1 - 19) and (3.1 - 20) that the tensors $\underline{K}$, $\underline{L}$ and M are vector functions of only $\underline{v}_i$.

If we then change variables from $\underline{v}_i$ to $\underline{V}_i$ in equations (3.2 - 28), (3.2 - 29) and (3.2 - 30) and integrate over the angles of $\underline{V}_i$, the resulting integrals must be isotropic. Since there are no isotropic odd order tensors and the only second order isotropic tensor $\underline{U}$ is not traceless, equations (3.2 - 28), (3.2 - 29) and (3.2 - 30) can be simplified to

$$\int \underline{v}_i \underline{K} d\underline{v}_i = 0 \quad (3.2 - 31)$$

$$\int M d\underline{v}_i = 0 \quad (3.2 - 32)$$

and

$$\int v_i^2 M d\underline{v}_i = 0 \quad (3.2 - 33)$$

These integral conditions have been verified by Snider and Curtiss. Equations (3.2 - 31) and (3.2 - 32) result from straightforward integration; however, the condition in equation (3.2 - 33) is much more difficult to prove. The problem involves the evaluation of the integral

$$\int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i$$

This integral which also arises later on in the treatment is evaluated in Appendix B. The integral equations we wish to solve are thus consistent.

Closely connected with the question of consistency of the integral equations is that of uniqueness of solution. We defer a discussion of this important question until the next section where it is answered in a natural manner in the course of the solution of the integral equations.

The integral equations (3.2 - 6), (3.2 - 7) and (3.2 - 8) can be simplified by considering their tensor properties. Let us consider a second order tensor $\underline{\underline{\gamma}}$ which is vectorally a function of only the vector $\underline{w}$. The tensor $\underline{\underline{\gamma}}$ must be invariant to a rotation about the axis of $\underline{w}$, and hence can depend only on the isotropic tensor $\underline{\underline{U}}$ and the dyad $\underline{w}\underline{w}$. If we require in addition that $\underline{\underline{\gamma}}$ be traceless, it must depend on the particular combination

$$\underline{w}\underline{w} - \frac{1}{3} w^2 \underline{\underline{U}} = \underline{w}\underline{w} : \left[\underline{\underline{U}} - \left(\frac{1}{3}\right) \underline{\underline{U}}\underline{\underline{U}} \right] \quad (3.2 - 34)$$

We can thus write

$$\underline{\underline{\gamma}} = \gamma(w) \left\{ \underline{w}\underline{w} : \left[\underline{\underline{U}} - \frac{1}{3} \underline{\underline{U}}\underline{\underline{U}} \right] \right\} \quad (3.2 - 35)$$

where $\gamma(w)$ is a function of the invariant scalar w . Similar arguments hold for a tensor of any order. The tensors in equations (3.2 - 6), (3.2 - 7) and (3.2 - 8) depend vectorally on only the vector $\underline{w}$, and thus we can deduce their tensor forms. This allows us to reduce the tensor integral equations to the scalar equations

$$K = \Delta'(A) \quad (3.2 - 36)$$

$$L = \Delta''(B,) \quad (3.2 - 37)$$

and

$$M = \Delta(C,) \quad (3.2 - 38)$$

The defining equations for $A,$, $B,$, K , and L and the operators Δ' and Δ'' are

$$\underline{A}, = A, \underline{w}, \quad (3.2 - 39)$$

$$\underline{\underline{B}}, = B, \underline{w}, \underline{w}, : \left[\underline{\underline{U}} - \left(\frac{1}{3}\right) \underline{\underline{U}} \underline{\underline{U}} \right] \quad (3.2 - 40)$$

$$\underline{K} = K \cdot \underline{w}, \quad (3.2 - 41)$$

$$L = \underline{\underline{L}} : \underline{w}, \underline{w}, \quad (3.2 - 42)$$

$$\Delta'(A,) = \underline{w}, \cdot \Delta(\underline{A},) \quad (3.2 - 43)$$

and

$$\Delta''(B,) = \underline{w}, \underline{w}, : \Delta(\underline{\underline{B}},) \quad (3.2 - 44)$$

The quantities $A,$, $B,$, $C,$, K , L and M are functions of the invariant scalar $w,$.

Section 3.3 Solution of the Integral Equations

In the preceding section we showed that the summational invariants are solutions to the homogeneous equation for the operator Δ . We can find the solutions to the homogeneous

equations that are functions of W_1 for the operators Δ , Δ' and Δ'' from a knowledge of the general solutions to the homogeneous equation for the operator Δ . We find that Δ has the homogeneous solutions 1 and W_1^2 , the operator Δ' has the homogeneous solution 1, and the operator Δ'' has no homogeneous solutions. The transposed operators also have these homogeneous solutions. As we shall see, there is a one to one correspondence between the solutions to the homogeneous equations and the arbitrary constants in the solutions of the integral equations. There are just enough arbitrary parameters in the solutions of the integral equations to allow us to impose the integral conditions of equations (2.7 - 21), (2.7 - 22) and (2.7 - 23).

Let us first consider equation (3.2 - 36). In order to solve this equation we must invert the operator Δ' . However, Δ' can not be inverted in a straightforward manner because it is singular. That is, the homogeneous equation has a solution. This problem can be avoided by writing equation (3.2 - 36) in a matrix representation. Let us expand $A(W)$ in a complete set of Sonine polynomials of order $3/2$. The m th polynomial of the set of Sonine polynomials of order n is represented by $S_n^{(m)}$ and is defined by

$$S_n^{(m)}(x) = \sum_{p=0}^m (-x)^p \frac{(m+n)!}{(n+p)!(m-p)!p!} \quad (3.3 - 1)$$

These polynomials have the orthogonality property

$$\int_0^\infty e^{-W_1^2} W_1^{2n+1} S_n^{(m)}(W_1^2) S_n^{(m')}(W_1^2) dW_1 = \frac{\Gamma(n+m+1)}{2 \Gamma(m+1)} \delta_{mm'} \quad (3.3 - 2)$$

where Γ is the gamma function. In terms of the expansion coefficients a_i , we have

$$A(w) = \sum_{i=0}^{\infty} a_i S_{\frac{j}{2}}^{(i)}(w^2) \quad (3.3 - 3)$$

Since Δ' is a linear operator, equation (3.2 - 36) can be written

$$K = \sum_{i=0}^{\infty} a_i \Delta' \left(S_{\frac{j}{2}}^{(i)}(w, z) \right) \quad (3.3 - 4)$$

If we now expand K in this representation, we have for all $j'=0$ to ∞

$$(K)_{j'} = \int S_{\frac{j}{2}}^{(j)}(w, z) K d\underline{w}, \quad (3.3 - 5)$$

$$= \sum_{i=0}^{\infty} a_i \int S_{\frac{j}{2}}^{(j)}(w, z) \Delta' \left(S_{\frac{j}{2}}^{(i)}(w, z) \right) d\underline{w} = \sum_{i=0}^{\infty} \Delta'_{ji} a_i$$

where

$$\Delta'_{ji} = \int S_{\frac{j}{2}}^{(j)}(w, z) \Delta' \left(S_{\frac{j}{2}}^{(i)}(w, z) \right) d\underline{w}, \quad (3.3 - 6)$$

Thus equation (3.2 - 36) is reduced to a matrix equation.

Since $S_{\frac{j}{2}}^{(0)}(w, z) = 1$ is a solution of the homogeneous equation and also the transposed homogeneous equation, we have for all $j'=0$ to ∞

$$(K)_0 = \Delta'_{j0} = \Delta'_{0j} = 0 \quad (3.3 - 7)$$

Equation (3.3 - 5) for $(K)_0$ is thus an identity. Further the constant a_0 does not help to determine any of the $(K)_{j'}$. Hence,

we can ignore the first row and the first column of the matrix $\Delta'_{j,i}$. The new matrix $\Delta'_{j,i}$ $j=1$ to ∞ $i=1$ to ∞ has no zero eigenvalues and thus is non-singular and can be inverted.

Equation (3.3 - 5), when inverted, can be written for $i=1$ to ∞

$$a_i = \sum_{j=1}^{\infty} (\Delta')^{-1}_{i,j} \cdot (K)_j \quad (3.3 - 8)$$

where $(\Delta')^{-1}_{i,j}$ is the i,j element of the inverted matrix.

Thus A_i is given by

$$A_i = A(\omega_i) = \sum_{j=1}^{\infty} (\Delta')^{-1}_{i,j} \cdot (K)_j \cdot \int_{\frac{1}{2}}^{\infty} \omega_i^2 \omega_j^2 + a_0 \cdot \int_{\frac{1}{2}}^{\infty} \omega_i^2 \quad (3.3 - 9)$$

where a_0 is an arbitrary constant. We fix a_0 by the relation

$$\int f_{i,j}'' \psi_i \psi_j = 0 \quad (3.3 - 10)$$

discussed in Sec. 2.7. Because of the orthogonality condition of equation (3.3 - 2) the integral relation of equation (3.3 - 10) requires

$$a_0 = 0 \quad (3.3 - 11)$$

We can solve equations (3.2 - 37) and (3.2 - 38) by the same technique. To solve equation (3.2 - 37), we use as expansion polynomials the Sonine polynomials of order 5/2. The operator has no solutions to its homogeneous equation. Hence, we can immediately invert its matrix representation and obtain the expression for B_i :

$$B, = B(w_1) = \sum_{i,j=0}^{\infty} (\Delta'')^{-1}_{ij} (L)_j \cdot S_{\frac{z}{2}}^{(i)}(w_1^2) \quad (3.3 - 12)$$

To solve equation (3.2 - 38), we choose as expansion polynomials the Sonine polynomials of order 1/2. The operator Δ has two solutions to its homogeneous equation. These two solutions 1 and w_1^2 can be written as a linear combination of the first two Sonine polynomials: $S_{\frac{1}{2}}^{(0)}(w_1^2) = 1$ and $S_{\frac{1}{2}}^{(1)}(w_1^2) = (\frac{z}{2} - w_1^2)$. We obtain a non-singular matrix from the matrix representation of Δ'' by ignoring the first two rows and columns of the matrix. We then obtain the expression for $C,$

$$C, = C(w_1) = \sum_{i,j=2}^{\infty} (\Delta'')^{-1}_{ij} (M)_j \cdot S_{\frac{z}{2}}^{(i)}(w_1^2) + c_0 \int_{\frac{z}{2}}^{(0)}(w_1^2) + c_1 \int_{\frac{z}{2}}^{(1)}(w_1^2) \quad (3.3 - 13)$$

where C_0 and $C,$ are arbitrary constants. These constants are uniquely determined by the relations

$$\int f_{i,r,j}^{(n)} d\underline{u}_1 = 0 \quad (3.3 - 14)$$

and

$$\int f_{i,r,j}^{(n)} v_1^2 d\underline{u}_1 = 0 \quad (3.3 - 15)$$

which were discussed in Sec. 2.7. Because of the orthogonality condition of equation (3.2 - 2) we have

$$C_0 = 0$$

(3.3 - 16)

and

$$C_1 = 0$$

(3.3 - 17)

Section 3.4 Approximations to the Solutions

Equations (3.3 - 9), (3.3 - 13) and (3.3 - 15) are solutions to equations (3.2 - 36), (3.2 - 37) and (3.2 - 38). However, the inversion of the operators Δ , Δ' and Δ'' presents some difficulty. We, of course, mean by these operators the non-singular matrices formed from the singular matrices by eliminating the appropriate rows and columns as discussed in the last section. This difficulty can be met by an approximate inversion technique which has been discussed by Chapman and Cowling³⁰.

Let us consider the operator Δ' and define a matrix $\Delta'^{(m)}$ as the first m rows and columns of the matrix representation of Δ' . This finite matrix may be inverted by the method of minors. In analogy with equation (3.3 - 8), we can now write an approximation to a_i' which we will call $a_i^{(m)}$. For $i \leq m$ we have

$$a_i^{(m)} = \sum_{j=1}^m (\Delta'^{(m)})_{ij}^{-1} (K)_j = \frac{1 \Delta'_{ij}^{(m)}}{1 \Delta'^{(m)}} \quad (3.4 - 1)$$

and for $i > m$ we have

$$a_i^{(m)} = 0 \quad (3.4 - 2)$$

In Equation (3.4 - 1), $|\Delta^{(m)}|$ is the determinant of $\Delta^{(m)}$ and $|\Delta_{i'}^{(m)}|$ is the determinant of the matrix formed from $\Delta^{(m)}$ by replacing the elements $\Delta_{j'i'}^{(m)}$ by $(K)_{j'}$ for all $j' = 1$ to m . The determinant form in equation (3.4 - 1) results from the inversion of $\Delta^{(m)}$ by minors and is a standard form of solution of a system of linear algebraic equations. We assume that

$$\lim_{m \rightarrow \infty} a_{i'}^{(m)} = a_{i'} \quad (3.4 - 3)$$

In the simplest approximation, where $m = 1$, we have

$$a_{i'}^{(1)} = \frac{(K)_{i'}}{\Delta_{ii}'} \quad (3.4 - 4)$$

and for all $i' \neq 1$

$$a_{i'}^{(1)} = 0 \quad (3.4 - 5)$$

In an analogous manner, we find that the first approximation to b_0 (which in accord with the above discussion we denote by $b_0^{(1)}$) is given by

$$b_0^{(1)} = \frac{(L)_0}{\Delta_{00}''} \quad (3.4 - 6)$$

and for $i' \neq 0$:

$$b_{i'}^{(1)} = 0 \quad (3.4 - 7)$$

Similarly, the first approximation to c_2 is

$$C_2^{(1)} = \frac{(M)_2}{\Delta_{22}} \quad (3.4 - 8)$$

and for $i \neq 2$:

$$C_i^{(1)} = 0 \quad (3.4 - 9)$$

Section 3.5 Components of the Non-homogeneous Terms

We now evaluate the integrals $(K)_i$, $(L)_0$ and $(M)_2$. Let us consider $(K)_i$, which, according to equations (3.2 - 41) and (3.3 - 5), is given by

$$(K)_i = \int K \int_{\frac{5}{2}}^{(1)} (w_i^2) d\underline{w}_i \quad (3.5 - 1)$$

$$= \int K \left(\frac{5}{2} - w_i^2 \right) d\underline{w}_i = \int \underline{K} \cdot \underline{w}_i \left(\frac{5}{2} - w_i^2 \right) d\underline{w}_i$$

From the orthogonality condition given in equation (3.2 - 31) we have

$$(K)_i = - \int \underline{K} \cdot \underline{w}_i w_i^2 d\underline{w}_i \quad (3.5 - 2)$$

If we substitute the expression for $\underline{K}$ given in equation (3.1 - 18) into equation (3.5 - 2), we find

$$(K)_i = -(1+nB) \int_{I_0}^{(1)} \left(\frac{5}{2} w_i^2 - w_i^4 \right) \underline{v}_i \cdot \underline{w}_i d\underline{w}_i \quad (3.5 - 3)$$

$$+ \frac{n^2}{4} \int \left(\frac{\partial}{\partial \underline{v}_i} \cdot \underline{I} \right) \cdot \underline{w}_i w_i^2 d\underline{w}_i$$

The first integral in this expression can be evaluated immediately and the second can be rewritten by manipulating the divergence in the integrand. Thus we have

$$(K)_1 = \frac{15}{4} n \left(\frac{m}{2kT} \right) (1 + nB) \quad (3.5 - 4)$$

$$+ \frac{n^2}{4} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left\{ \int \frac{\partial}{\partial \underline{w}_i} \cdot (\underline{I} \cdot \underline{w}_i w_i^2) d\underline{w}_i - \int (\underline{U} : \underline{I}) w_i^2 d\underline{w}_i - 2 \int \underline{I} : \underline{w}_i \underline{w}_i d\underline{w}_i \right\}$$

The integral of the divergence can be converted to a vanishing surface integral yielding

$$(K)_1 = \frac{15}{4} n \left(\frac{m}{2kT} \right) (1 + nB) \quad (3.5 - 5)$$

$$- \frac{n^2}{4} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left\{ \int (\underline{U} : \underline{I}) w_i^2 d\underline{w}_i + 2 \int \underline{I} : \underline{w}_i \underline{w}_i d\underline{w}_i \right\}$$

We can evaluate $(L)_0$ and $(M)_2$ in a similar manner to obtain

$$(L)_0 = -5n(1 + nB) \left(\frac{m}{2kT} \right)^{\frac{3}{2}} \quad (3.5 - 6)$$

$$+ \left(\frac{m n^2}{2kT} \right) \left\{ \int \underline{I} : \underline{w}_i \underline{w}_i d\underline{w}_i - \frac{1}{3} \int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i \right\}$$

and

$$(M)_2 = \left(\frac{m n^2}{12kT} \right) \left\{ -5 \int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i + \int (\underline{I} : \underline{U}) w_i^4 d\underline{w}_i \right\} \quad (3.5 - 7)$$

In Appendix B, the integrals $\int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i$ and $\int (\underline{I} : \underline{U}) w_i^4 d\underline{w}_i$ are evaluated in terms of the second virial coefficient, B , and its temperature derivatives. Thus,

the problem of determining (K) , and $(L)_0$ is reduced to the evaluation of the integral

$$\int \underline{I} : \underline{w}_1 \underline{w}_1 d\underline{w}_1$$

This integral must be evaluated numerically because the integrand depends on the detailed dynamics of binary collisions. The numerical problems involved in this integration will be considered in detail in Chapter V.

Section 3.6 Evaluation of the Matrix Elements

We now evaluate the matrix elements Δ'_{11} , Δ''_{00} and Δ_{22} . Let us consider Δ'_{11} , which is defined in equation (3.3 - 6) by

$$\Delta'_{11} = \int S_{\frac{1}{2}}''(w_1^2) \Delta'(S_{\frac{1}{2}}''(w_1^2)) d\underline{w}_1 \quad (3.6 - 1)$$

From equation (3.2 - 43) we have

$$\Delta'_{11} = \int S_{\frac{1}{2}}''(w_1^2) \underline{w}_1 \cdot \Delta(S_{\frac{1}{2}}''(w_1^2) \underline{w}_1) d\underline{w}_1 \quad (3.6 - 2)$$

and from the definition of Δ given in equation (3.2 - 3) we have

$$\Delta'_{11} = \frac{2}{m} \int d\underline{w}_1 d\underline{g} d\underline{h} S_{\frac{1}{2}}''(w_1^2) \underline{w}_1 \cdot \left(\frac{\partial \phi''(z)}{\partial \underline{h}} \right) \cdot \left(\frac{\partial \phi}{\partial \underline{g}} \right) \quad (3.6 - 3)$$

$$\left\{ \bar{y}_{[0]} \bar{f}_{[0]}' \bar{f}_{[2]}' \left[S_{\frac{1}{2}}''(w_1^2) \underline{w}_1' \cdot \underline{w}_1 + S_{\frac{1}{2}}''(w_2^2) \underline{w}_2' \cdot \underline{w}_1 \right] \right\}$$

We can rewrite this equation by making use of the identity of equation (2.6 - 18). Thus

$$\Delta_{II}' = \int d\underline{w}_1 d\underline{g} d\underline{h} \underline{g} \cdot \frac{\partial}{\partial \underline{h}} \left\{ S_{\frac{3}{2}}^{(1)}(w_1^2) \bar{y}_{[0]} \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(1)'} \left[\begin{array}{c} S_{\frac{3}{2}}^{(1)}(w_1'^2) \underline{w}_1' \cdot \underline{w}_1 \\ + \\ S_{\frac{3}{2}}^{(1)}(w_2'^2) \underline{w}_2' \cdot \underline{w}_1 \end{array} \right] \right.$$

(3.6 - 4)

$$\left. - \int d\underline{w}_1 d\underline{g} d\underline{h} \underline{g} \cdot \left(\frac{\partial}{\partial \underline{h}}, \bar{y}_{[0]} \right)_{\underline{g}} \left\{ S_{\frac{3}{2}}^{(1)}(w_1^2) \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(1)'} \left[\begin{array}{c} S_{\frac{3}{2}}^{(1)}(w_1'^2) \underline{w}_1' \cdot \underline{w}_1 \\ + \\ S_{\frac{3}{2}}^{(1)}(w_2'^2) \underline{w}_2' \cdot \underline{w}_1 \end{array} \right] \right\} \right.$$

The first integral of this equation can be converted to a surface integral on a sphere of sufficient radius that $\bar{y}_{[0]} = 1$ on the surface. This surface integral can be written in terms of the "square brackets" discussed by Chapman and Cowling³¹. The square brackets have been evaluated³² and from these results we find that

$$\Delta_{II}' = -8\pi^2 \sigma^2 \left(\frac{M}{2kT} \right)^{\frac{3}{2}} \left(\frac{\pi kT}{m} \right)^{\frac{1}{2}} \Omega^{(2,2)*}$$

(3.6 - 5)

$$- \int d\underline{w}_1 d\underline{g} d\underline{h} \underline{g} \cdot \left(\frac{\partial}{\partial \underline{h}}, \bar{y}_{[0]} \right)_{\underline{g}} \left\{ S_{\frac{3}{2}}^{(1)}(w_1^2) \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(1)'} \left[\begin{array}{c} S_{\frac{3}{2}}^{(1)}(w_1'^2) \underline{w}_1' \cdot \underline{w}_1 \\ + \\ S_{\frac{3}{2}}^{(1)}(w_2'^2) \underline{w}_2' \cdot \underline{w}_1 \end{array} \right] \right\}$$

Here σ is an arbitrary constant with the dimensions of length.

It is conveniently chosen as a parameter of the intermolecular potential and is introduced to make $\Omega^{(2,2)*}$ dimensionless. The reduced omega integral, $\Omega^{(2,2)*}$, is defined by

$$\Omega^{(2,2)*} = \frac{\pi}{\sigma^2 (5+1)! \left[1 - \frac{1}{2} \left(\frac{1+(-1)^2}{1+1} \right) \right]} \int_0^\infty \int_0^\pi e^{-\gamma^2} \gamma^{(2+2)} (1-\cos^2 \chi) d\chi d\gamma$$

(3.6 - 6)

where $\underline{g} = \left(\frac{m}{2kT}\right)^{\frac{1}{2}} \underline{g}$ and where b and χ are respectively the impact parameter and the angle of deflection. The quantities b and χ are discussed in Sec. 2.6. The integral $\Omega^{(2,2)*}$ is a tabulated function of the temperature.

By the identity of equation (2.6 - 18) we have

$$\underline{g}' \cdot \left(\frac{\partial}{\partial \underline{g}}, \bar{\underline{y}}_{[0]}\right)_{\underline{g}} = \underline{g} \cdot \left(\frac{\partial}{\partial \underline{g}}, \bar{\underline{y}}_{[0]}\right) \quad (3.6 - 7)$$

Hence we can write equation (3.6 - 5) in the form:

$$\Delta'_{11} = -8 n^2 \sigma^2 \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left(\frac{kT}{m}\right)^{\frac{1}{2}} \Omega^{(2,2)*} \quad (3.6 - 8)$$

$$- \int d\underline{w}_1 d\underline{g} d\underline{g}' \underline{g} \cdot \left(\frac{\partial}{\partial \underline{g}}, \bar{\underline{y}}_{[0]}\right) \left\{ S_{\frac{1}{2}}^{(1)}(\underline{w}_1^2) \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(1)'} \left[S_{\frac{1}{2}}^{(1)}(\underline{w}_1'^2) \underline{w}_1' \cdot \underline{w}_1 + S_{\frac{1}{2}}^{(1)}(\underline{w}_2'^2) \underline{w}_2' \cdot \underline{w}_1 \right] \right\}$$

Let us make the variable transformation $\underline{g} \rightarrow \underline{w}_2$. The Jacobian of this transformation is such that

$$d\underline{g} = \left(\frac{2kT}{m}\right)^{\frac{3}{2}} d\underline{w}_2 \quad (3.6 - 9)$$

If we then write the integral in equation (3.6 - 8) in a form symmetric in particles 1 and 2, we have

$$\Delta'_{11} = -8 n^2 \sigma^2 \left(\frac{m}{2kT}\right)^{\frac{3}{2}} \left(\frac{kT}{m}\right)^{\frac{1}{2}} \Omega^{(2,2)*} \quad (3.6 - 10)$$

$$- \frac{1}{2} \left(\frac{2kT}{m}\right)^{\frac{3}{2}} \int d\underline{w}_1 d\underline{w}_2 d\underline{g} \underline{g} \cdot \left(\frac{\partial}{\partial \underline{g}}, \bar{\underline{y}}_{[0]}\right) \bar{f}_{[0]}^{(1)'} \bar{f}_{[0]}^{(1)'} \left[\begin{array}{c} S_{\frac{1}{2}}^{(1)}(\underline{w}_1^2) \underline{w}_1 \\ + \\ S_{\frac{1}{2}}^{(1)}(\underline{w}_2^2) \underline{w}_2 \end{array} \right] \cdot \left[\begin{array}{c} S_{\frac{1}{2}}^{(1)}(\underline{w}_1'^2) \underline{w}_1' \\ + \\ S_{\frac{1}{2}}^{(1)}(\underline{w}_2'^2) \underline{w}_2' \end{array} \right]$$

Let us define the vectors $\underline{\rho}$ and $\underline{\gamma}$ by the relations

$$\underline{\rho} = \frac{1}{\sqrt{2}} (\underline{w}_1 + \underline{w}_2) \quad (3.6 - 11)$$

and

$$\underline{\gamma} = \frac{1}{\sqrt{2}} (\underline{w}_2 - \underline{w}_1) \quad (3.6 - 12)$$

Then

$$\begin{aligned} & \int \frac{''}{2} (w_1^2) \underline{w}_1 + \int \frac{''}{2} (w_2^2) \underline{w}_2 \\ &= \left[\left(\frac{\epsilon}{2} \underline{w}_1 - w_1^2 \underline{w}_1 \right) + \left(\frac{\epsilon}{2} \underline{w}_2 - w_2^2 \underline{w}_2 \right) \right] \quad (3.6 - 13) \\ &= \left[\frac{1}{\sqrt{2}} (5 - \rho^2 - \gamma^2) \underline{\rho} - \sqrt{2} (\underline{\gamma} \cdot \underline{\rho}) \underline{\gamma} \right] \end{aligned}$$

In terms of $\underline{\gamma}$ and $\underline{\rho}$ the product $\bar{f}_{1[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'}$ is given by

$$\bar{f}_{1[0]}^{(1)'} \bar{f}_{2[0]}^{(1)'} = n^2 \left(\frac{m}{2\pi\hbar T} \right)^3 e^{-\frac{\phi^{(1,2)}}{\hbar T}} e^{-\frac{\gamma^2 - \rho^2}{c}} \quad (3.6 - 14)$$

The Jacobian of the transformation $(\underline{w}_1, \underline{w}_2) \rightarrow (\underline{\gamma}, \underline{\rho})$ is unity.

Hence, if we substitute equations (3.6 - 13) and (3.6 - 14) into equation (3.6 - 10) we find

$$\Delta'_{11} = -8\pi^2 \sigma^2 \left(\frac{m}{2kT}\right)^{3/2} \left(\frac{4kT}{m}\right)^{1/2} \Omega^{(2,2)*} \quad (3.6 - 15)$$

$$-\frac{\pi^2}{2} \left(\frac{m}{2kT}\right)^{3/2} \int d\underline{x} d\underline{y} d\underline{r} \left(\underline{g} \cdot \frac{\underline{x}}{\partial \underline{x}} \bar{y}_{(0)}\right) e^{-\frac{g^2}{2kT} - \underline{x}^2 - \underline{r}^2} \chi$$

$$\left[\frac{1}{\sqrt{2}} (5 - r^2 - x^2) \underline{r} - \sqrt{2} (\underline{x} \cdot \underline{r}) \underline{x} \right] \cdot \left[\frac{1}{\sqrt{2}} (5 - r'^2 - x'^2) \underline{r}' - \sqrt{2} (\underline{x}' \cdot \underline{r}') \underline{x}' \right]$$

We can integrate over the angles of $\underline{r}$ making use of the fact that

$$\int \hat{r} \hat{r} d\hat{r} = \frac{4\pi}{3} \underline{0} \quad (3.6 - 16)$$

where $\hat{r}$ is a unit vector in the direction of $\underline{r}$. Thus we have

$$\Delta'_{11} = -8\pi^2 \sigma^2 \left(\frac{m}{2kT}\right)^{3/2} \left(\frac{4kT}{m}\right)^{1/2} \Omega^{(2,2)*} \quad (3.6 - 17)$$

$$-\frac{\pi^2}{2} \left(\frac{m}{2kT}\right)^{3/2} \int d\underline{x} d\underline{y} d\underline{r} r' \left(\underline{g} \cdot \frac{\underline{x}}{\partial \underline{x}} \bar{y}_{(0)}\right) e^{-\frac{g^2}{2kT} - \underline{x}^2 - \underline{r}^2} \chi$$

$$\left[\frac{1}{2} (5 - r^2 - x^2) (5 - r'^2 - x'^2) r^2 - \frac{1}{3} (5 - r^2 - x'^2) x^2 - \frac{1}{3} (5 - r^2 - x^2) x'^2 + \frac{2}{3} (\underline{x} \cdot \underline{x}')^2 \right]$$

If we write

$$\underline{g} \cdot \frac{\underline{x}}{\partial \underline{x}} = \left(\frac{4kT}{m}\right)^{1/2} \underline{x} \cdot \frac{\underline{x}}{\partial \underline{x}} \quad (3.6 - 18)$$

and make use of the fact that

$$\int \hat{\gamma} \cdot \hat{\gamma} = 0 \quad (3.6 - 19)$$

where $\hat{\gamma}$ is a unit vector, then our expression for $\Delta'_{||}$ can be simplified to

$$\Delta'_{||} = -8 n^2 \sigma^2 \left(\frac{m}{2 k T} \right)^{\frac{3}{2}} \left(\frac{\pi k T}{m} \right)^{\frac{1}{2}} \Omega^{(2,2)*} \quad (3.6 - 20)$$

$$- \frac{4 n^2}{3 \sqrt{2} \pi^2} \left(\frac{m}{k T} \right) \int d\underline{R} \, d\underline{\gamma} \, d\underline{r} \, d\underline{r}' \left(\underline{\gamma} \cdot \frac{\partial}{\partial \underline{R}} \bar{\psi}_{[0]} \right) e^{-\frac{\underline{R}^2}{k T}} e^{-\frac{\underline{r}^2}{k T}} e^{-\frac{\underline{r}'^2}{k T}} (\underline{\gamma} \cdot \underline{\gamma}')^2$$

The integral over $\underline{r}$ can be carried out to yield

$$\Delta'_{||} = -8 n^2 \sigma^2 \left(\frac{m}{2 k T} \right)^{\frac{3}{2}} \left(\frac{\pi k T}{m} \right)^{\frac{1}{2}} \Omega^{(2,2)*} \quad (3.6 - 21)$$

$$- \frac{n^3}{(2 \pi^3)^{\frac{1}{2}}} \left(\frac{m \sigma^2}{2 k T} \right) R$$

where

$$R = \frac{1}{n \sigma^2} \int d\underline{R} \, d\underline{\gamma} \left(\underline{\gamma} \cdot \frac{\partial}{\partial \underline{R}} \bar{\psi}_{[0]} \right) e^{-\frac{\underline{R}^2}{k T}} e^{-\frac{\underline{r}^2}{k T}} (\underline{\gamma} \cdot \underline{\gamma}')^2 \quad (3.6 - 22)$$

The integral R must be calculated numerically. We discuss this calculation in detail in Chapter V.

In a manner analogous to the above procedure we find that

$$\Delta''_{\circ\circ} = \Delta'_{||} \quad (3.6 - 23)$$

and

$$\Delta_{zz} = \frac{1}{2} \Delta'_{||} \quad (3.6 - 24)$$

The evaluation of the matrix elements Δ'_{11} , Δ''_{00} and Δ_{22} completes the determination of the coefficients a''_1 , b''_0 and c''_2 .

Section 3.7 The Density Expansion of the Perturbation of the Distribution Function

In Sec. 3.1 we restricted our attention to the constant and linear terms in the density expansion of f''_{11} and simplified our equation for f''_{11} accordingly. Equivalently, we are justified in retaining only those terms of a''_1 , b''_0 and c''_2 which are of order $\frac{1}{n}$ or constant in the density. We note that $\mathcal{R}$ (as defined in equation (3.6 - 22)) is density independent, if only the constant and linear terms of $\bar{y}_{10j}$ are used in its evaluation. Similarly, we note that $\mathcal{I}$ and $\Omega^{(2,2)*}$ (defined respectively by equations (3.1 - 12) and (3.6 - 6)) are also density independent. Then from our formulae for $(K)_1$, $(L)_0$ and $(M)_2$ and the matrix elements Δ'_{11} , Δ''_{00} and Δ_{22} we can cast equations (3.4 - 4), (3.4 - 6) and (3.4 - 8) which determine a''_1 , b''_0 and c''_2 in the general form:

$$x = \frac{\alpha n + \beta n^2}{\delta n^2 + \epsilon n^3} \quad (3.7 - 1)$$

(For example we can write $x = a''_1$, $\alpha n + \beta n^2 = (K)_1$, and $(\delta n^2 + \epsilon n^3) = \Delta'_{11}$. If we expand x in the density, we find

$$x = \frac{\alpha}{\delta} \left(\frac{1}{n} \right) + \frac{1}{\delta} \left(\beta - \frac{\alpha \epsilon}{\delta} \right) \quad (3.7 - 2)$$

through the constant term.

The present treatment differs from that of Snider and Curtiss only in the terms in the matrix elements involving the integral $\mathcal{R}$. We can reduce the present results to those of Snider and Curtiss by setting these terms, represented by ϵ in equations (3.7 - 1) and (3.7 - 2), to zero. Thus, if we represent the results of Snider and Curtiss by $(\chi)_{s.c.}$, equation (3.7 - 2) can be written

$$\chi = (\chi)_{s.c.} - \frac{\alpha \epsilon}{\delta^2} \quad (3.7 - 3)$$

In particular we have

$$a_i^{(1)} = (a_i^{(1)})_{s.c.} + \frac{15}{128} \left(\frac{\mathcal{R}}{(2\pi^5)^{\frac{1}{2}} [\sigma \Omega^{(2,2)*}]^2} \right) \quad (3.7 - 4)$$

$$b_0^{(1)} = (b_0^{(1)})_{s.c.} - \left(\frac{5}{64\pi^4} \right) \left(\frac{m}{kT} \right)^{\frac{1}{2}} \frac{\mathcal{R}}{[\sigma \Omega^{(2,2)*}]^2} \quad (3.7 - 5)$$

and

$$c_z^{(1)} = (c_z^{(1)})_{s.c.} \quad (3.7 - 6)$$

There is no correction in equation (3.7 - 6); since $\alpha = 0$ in $(M)_2$. For the same reason, $c_z^{(1)}$ has no $\frac{1}{n}$ term.

CHAPTER IV

TRANSPORT COEFFICIENTS

In the last chapter we solved an approximate $f^{(1)}$ equation. We now derive expressions for the transport coefficients based on this solution.

Section 4.1 Flux Vectors

The pressure tensor and energy flux vector represent fluxes of momentum and energy respectively. They arise from the transport of these quantities within the fluid in two distinct ways. The kinetic contribution to the transport is due to the movement of the individual molecules and the accompanying transfer of momentum and energy. Since the kinetic contributions to the fluxes result from a uni-molecular process, they can be expressed in terms of the distribution function $f^{(1)}$. The collisional contributions, on the other hand, arise from the transfer of momentum and energy from one molecular center to another by interaction through the intermolecular potential. Since this is a bi-molecular transfer process, the collisional contributions to the fluxes are given in terms of $f^{(2)}$.

Irving and Kirkwood³³ have developed general expressions for the kinetic and collisional contributions to the fluxes. From their expressions, Snider and Curtiss¹¹ have written the fluxes to first order in a perturbation expansion. The kinetic portion of the pressure tensor, $\underline{p}^k$, which we write $\underline{p}^k$, is

$$\underline{p}^k = m \int f^{(1)} \underline{v}_1 \underline{v}_1 d\underline{v}_1 \quad (4.1 - 1)$$

and the collisional portion, $\mathbb{P}^c$, is

$$\mathbb{P}^c = -\frac{1}{2} \int \frac{1}{k} \frac{\partial \phi^{(1,2)}}{\partial k} \mathbb{A} \mathbb{A} \left[f^{(2)} - \frac{1}{2} \mathbb{A} \cdot \frac{\partial f^{(2)}}{\partial \mathbb{A}_1} \right] d\mathbb{A} d\mathbb{A}_1 d\mathbb{A}_2 \quad (4.1 - 2)$$

The total pressure tensor is

$$\mathbb{P} = \mathbb{P}^K + \mathbb{P}^c \quad (4.1 - 3)$$

Similarly, for the energy flux vector, $\mathbb{Q}$, we have

$$\mathbb{Q}^K = \frac{1}{2} m \int f_1^{(1)} V_1^2 \underline{V}_1 d\underline{V}_1 \quad (4.1 - 4)$$

$$\mathbb{Q}^c = -\frac{1}{2} \int \frac{1}{k} \frac{\partial \phi^{(1,2)}}{\partial k} \mathbb{A} \mathbb{A} \left[f^{(2)} - \frac{1}{2} \mathbb{A} \cdot \frac{\partial f^{(2)}}{\partial \mathbb{A}_1} \right] - \phi f \frac{\underline{V}}{x} \} \cdot \underline{Q} d\mathbb{A} d\mathbb{A}_1 d\mathbb{A}_2 \quad (4.1 - 5)$$

and

$$\mathbb{Q} = \mathbb{Q}^K + \mathbb{Q}^c \quad (4.1 - 6)$$

Through first order in the perturbation expansion, $f_1^{(1)}$ is given by

$$f_1^{(1)} = f_{1[0]}^{(1)} + f_{1[0]}^{(1)} \phi_1 \quad (4.1 - 7)$$

Similarly $f^{(2)}$ and $\left[f^{(2)} - \frac{1}{2} \mathbb{A} \cdot \frac{\partial f^{(2)}}{\partial \mathbb{A}_1} \right]$ are given by

$$f^{(2)} = \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} \left[1 + \bar{y}_{[0]} (\phi_1' + \phi_2') \right] \quad (4.1 - 8)$$

$$- \frac{\partial}{\partial \mathbb{A}_1} \cdot (a B \underline{V}_1 f_{1[0]}^{(1)}) + \frac{m n^2}{2 k T} \left\{ \frac{\partial \mu}{\partial \mathbb{A}_1} - \left(\frac{k T}{2 m} \right) \left(\frac{\partial^2 n T}{\partial \mathbb{A}_1^2} \right) \frac{\partial}{\partial \underline{V}_1} \right\} \cdot \underline{I}$$

and

$$f^{(2)} - \frac{1}{2} n \cdot \frac{\partial}{\partial \underline{x}_1} f^{(2)} = \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} [1 + \bar{\gamma}_{[0]} (\phi'_1 + \phi'_2)]$$

(4.1 - 9)

$$+ \frac{m n^2}{2 k T} \left\{ \frac{\partial \underline{u}}{\partial \underline{x}_1} - \left(\frac{k T}{2 m} \right) \left(\frac{\partial^2 m T}{\partial \underline{x}_1^2} \right) \frac{\partial}{\partial \underline{v}_1} \right\} : \underline{I}$$

where terms of higher order than n^2 in the density have been deleted.

Since we have obtained $f_{1[0]}^{(1)} = f_{1[0]}^{(1)} \phi$ through order n in the density, it follows from equations (4.1 - 1) and (4.1 - 4) that we can write the kinetic portion of the fluxes to that order. Furthermore, the constant term of the kinetic portion does not involve the integral $\mathcal{R}$ because the $\frac{1}{n}$ terms of $a_{1'}^{(1)}$ and $b_{0'}^{(1)}$ do not involve $\mathcal{R}$. Similar reasoning shows that we can write the collisional portion of the fluxes to order n^2 and that to order n they are independent of $\mathcal{R}$.

Section 4.2 The Density Expansions of the Transport Coefficients

The above considerations hold also for the transport coefficients which are simply related to the fluxes as discussed in Chapter I. Since the total transport coefficient is the sum of its kinetic and collisional parts, it follows from the remarks of the last section that if the kinetic part is non-zero, we can calculate the total transport coefficient only through order n . This is the case with the coefficients η and λ . It also follows from the last section that only the kinetic portion of the transport coefficient involves the integral $\mathcal{R}$ to order n . Since the expression for the collisional portion of the fluxes to order n can be written by

letting $\bar{y}_{i0j} = 1$, it follows that our treatment to this order gives expressions for the collisional portion of the transport coefficients identical with those of Snider and Curtiss.

From equations (1 - 11) and (1 - 12) of Chapter I, we see that ζ is the coefficient of a traceless second order tensor, $\kappa \left(\frac{\partial \underline{u}}{\partial \underline{x}_i} \cdot \underline{u} \right)$ is the coefficient of $\underline{U}$ and λ is the coefficient of a first order tensor. These tensor properties, along with the definitions of $\underline{A}$, $\underline{B}$ and $\underline{C}$ given in equation (3.2 - 5), insure that ζ depends only on the coefficient $b_0^{(1)}$, κ depends only on $c_z^{(1)}$, and λ on $a_1^{(1)}$.

As we shall presently demonstrate, there is no kinetic contribution to κ . Thus κ can be written to order n^2 . Since $c_z^{(1)}$, as given in equation (3.7 - 6), does not depend on $\mathcal{R}$ neither does κ . Also, since $c_z^{(1)}$ has no $\frac{1}{\pi}$ term, we can set $\bar{y}_{i0j} = 1$ to calculate the collisional contribution to κ to order n^2 . Thus, our κ is identical to that of Snider and Curtiss.

Let us examine the kinetic portion of ζ . To do this we find ϕ_K from equation (4.1 - 1).

$$\begin{aligned} \phi_K &= m \int f_{i0j}^{(1)} \underline{v}_i \underline{v}_j d\underline{v}_i + m \int f_{i0j}^{(1)} \phi_i \underline{v}_i \underline{v}_j d\underline{v}_i \\ &= m \int f_{i0j}^{(1)} \underline{v}_i \underline{v}_j d\underline{v}_i - m \int f_{i0j}^{(1)} \left[\underline{A}_i \cdot \frac{\partial \underline{u}}{\partial \underline{x}_i} + \underline{B}_i \cdot \frac{\partial \underline{u}}{\partial \underline{x}_i} + \underline{C}_i \cdot \frac{\partial \underline{u}}{\partial \underline{x}_i} \right] \underline{v}_i \underline{v}_j d\underline{v}_i \end{aligned} \quad (4.2 - 1)$$

From equation (2.7 - 23) we have

$$\left\{ m \int f_{[0]}^{(1)} \phi, \underline{v}_i \underline{v}_i d\underline{v}_i \right\} : \underline{U} = 0 \quad (4.2 - 2)$$

The term involving $\underline{A}$ does not contribute to $\underline{p}^*$ in equation (4.2 - 1) since integration over $\underline{v}_i$ yields a third order isotropic tensor. The term involving $\underline{C}$ also does not contribute because integration of this term over the angles of $\underline{v}_i$ yields the unit tensor $\underline{U}$, and, according to equation (4.2 - 2), the coefficient of this term is zero. Thus the perturbation of the distribution function gives rise to only a traceless symmetric contribution to the kinetic portion of the pressure tensor and, correspondingly, there is no kinetic contribution to $\mathcal{H}$.

From equation (2.7 - 17) we have

$$\underline{p}^* : \underline{U} = 3 n k T \quad (4.2 - 3)$$

and hence, from equation (4.2 - 1), it follows that

$$\begin{aligned} \underline{p}^* &= n k T \underline{U} - m \int f_{[0]}^{(1)} \left(\underline{B}_i : \frac{\partial \underline{u}}{\partial \underline{x}_i} \right) \underline{v}_i \underline{v}_i d\underline{v}_i \quad (4.2 - 4) \\ &= n k T \underline{U} - m b_0^{(1)} \left\{ \int f_{[0]}^{(1)} \underline{v}_i \underline{v}_i \underline{w}_i \underline{w}_i d\underline{v}_i \right\} : \left\{ \frac{\partial \underline{u}}{\partial \underline{x}_i} - \frac{1}{3} \left(\frac{\partial}{\partial \underline{x}_i} : \underline{u} \right) \underline{U} \right\} \\ &= n k T \underline{U} - \frac{2 n k T b_0^{(1)}}{\pi^{\frac{3}{2}}} \left\{ \int e^{-\underline{w}_i^2} \underline{w}_i \underline{w}_i \underline{w}_i \underline{w}_i d\underline{w}_i \right\} : \left\{ \frac{\partial \underline{u}}{\partial \underline{x}_i} - \frac{1}{3} \left(\frac{\partial}{\partial \underline{x}_i} : \underline{u} \right) \underline{U} \right\} \end{aligned}$$

we find in a similar manner that

$$\begin{aligned} \eta_K &= \frac{m}{2} \int f_1^{(1)} v_1^2 \underline{v}_1 d\underline{v}_1 \\ &= \frac{5}{4} n k \left(\frac{2 k T}{m} \right)^{\frac{1}{2}} a_1^{(1)} \left(\frac{\partial T}{\partial x_1} \right) \end{aligned} \quad (4.2 - 11)$$

We then conclude from equation (1 - 12) that

$$\lambda_K = -\frac{5}{4} n k \left(\frac{2 k T}{m} \right)^{\frac{1}{2}} a_1^{(1)} \quad (4.2 - 12)$$

We can now write the transport coefficients in terms of the integral R and the results of Snider and Curtiss by making use of equations (4.2 - 10) and (4.2 - 12) and the expressions for $a_1^{(1)}$, $b_0^{(1)}$ and $c_2^{(1)}$ of equations (3.7 - 4), (3.7 - 5) and (3.7 - 6).

We also make use of the fact that our treatment does not affect the collisional portions of the transport coefficients given by Snider and Curtiss. Thus we have

$$\eta = (\eta)_{S.C.} - \left(\frac{5}{128 \pi^{\frac{1}{2}}} \right) (m k T)^{\frac{1}{2}} \left(\frac{n R}{[\sigma \Omega^{(2,2)*}]^2} \right) \quad (4.2 - 13)$$

$$\lambda = (\lambda)_{S.C.} - \left(\frac{75}{512} \right) \left(\frac{k T}{m} \right)^{\frac{1}{2}} \left(\frac{n k R}{\pi^{\frac{5}{2}} [\sigma \Omega^{(2,2)*}]^2} \right) \quad (4.2 - 14)$$

and

$$\mathcal{H} = (\mathcal{H})_{S.C.} \quad (4.2 - 15)$$

Here the subscript S.C. denotes the result of Snider and Curtiss.

It is convenient to write the density expansion of the transport coefficients in the form

$$\lambda = \lambda^{(0)} (1 + (n\sigma^3) B_\lambda^* + (n\sigma^3)^2 C_\lambda^* + \dots) \quad (4.2 - 16)$$

$$\eta = \eta^{(0)} (1 + (n\sigma^3) B_\eta^* + (n\sigma^3)^2 C_\eta^* + \dots) \quad (4.2 - 17)$$

and

$$\chi = \eta^{(0)} ((n\sigma^3)^2 C_\chi^* + \dots) \quad (4.2 - 18)$$

where $\lambda^{(0)}$ and $\eta^{(0)}$ are the constant terms in the density expansions of λ and η . The quantities B_λ^* , C_λ^* , B_η^* , C_η^* , C_χ^* etc. are dimensionless and density independent and are referred to as the reduced transport virial coefficients. From the density arguments given previously in this section, we note that it is possible to calculate the quantities $\lambda^{(0)}$, $\eta^{(0)}$, B_λ^* , B_η^* and C_χ^* from our treatment. The quantities $\lambda^{(0)}$ and $\eta^{(0)}$ can be calculated from the $\frac{1}{n}$ terms of $a_1^{(1)}$ and $b_0^{(1)}$ and equations (4.2 - 10) and (4.2 - 12). We find that

$$\lambda^{(0)} = \left(\frac{75 k}{64 \sigma^2 \Omega^{(2,2)*}} \right) \left(\frac{k T}{\pi m} \right)^{\frac{1}{2}} \quad (4.2 - 19)$$

and

$$\eta^{(0)} = \left(\frac{5}{16 \sigma^2 \Omega^{(2,2)*}} \right) \left(\frac{m k T}{\pi} \right)^{\frac{1}{2}} \quad (4.2 - 20)$$

It then follows from equations (4.2 - 13), (4.2 - 14) and (4.2 - 15), that

$$B_{\lambda}^* = (B_{\lambda}^*)_{s.c.} - \frac{R}{8\pi^2\sigma^3\Omega^{(2,2)*}} \quad (4.2 - 21)$$

$$B_{\eta}^* = (B_{\eta}^*)_{s.c.} - \frac{R}{8\pi^2\sigma^3\Omega^{(2,2)*}} \quad (4.2 - 22)$$

and

$$C_{\kappa}^* = (C_{\kappa}^*)_{s.c.} \quad (4.2 - 23)$$

In Chapter V we consider the evaluation of these coefficients for a particular molecular potential and compare the results of a number of experimental measurements and theoretical calculations.

Section 4.3 The Rigid Sphere Limit and the Enskog Dense Gas Transport Coefficients.

We now consider the correction to the results of Snider and Curtiss for the special case of rigid spheres. To do this we evaluate the integral R which is defined in equation (3.6 - 22) as

$$R = \frac{1}{n\sigma^2} \int d\underline{r} d\underline{s} \left(\underline{s} \cdot \frac{\partial}{\partial \underline{r}} \bar{y}_{[0]} \right) e^{-\frac{\phi^{(1,2)}}{kT}} e^{-\underline{s}^2} (\underline{s} \cdot \underline{s}')^2 \quad (4.3 - 1)$$

From the identity of equation (2.6 - 18) we have

$$\underline{s} \cdot \frac{\partial}{\partial \underline{r}} \bar{y}_{[0]} = \underline{s}' \cdot \frac{\partial}{\partial \underline{r}'} \bar{y}_{[0]} \quad (4.3 - 2)$$

and hence (since $\underline{s}'^2 = \underline{s}^2 + \frac{\phi^{(1,2)}}{kT}$)

$$R = \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} \left(\underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} \cdot \bar{y}_{[0J]} \right) e^{-\underline{x}'^2 (\underline{x} \cdot \underline{x}')^2} \quad (4.3 - 3)$$

We can rewrite R in the form

$$R = \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} \underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} \left\{ \bar{y}_{[0J]} e^{-\underline{x}'^2 (\underline{x} \cdot \underline{x}')^2} \right\} \quad (4.3 - 4)$$

$$= \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} \bar{y}_{[0J]} e^{-\underline{x}'^2} \left\{ \underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} (\underline{x} \cdot \underline{x}') \right\} : \underline{x}' \underline{x}'$$

From the identity of equation (2.6 - 18) we have

$$\underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} (\underline{x} \cdot \underline{x}') = -\frac{1}{2k\tau} \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \cdot \frac{\partial}{\partial \underline{x}} (\underline{x} \cdot \underline{x}') \quad (4.3 - 5)$$

$$= -\frac{1}{2k\tau} \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \underline{x} + \underline{x} \frac{\partial \phi^{(1,2)}}{\partial \underline{h}} \right)$$

Thus, the integrand of the second integral in equation (4.3 - 4)

contains the quantity

$$\frac{\partial \phi^{(1,2)}}{\partial \underline{h}} e^{-\frac{\phi^{(1,2)}}{k\tau}}$$

Since for $h < \sigma$ $e^{-\frac{\phi^{(1,2)}}{k\tau}} = 0$, and for $h > \sigma$ $\frac{\partial \phi^{(1,2)}}{\partial \underline{h}} = 0$ and $\phi^{(1,2)}$ has a discontinuity at $h = \sigma$; this quantity has a

δ -function behavior at $h = \sigma$. We can thus replace $y_{[0J]}(\underline{h}', \underline{x})$

by $y_{[0J]}(\underline{h}', \sigma)$ in the integrand of the second integral in

equation (4.3 - 4). We then have

$$R = \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} \underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} \left\{ \bar{y}_{[0J]} e^{-\underline{x}'^2 (\underline{x} \cdot \underline{x}')^2} \right\} \quad (4.3 - 6)$$

$$= \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} y_{[0J]}(\underline{h}', \sigma) e^{-\underline{x}'^2} \left\{ \underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} (\underline{x} \cdot \underline{x}') \right\} : \underline{x}' \underline{x}'$$

$$= \frac{1}{n\sigma^2} \int d\underline{h} d\underline{x} \underline{x}' \cdot \frac{\partial}{\partial \underline{h}'} \left\{ (\bar{y}_{[0J]} - y_{[0J]}(\underline{h}', \sigma)) e^{-\underline{x}'^2 (\underline{x} \cdot \underline{x}')^2} \right\}$$

Let us now make the variable transformation $(\underline{r}, \underline{x}) \rightarrow (\underline{r}', \underline{x}')$ discussed in Sec. 2.6. From equations (2.6 - 16) and (2.6 - 19) we have

$$R = \frac{1}{n \pi^2} \int d\underline{x}' d\underline{e} d\underline{z} d\underline{b} b(\underline{x}') \frac{\underline{x}' \cdot \underline{z}}{|\underline{z}|^2} \left\{ \left(\bar{y}_{[0]} - y_{[0]}(\underline{r}', \sigma) \right) e^{-\underline{x}' \cdot \underline{x}'^2} \right\} \quad (4.3 - 7)$$

Integration over $\underline{z}$ yields

$$\begin{aligned} R &= \frac{1}{n \pi^2} \left(1 - y_{[0]}(\underline{r}', \sigma) \right) \int d\underline{x}' d\underline{e} d\underline{b} b(\underline{x}') e^{-\underline{x}' \cdot \underline{x}'^2} [\cos^2 \chi - 1] \\ &= \frac{8 \pi^2}{n \pi^2} \left(y_{[0]}(\underline{r}', \sigma) - 1 \right) \int d\underline{x}' d\underline{b} b(\underline{x}')^2 e^{-\underline{x}' \cdot \underline{x}'^2} [1 - \cos^2 \chi] \end{aligned} \quad (4.3 - 8)$$

which from equation (3.6 - 6) is

$$R = \left(\frac{8 \pi^2}{n} \right) \left(y_{[0]}(\underline{r}', \sigma) - 1 \right) \Omega^{(2,2)*} \quad (4.3 - 9)$$

For rigid spheres

$$\Omega^{(2,2)*} = 1 \quad (4.3 - 10)$$

and, from equation (2.9 - 9)

$$y_{[0]}(\underline{r}', \sigma) - 1 = n \frac{C}{B} \quad (4.3 - 11)$$

where B and C are respectively the second and third rigid sphere virial coefficients. Thus we have

$$R = 8 \pi^2 \frac{C}{B} \quad (4.3 - 12)$$

From equations (4.2 - 21), (4.2 - 22) and (4.2 - 23), we have

$$B_{\lambda}^* = (B_{\lambda}^*)_{s.c.} - \frac{C}{\sigma^3 B} \quad (4.3 - 13)$$

$$B_{\eta}^* = (B_{\eta}^*)_{s.c.} - \frac{C}{\sigma^3 B} \quad (4.3 - 14)$$

and

$$C_{\kappa}^* = (C_{\kappa}^*)_{s.c.} \quad (4.3 - 15)$$

The Enskog dense gas equation for rigid spheres, which is given by equation (2.9 - 8), differs from the ordinary Boltzmann equation in two respects. First, in the ordinary Boltzmann equation, the product of one particle distribution functions in the collision integral are evaluated at the gross position $\underline{r}_i$. Second, the factor $\psi_{[0]}$ in the ordinary Boltzmann equation is unity. Snider and Curtiss³⁴ have shown that the transport virial coefficients $(B_{\lambda}^*)_{s.c.}$, $(B_{\eta}^*)_{s.c.}$ and $(C_{\kappa}^*)_{s.c.}$, in the special case of rigid spheres, are identical to those obtained by direct solution of the Enskog equation when the deviation of $\psi_{[0]}$ from unity is not considered. Our treatment in this limit gives rise to the full transport virial coefficients obtained from the Enskog treatment through the inclusion of the correction $-\frac{C}{\sigma^3 B}$ in the coefficients B_{λ}^* and B_{η}^* . This correction arises from the linear term in $\psi_{[0]}$.

CHAPTER V

EVALUATION OF THE TRANSPORT COEFFICIENTS

In this chapter we consider the transport coefficients of a gas composed of molecules which interact through a realistic potential which is repulsive at short separations but is attractive at large separations. The theoretical development in the preceding chapters is applicable only to purely repulsive potentials. We can, however, separately consider contributions to the transport coefficients which arise from bound states and non-bound states. The non-bound state contributions can be treated formally in much the same manner as we have discussed for purely repulsive potentials. The bound state contributions have not been handled satisfactorily from a theoretical point of view.

Section 5.1 The Reduction of the Integrals to Computation Form

A family of two constant potentials can be defined by

$$\phi(r) = \epsilon F\left(\frac{r}{\sigma}\right) \quad (5.1 - 1)$$

The function F is defined in such a way that the zero of the potential occurs at $\frac{r}{\sigma} = 1$; and at the minimum of the potential well $F = -1$. A typical potential of this type is the Lennard-Jones potential defined by

$$F(x) = 4 \left[\frac{1}{x^{12}} - \frac{1}{x^6} \right] \quad (5.1 - 2)$$

The Lennard-Jones potential is illustrated in Fig. 2.

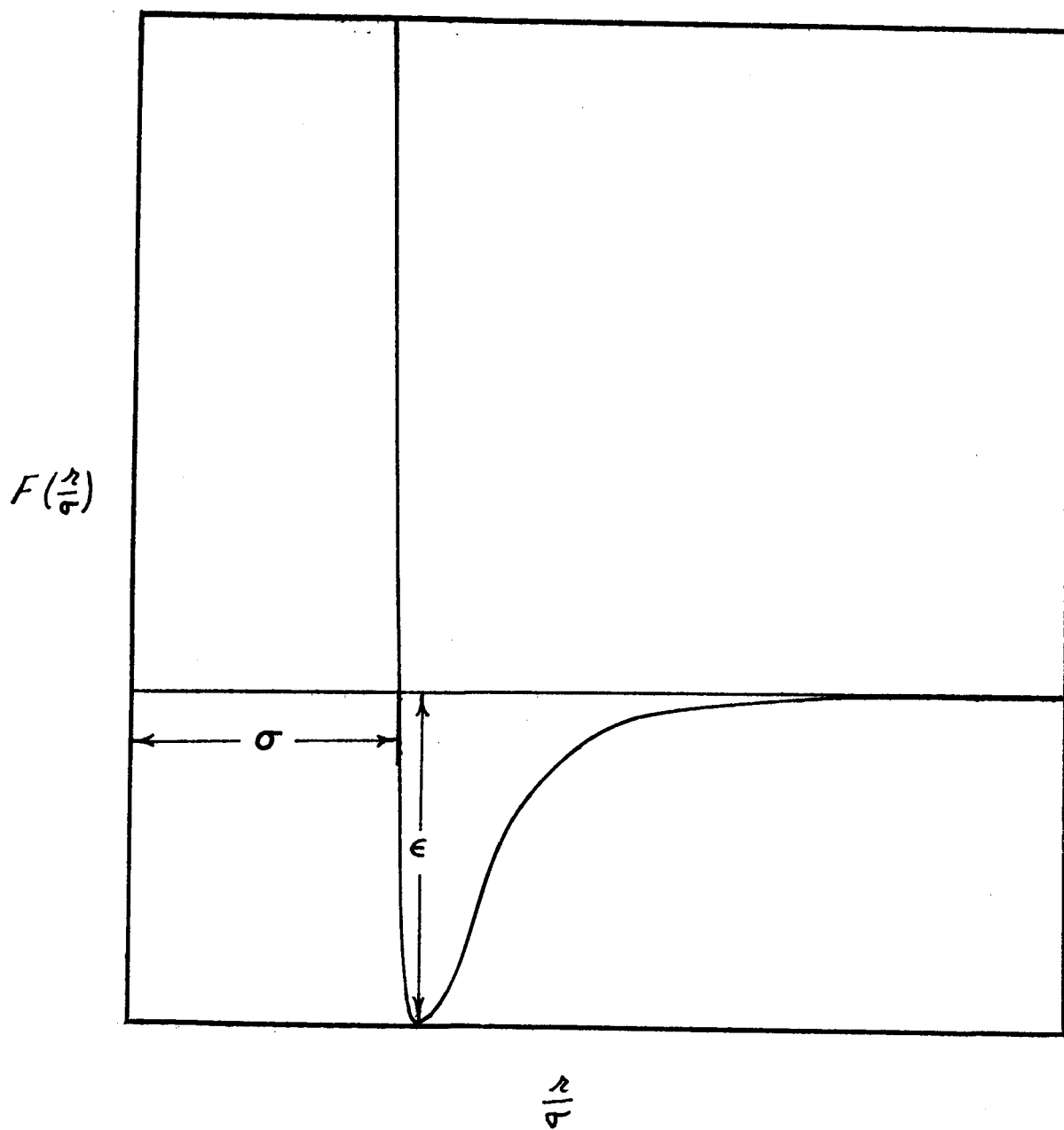


Fig. 2

The Lennard-Jones Potential

For convenience we define the dimensionless quantities:

$$r^* = \frac{r}{\sigma} \quad (5.1 - 3)$$

$$T^* = \frac{kT}{\epsilon} \quad (5.1 - 4)$$

$$g^* = (T^*)^{\frac{1}{2}} g = \frac{1}{2} \left(\frac{m}{\epsilon} \right)^{\frac{1}{2}} g \quad (5.1 - 5)$$

$$\omega_s^* = \frac{\omega_s}{\sigma} \quad (5.1 - 6)$$

$$\Delta \omega^* = \frac{\Delta \omega}{\sigma} \quad (5.1 - 7)$$

and

$$E^* = \frac{E}{\sigma} \quad (5.1 - 8)$$

These reduced variables are convenient since only one calculation for the corresponding states of a series of gases is then necessary.

Since, in general, the potential is not purely repulsive, bound states are possible. A typical pseudo-potential for a particular angular momentum and energy is shown in Fig. 3. Depending on the energy and angular momentum, there can be one, two or three turning points. Two turning points arise when the well in the pseudo-potential is below the zero of energy and the energy is negative. These are turning points on a bound trajectory. For energies, above zero,

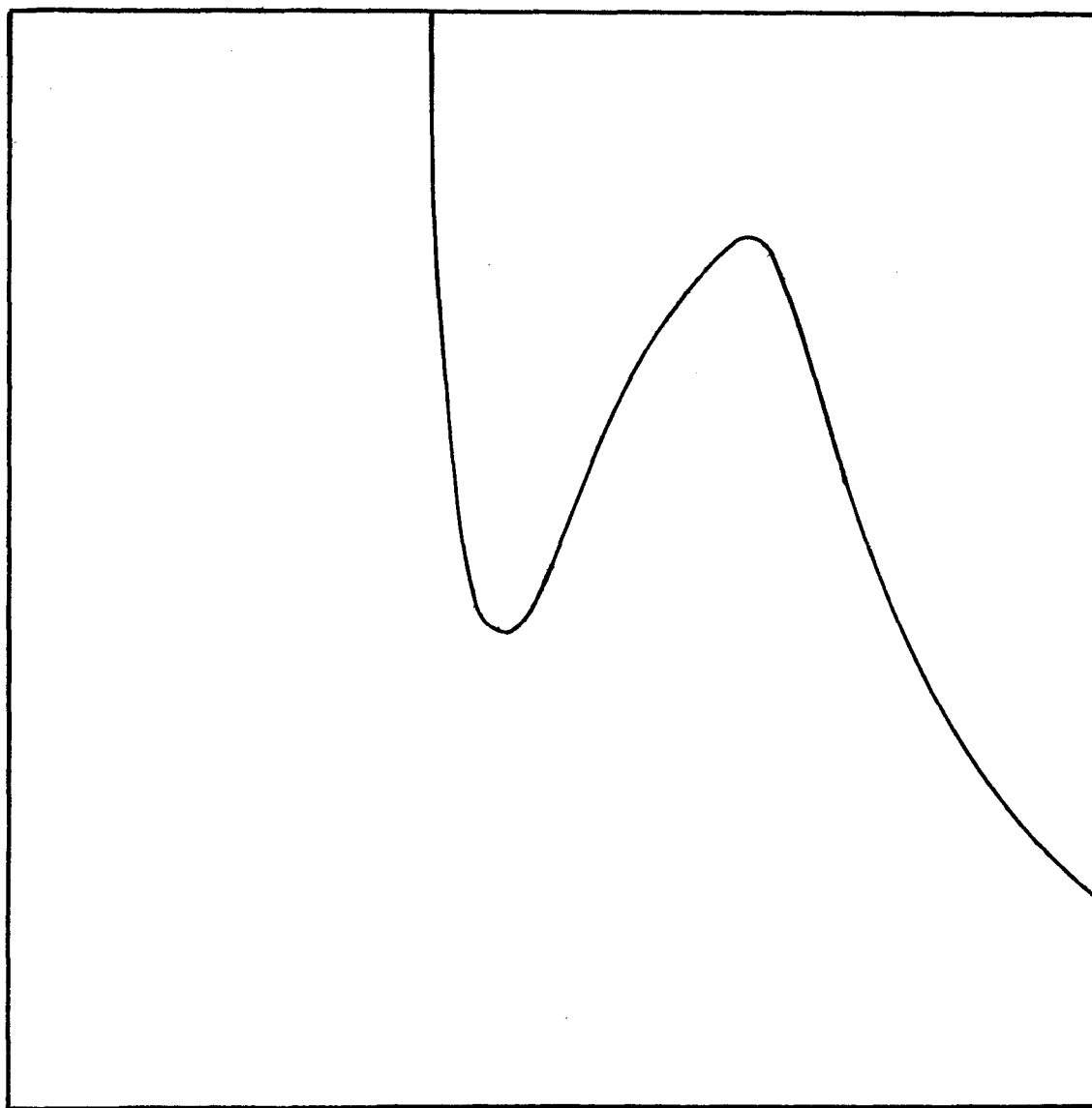


Fig. 3

The Pseudo-potential $F(r^*) \neq \frac{f^{*2}}{r^{*2}} g^{*2}$
 for an Orbiting Angular Momentum

the outermost turning point is always on a non-bound trajectory.

When there are three turning points, the energy and angular momentum do not uniquely specify a single trajectory. However, every choice of b and g corresponds to one and only one non-bound trajectory.

Most of the discussion of Sec. 2.6 holds for the non-bound trajectories of any potential. In the manner given there, we can define the quantities α' and g' . The specific coordinate systems for these quantities which were discussed in Sec. 2.6 are still valid. Further, the identity equation (2.6 - 18) holds; and we can integrate over the non-bound portion of the position-velocity space by integrating over (α', g') .

For purely repulsive potentials, the scattering angle χ is always positive. For a general potential this is not true. A phenomena known as near orbiting occurs when the energy and angular momentum are such that the energy is approximately equal to the maximum in the pseudo-potential. Under these conditions the particle orbits the scatterer a number of times; and the scattering angle is large and negative. If the energy is slightly greater than the potential maximum, the radial velocity of an incoming particle falls nearly to zero; but remains negative as the radial separation approaches the maximum of the pseudo-potential. The particle thus travels in a nearly circular orbit with a slight inward spiral. Depending on how close the incoming energy is to that of the potential maximum, the particle may make several such orbits. Finally, the particle spirals in over the maximum, and the radial velocity decreases then increases sharply to zero at the turning point.

The radial velocity then becomes positive and the particle spirals outward on a trajectory symmetric to the incoming trajectory. If the incoming particle has energy slightly less than the maximum in the pseudo-potential, the particle undergoes a similar type of orbiting but does not pass over the maximum. Near orbiting presents no theoretical difficulties; but computationally it introduces difficulties because the scattering angle and the duration of a collision are very large.

The transport coefficient expressions of Snider and Curtiss¹¹ have been written in terms of five basic integrals over the two particle position velocity space by Snider and McCourt³⁵. (Only three of these integrals comprise part of B_{λ}^* , B_{η}^* and $C_{\mathcal{H}}^*$. The other two give portions of C_{λ}^* and C_{η}^*). One of these integrals is closely related to $\int (\underline{I} : \underline{W}, \underline{W}) d\underline{W}$ which, as we have shown, arises in the solution of the integral equations. The other four integrals arise in the evaluation of the flux vectors. Our treatment leads to an additional integral, $\mathcal{R}$.

The five basic integrals in the Snider and Curtiss treatment have been evaluated for the Lennard-Jones potential by Curtiss, McElroy, and Hoffman³⁶. These integrals over the non-bound state regions of the two particle position-velocity space are evaluated by first transforming to the reduced variables mentioned previously. The integrations over the three angles which determine the plane of collision and its orientation in the plane can be carried out immediately. The remaining variables determine a trajectory in the collision plane and a point on the trajectory. If the integrations are carried out in the $(\underline{r}^*, \underline{f}^*)$ coordinate system, the remaining

three integrations are over r^* , g^* and the angle φ between r^* and $-g^*$.

By manipulating the φ integrations we can transform the integrals to integrals only over the incoming portions of the trajectories. If we represent the integrand of a typical φ integral by $H(r^*, g^*, \varphi)$, then the φ integral is $\int_0^\pi H(r^*, g^*, \varphi) \sin \varphi d\varphi$. On the incoming portion of the trajectory $0 \leq \varphi \leq \frac{\pi}{2}$; and at the distance of closest approach, $\varphi = \frac{\pi}{2}$. We can write

$$\begin{aligned} \int_0^\pi H(r^*, g^*, \varphi) \sin \varphi d\varphi &= \int_0^{\frac{\pi}{2}} H(r^*, g^*, \varphi) \sin \varphi d\varphi + \int_{\frac{\pi}{2}}^\pi H(r^*, g^*, \varphi) \sin \varphi d\varphi \\ &= \int_0^{\frac{\pi}{2}} H(r^*, g^*, \varphi) \sin \varphi d\varphi + \int_{\frac{\pi}{2}}^0 H(r^*, g^*, \pi - \varphi) \sin(\pi - \varphi) d(\pi - \varphi) \\ &= \int_0^{\frac{\pi}{2}} [H(r^*, g^*, \varphi) + H(r^*, g^*, \pi - \varphi)] \sin \varphi d\varphi \quad (5.1 - 9) \end{aligned}$$

The integral is over the domain of φ from 0 to $\frac{\pi}{2}$ and is thus an integral over the incoming portion of the trajectory. The integrand

$$[H(r^*, g^*, \varphi) + H(r^*, g^*, \pi - \varphi)]$$

contains equal contributions from the point (r^*, g^*, φ) on the incoming portion of the trajectory and the corresponding point (through symmetry) $(r^*, g^*, \pi - \varphi)$ on the outgoing portion of the trajectory.

There are several choices of coordinates we can use to carry out the integrations over the incoming portion of the trajectory. A convenient choice is $(g')^*$, ξ^* and λ^* . The coordinates $(g')^*$ and ξ^* specify a trajectory and λ^* specifies a point on the incoming portion of this trajectory. From equations (2.6 - 2) and (2.6 - 3) we note that these coordinates have the advantage numerically of specifying b^* and g^* without the necessity of determining a root of an algebraic equation. The integration limits on λ^* are ξ^* and infinity. The integration over $(g')^*$ and ξ^* is restricted to the non-shaded areas of the first quadrant in Fig. 4. The area A is excluded in the integration because there the potential energy at ξ^* exceeds the total energy. The area B is excluded because it corresponds to bound states. Points in the integration region which lie near the boundary curve of B correspond to non-bound states with near-orbiting trajectories. Those points lying near the part of the boundary curve with positive slope, correspond to collisions where the particle energy is slightly greater than the maximum in the pseudo-potential; and those points lying near the part of the curve with negative slope, correspond to collisions where the particle energy is slightly less than the pseudo-potential maximum. As mentioned previously, points near the boundary curve of B present computational problems because the angle of scattering is large and the duration of the collision is long.

The Jacobian of the transformation $(\lambda^*, g^*, \epsilon) \rightarrow (\lambda^*, (g')^*, \xi^*)$ is

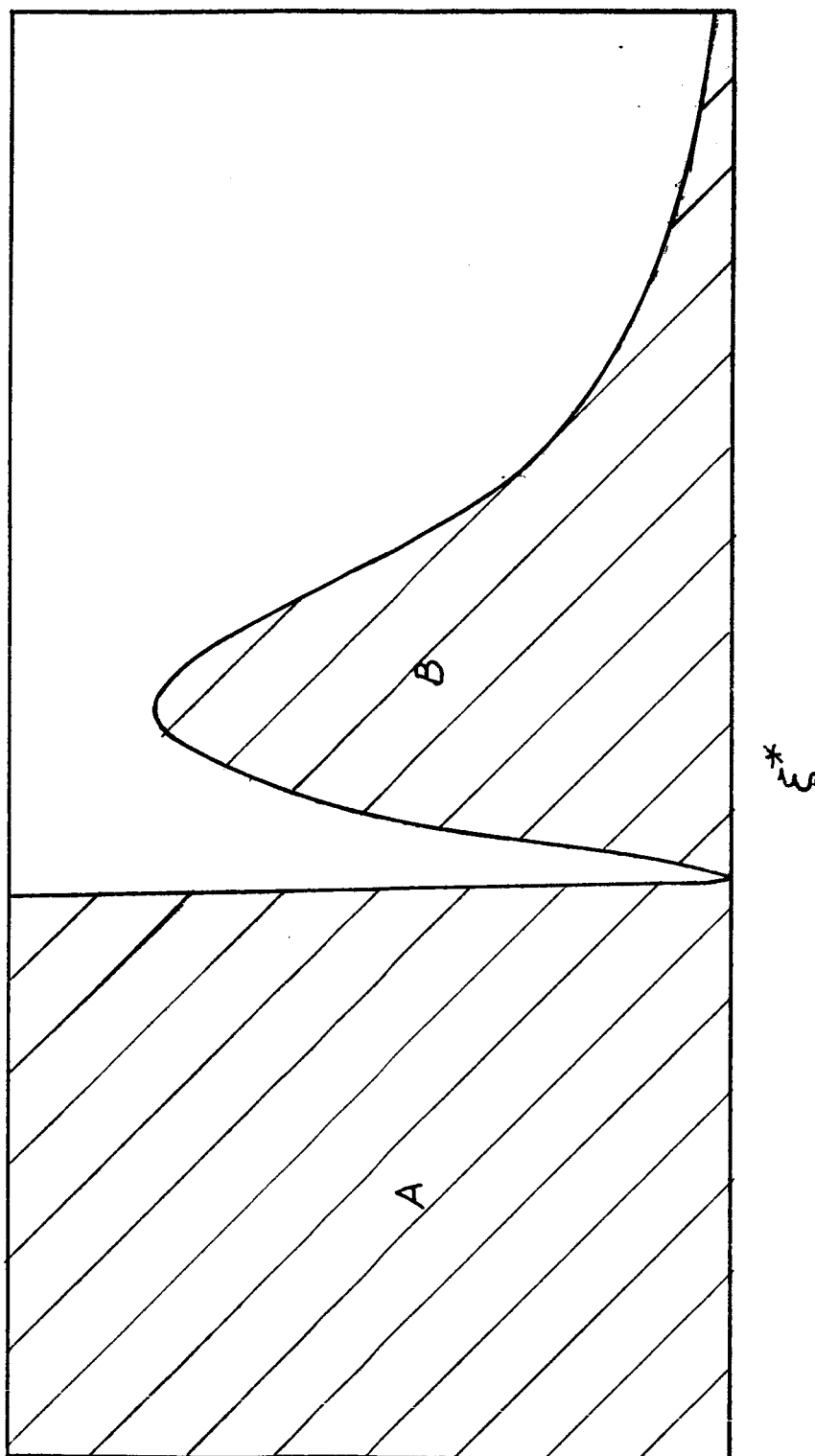


Fig. 4 $(g')^{*2}$

The Integration Region for $((g')^{*2}, \xi^*)$

$$\frac{\partial(\varphi, g^*)}{\partial(s^*, (g')^*)} = \begin{vmatrix} \frac{\partial \varphi}{\partial s^*} & \frac{\partial \varphi}{\partial (g')^*} \\ \frac{\partial g^*}{\partial s^*} & \frac{\partial g^*}{\partial (g')^*} \end{vmatrix} \quad (5.1 - 10)$$

$$= \frac{(g')^* \left\{ (g')^{*2} - F(s^*) - \frac{1}{2} s^* \frac{dF(s^*)}{ds^*} \right\}}{[(g')^{*2} - F(\lambda^*)]^{\frac{1}{2}} [(g')^{*2} - F(s^*)]^{\frac{1}{2}} \left\{ \lambda^{*2} [(g')^{*2} - F(\lambda^*)] - s^{*2} [(g')^{*2} - F(s^*)] \right\}^{\frac{1}{2}}}$$

To evaluate the determinant in equation (5.1 - 10) we make use of the relations:

$$g^* = [(g')^{*2} - F(\lambda^*)]^{\frac{1}{2}} \quad (5.1 - 11)$$

$$b^* = \frac{s^* [(g')^{*2} - F(s^*)]^{\frac{1}{2}}}{(g')^*} \quad (5.1 - 12)$$

$$\sin \varphi = \frac{s^* [(g')^{*2} - F(s^*)]^{\frac{1}{2}}}{\lambda^* [(g')^{*2} - F(\lambda^*)]^{\frac{1}{2}}} \quad (5.1 - 13)$$

and

$$\cos \varphi = \frac{\left\{ \lambda^{*2} [(g')^{*2} - F(\lambda^*)] - s^{*2} [(g')^{*2} - F(s^*)] \right\}^{\frac{1}{2}}}{\lambda^* [(g')^{*2} - F(\lambda^*)]^{\frac{1}{2}}} \quad (5.1 - 14)$$

which follow from equations (2.6 - 2), (2.6 - 3), (2.6 - 4) and

(2.6 - 5).

We can also write expressions for the quantities α , χ , ω_{ξ}^* and $\Delta\omega$ (which were discussed in Sec. 2.6) in terms of the coordinates ρ^* , $(g')^*$ and ξ^* . Then, from equations (2.6 - 1), (2.6 - 6), (2.6 - 27), (2.6 - 30), (5.1 - 11) and (5.1 - 12), we have

$$\alpha = \int_{\rho^*}^{\infty} \frac{\frac{\xi^* [(g')^{*2} - F(\xi^*)]^{\frac{1}{2}}}{\rho^{*2} (g')^*} d\rho^*}{\sqrt{1 - \frac{F(\rho^*)}{(g')^{*2}} - \frac{\xi^{*2} [(g')^{*2} - F(\xi^*)]}{\rho^{*2} (g')^{*2}}} \quad (5.1 - 15)$$

$$\chi = \pi - 2 \int_{\xi^*}^{\infty} \frac{\frac{\xi^* [(g')^{*2} - F(\xi^*)]^{\frac{1}{2}}}{\rho^{*2} (g')^*} d\rho^*}{\xi^* \sqrt{1 - \frac{F(\rho^*)}{(g')^{*2}} - \frac{\xi^{*2} [(g')^{*2} - F(\xi^*)]}{\rho^{*2} (g')^{*2}}} \quad (5.1 - 16)$$

$$\omega_{\xi}^* = \int_{\xi^*}^{\rho^*} \frac{d\rho^*}{\sqrt{1 - \frac{F(\rho^*)}{(g')^{*2}} - \frac{\xi^{*2} [(g')^{*2} - F(\xi^*)]}{\rho^{*2} (g')^{*2}}} \quad (5.1 - 17)$$

and

$$\Delta\omega^* = \int_{\xi^*}^{\infty} \left[\frac{1}{\sqrt{1 - \frac{F(\rho^*)}{(g')^{*2}} - \frac{\xi^{*2} [(g')^{*2} - F(\xi^*)]}{\rho^{*2} (g')^{*2}}} - 1 \right] d\rho^* - \xi^* \quad (5.1 - 18)$$

From Sec. 2.6 we have, on the incoming portion of a trajectory,

$$(\underline{r}')^* = (\Delta\omega^* - \omega_s^*) \hat{g}' + b^* \hat{b} \quad (5.1 - 19)$$

$$\hat{g}' \cdot \hat{r} = -\cos \alpha \quad (5.1 - 20)$$

$$\hat{g}' \cdot \hat{g} = \cos \alpha \cos \varrho + \sin \alpha \sin \varrho \quad (5.1 - 21)$$

$$\hat{b} \cdot \hat{r} = \sin \alpha \quad (5.1 - 22)$$

and

$$\hat{b} \cdot \hat{g} = \cos \alpha \sin \varrho - \sin \alpha \cos \varrho \quad (5.1 - 23)$$

On the outgoing portion of the trajectory,

$$(\underline{r}')^* = (\Delta\omega^* + \omega_s^*) \hat{g}' + b^* \hat{b} \quad (5.1 - 24)$$

$$\hat{g}' \cdot \hat{r} = \cos(\alpha + \chi) \quad (5.1 - 25)$$

$$\hat{g}' \cdot \hat{g} = \cos(\alpha + \chi) \cos \varrho + \sin(\alpha + \chi) \sin \varrho \quad (5.1 - 26)$$

$$\hat{b} \cdot \hat{r} = \sin(\alpha + \chi) \quad (5.1 - 27)$$

and

$$\hat{b} \cdot \hat{g} = -\cos(\alpha + \chi) \sin \varrho + \sin(\alpha + \chi) \cos \varrho \quad (5.1 - 28)$$

We now reduce the integral $\int (\underline{I} : \underline{w}_1, \underline{w}_1) d\underline{w}_1$ to a form which is convenient for computation. From equation (3.1 - 12) we have

$$\begin{aligned}
 & \int (\underline{I} : \underline{w}_1, \underline{w}_1) d\underline{w}_1 \quad (5.1 - 29) \\
 &= \frac{2}{m n^2} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{w}_1 d\underline{w}_2 \underline{w}_1, \underline{w}_1 \left\{ \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \right) \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left[\underline{g}' \underline{r}' \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} e^{-\frac{\phi^{(1,2)}}{k T}} \right] \right\} \\
 &= \frac{2}{m n^2} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{w}_1 d\underline{w}_2 \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \right) \cdot \left(\frac{\partial}{\partial \underline{g}} \right)_{\underline{g}} \left[(\underline{w}_1, \underline{w}_1 : \underline{g}' \underline{r}') \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} e^{-\frac{\phi^{(1,2)}}{k T}} \right] \\
 &- \frac{2}{m n^2} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{w}_1 d\underline{w}_2 \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \right) \cdot \left(\frac{\partial}{\partial \underline{g}} (\underline{w}_1, \underline{w}_1) \right)_{\underline{g}} \left\{ \underline{g}' \underline{r}' \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} e^{-\frac{\phi^{(1,2)}}{k T}} \right\}
 \end{aligned}$$

If we make the variable transformation $(\underline{w}_1, \underline{w}_2) \rightarrow (\underline{r}, \underline{r}')$ which was discussed in Sec. 3.6, then the first integral in equation (5.1 - 29) is zero by Gauss' theorem. Thus,

$$\begin{aligned}
 & \int (\underline{I} : \underline{w}_1, \underline{w}_1) d\underline{w}_1 \quad (5.1 - 30) \\
 &= - \frac{2}{m n^2} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{r} d\underline{r}' \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \right) \cdot \left(\frac{\partial (\underline{w}_1, \underline{w}_1)}{\partial \underline{r}} \right)_{\underline{r}'} \left\{ \underline{r}' \underline{r}' \bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} e^{-\frac{\phi^{(1,2)}}{k T}} \right\}
 \end{aligned}$$

The quantity $\underline{w}_i \underline{w}_j$ is given by

$$\underline{w}_i \underline{w}_j = \frac{1}{2} (\underline{r}_i \underline{r}_j - \underline{r}_i \underline{x} - \underline{x} \underline{r}_j + \underline{x} \underline{x}) \quad (5.1 - 31)$$

There is no contribution to $\int (\underline{I} : \underline{w}_i \underline{w}_j) d\underline{w}_i$ from the term $\frac{1}{2} \underline{r}_i \underline{r}_j$ by virtue of the gradient $\left(\frac{\partial}{\partial \underline{x}}\right)_{\underline{r}_i}$. Also, the terms $\frac{1}{2} \underline{x} \underline{r}_i$ and $\frac{1}{2} \underline{r}_j \underline{x}$ do not contribute after integration over the angles of $\underline{r}_i$. Hence,

$$\begin{aligned} & \int (\underline{I} : \underline{w}_i \underline{w}_j) d\underline{w}_i \\ &= -\frac{1}{m} \left(\frac{2kT}{m}\right)^{\frac{3}{2}} \left(\frac{m}{2\pi kT}\right)^3 \int d\underline{r}_j d\underline{x} d\underline{r}_i \left(\frac{\partial \phi^{(1,2)}}{\partial \underline{r}_j} \cdot \frac{\partial}{\partial \underline{x}} (\underline{x} \underline{x})\right) \left\{ \underline{x}' \underline{r}_j' e^{-\underline{x}'^2 - \underline{r}_j'^2 - \frac{\phi^{(1,2)}}{kT}} \right\} \end{aligned} \quad (5.1 - 32)$$

Integrating over $\underline{r}_i$ yields

$$\begin{aligned} & \int (\underline{I} : \underline{w}_i \underline{w}_j) d\underline{w}_i \\ &= -\frac{1}{m} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int d\underline{r}_j d\underline{x} \frac{1}{r_j} \frac{\partial \phi^{(1,2)}}{\partial r_j} \left\{ (\underline{r}_j \cdot \underline{x}') (\underline{x} \cdot \underline{r}_j') + (\underline{r}_j \cdot \underline{r}_j') (\underline{x} \cdot \underline{x}') \right\} e^{-\underline{x}'^2 - \frac{\phi^{(1,2)}}{kT}} \\ &= -\frac{8\pi^2}{m} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int d\underline{r}_j d\underline{x} d\Omega \, r_j^2 \sin \vartheta \frac{\partial \phi}{\partial r_j} \left\{ (\underline{r}_j \cdot \underline{x}') (\underline{x} \cdot \underline{r}_j') + (\underline{r}_j \cdot \underline{r}_j') (\underline{x} \cdot \underline{x}') \right\} e^{-\underline{x}'^2 - \frac{\phi^{(1,2)}}{kT}} \end{aligned} \quad (5.1 - 33)$$

In the manner previously discussed, this expression for

$\int (\underline{I} : \underline{w}_i \underline{w}_j) d\underline{w}_i$ can be transformed to an integral over the incoming trajectories. If we use as integration variables the coordinates $\underline{r}^*$, $(\underline{g}')^*$ and $\underline{\xi}^*$, we have

$$\int (I : \underline{w}, \underline{w}_1) d\underline{w}, \quad (5.1 - 34)$$

$$= -2^{\frac{3}{2}} \left(\frac{\pi m}{\epsilon} \right)^{\frac{1}{2}} \sigma^3 \left(\frac{1}{T^*} \right)^{\frac{1}{2}} \int d\underline{r}^* d(\underline{g}')^* d\underline{s}^* \frac{\partial(\underline{w}, \underline{g}^*)}{\partial(\underline{g}', \underline{s}^*)} r^* (g^*)^2 \sin \varpi$$

$$\left[\frac{dF}{d\underline{r}^*} e^{-\frac{(g')^2}{T^*}} \left\{ \begin{aligned} & \left\{ [\underline{r}^* \cdot (\underline{g}')^*] [\underline{g}^* \cdot (\underline{r}')^*] + [\underline{r}^* \cdot (\underline{r}')^*] [\underline{g}^* \cdot (\underline{g}')^*] \right\} \text{incoming} \\ & \quad + \\ & \left\{ [\underline{r}^* \cdot (\underline{g}')^*] [\underline{g}^* \cdot (\underline{r}')^*] + [\underline{r}^* \cdot (\underline{r}')^*] [\underline{g}^* \cdot (\underline{g}')^*] \right\} \text{outgoing} \end{aligned} \right\} \right]$$

The integrand of the integral in equation (5.1 - 34) is a function of the reduced quantities $\underline{r}^*$, $(\underline{g}')^*$, $\underline{s}^*$ and T^* only. The various functional relations necessary to write the integrand in this form are given by equations (5.1 - 10) - (5.1 - 28). The integral itself is a function of only T^* and is applicable to the corresponding states of a series of gases.

The other four integrals basic to the results of Snider and Curtiss can be reduced to a convenient computational form in a similar manner. The numerical methods by which these integrations were performed are discussed in detail by Curtiss, McElroy and Hoffman³⁶.

The integral R which arises in our treatment can be reduced to a computational form in a similar manner. We find that

$$R = \frac{8\pi^2}{N(T^*)^4} \int d\underline{r}^* d(\underline{g}')^* d\underline{s}^* \frac{\partial(\underline{w}, \underline{g}^*)}{\partial(\underline{g}', \underline{s}^*)} \sin \varpi g^{*3} (g')^{*2} r^{*2} [\bar{Y}_{[0]}^{-1}] e^{-\frac{(g')^2}{T^*}} \frac{dF}{d\underline{r}^*}$$

$$\left[(\hat{\underline{g}}' \cdot \hat{\underline{r}})(\hat{\underline{g}}' \cdot \hat{\underline{g}}) \text{incoming trajectory} + (\hat{\underline{g}}' \cdot \hat{\underline{r}})(\hat{\underline{g}}' \cdot \hat{\underline{g}}) \text{outgoing trajectory} \right] \quad (5.1 - 35)$$

The function $\frac{1}{n} (\bar{y}_{103} - 1)$ which appears in the integrand is itself an integral. From equation (2.8 - 12), we have

$$\frac{1}{n} (\bar{y}_{103} - 1) = \int (e^{-\frac{\phi^{(1,3)}}{kT} - 1}) (e^{-\frac{\phi^{(2,3)}}{kT} - 1}) d\underline{r}_3 \quad (5.1 - 36)$$

We can write this integral in confocal elliptic coordinates and perform the trivial angle integration to obtain

$$\frac{1}{n} (\bar{y}_{103} - 1) = \frac{2\pi k^3}{8} \int_{-1}^1 \int_{-1}^1 (e^{-\frac{\phi(\frac{r}{2}(\rho-\nu))}{kT} - 1}) (e^{-\frac{\phi(\frac{r}{2}(\rho+\nu))}{kT} - 1}) (\rho^2 - \nu^2) d\rho d\nu \quad (5.1 - 37)$$

If we then introduce the variable change

$$r_{13}^* = \frac{r}{2} (\rho - \nu) \quad (5.1 - 38)$$

and

$$r_{23}^* = \frac{r}{2} (\rho + \nu) \quad (5.1 - 39)$$

we obtain

$$\frac{1}{n} (\bar{y}_{103} - 1) = \frac{2\pi k^3}{n^*} \int_0^\infty \int_{|r^* - r_{13}^*|}^{r^* + r_{13}^*} d r_{13}^* \int_{r_{23}^*}^{\infty} d r_{23}^* (e^{-\frac{F(r_{13}^*)}{T^*} - 1}) (e^{-\frac{F(r_{23}^*)}{T^*} - 1}) r_{13}^* r_{23}^* \quad (5.1 - 40)$$

The integral $\mathcal{R}$ can be computed numerically from this expression for $\frac{1}{n} (\bar{y}_{103} - 1)$ and equation (5.1 - 35).

Section 5.2 Numerical Evaluation of $\mathcal{R}$

We see, from equations (5.1 - 35) and (5.1 - 40), that $\mathcal{R}$ is a five-fold integral. Straightforward numerical integration of $\mathcal{R}$ is difficult because the time required (on even a large computer) is prohibitively long. We, therefore, examine an approximate technique

based on a curve fitted analytic approximation to $\frac{1}{n} (\bar{y}_{r0} - 1)$

The rigid sphere expression for $\frac{1}{n} (\bar{y}_{r0} - 1)$ gives some indication of the type of analytic approximation which best fits the soft potential curve. For rigid spheres in the range $0 \leq \lambda^* \leq 2$ we have

$$\frac{1}{n} (\bar{y}_{r0} - 1) = \frac{4\pi\sigma^3}{3} \left[1 - \frac{3}{4}\lambda^* + \frac{\lambda^{*3}}{16} \right] \quad (5.2 - 1)$$

and for $\lambda^* > 2$

$$\frac{1}{n} (\bar{y}_{r0} - 1) = 0 \quad (5.2 - 2)$$

This curve is simply related to the radial distribution function for $\lambda^* > 1$. The cubic polynomial in the range $1 \leq \lambda^* \leq 2$ assumes its largest value at $\lambda^* = 1$, and decreases monotonically to zero at $\lambda^* = 2$. This corresponds to the fact that two rigid spheres at these separation distances can experience more collisions with a third molecule which force them together than that separate them. However, as the separation distance increases, this effect becomes smaller because less volume between the two colliding molecules is excluded from a third molecule.

Analogous regions exist in the soft potential case; but the demarcation between the regions is not sharp. The transition region at roughly two molecular diameters is highly temperature dependent for potentials which are attractive at large separations. At high temperatures this transition region is relatively unimportant and

$\frac{1}{n} (\bar{y}_{r0} - 1)$ is qualitatively similar to the rigid sphere

curve. The molecular size is relatively smaller, however, due to the increased penetration of two molecules in a high energy collision. At lower temperatures, there is a maximum in the curve at roughly two molecular diameters. This is due to the favorable packing of second nearest neighbors. There is no analogous maximum in the rigid sphere curve because there is no attraction to favor this separation.

For the purpose of curve fitting, the function $\frac{1}{n\sigma^3} [\bar{y}_{\text{LoJ}} - 1]$ was calculated for the Lennard-Jones potential at five widely separated temperatures and for a number of separation distances. The calculations were carried out on a CDC 1604; about 3-1/2 minutes being required for a given temperature and separation distance. The calculated results are given in Table 1. Included also (in parentheses) are a number of values obtained by de Boer and Michels³⁷. These results are illustrated in Fig. 5. For comparison, the rigid sphere curve is also given.

The integrand of the $\mathcal{R}$ integral heavily weights the region of λ^* between one and two molecular diameters. For smaller values of λ^* , the factor $e^{-\frac{\epsilon}{\lambda^*}}$ makes the integrand effectively zero; for larger values of λ^* the gradient of the potential has this effect. It is, therefore, most important to accurately curve fit $\frac{1}{n\sigma^3} [\bar{y}_{\text{LoJ}} - 1]$ in the region of λ^* between one and two molecular diameters. The function can be well fitted in this region by a cubic polynomial. From our rigid sphere analysis, such a behavior is reasonable. For values of λ^* exceeding two molecular diameters the function $\frac{1}{n\sigma^3} [\bar{y}_{\text{LoJ}} - 1]$ undergoes a decay to zero with increasing λ^* . This decay to zero is approximated (purely empirically) by an exponential function. As discussed previously,

TABLE I
VALUES OF $\frac{1}{n G^3} [\bar{y}_{[0]} - 1]$

λ^*	$T^*=1$	$T^*=1$	$T^*=2$	$T^*=2$	$T^*=8$	$T^*=30$	$T^*=100$
.4							1.2472
.5						1.4183	1.0754
.6						1.2108	0.9084
.7	3.1623		1.2064		1.2051	1.0134	0.7496
.8	2.3259		0.8225		0.9693	0.8285	0.6013
.9	1.6688	(1.652)		(0.501)	0.7547	0.6576	0.4655
1.0	1.1592	(1.204)		(0.237)	0.5617	0.5024	0.3438
1.2		(0.480)		(-0.147)	0.2423	0.2445	0.1496
1.4		(0.182)		(-0.362)	0.0167	0.0661	0.0313
1.6	0.1977	(0.178)		(-0.425)	-0.1075	-0.0215	-0.0068
1.8		(0.423)		(-0.329)	-0.1230	-0.0294	-0.0071
2.0		(0.886)		(-0.103)	-0.0708	-0.0167	-0.0039
2.2		(1.211)		(-0.080)	-0.0313	-0.0085	-0.0021
2.4	1.0221	(0.999)	0.1168	(0.134)	-0.0135	-0.0045	-0.0011
2.6	0.6948			(0.092)	-0.0062	-0.0025	-0.0007
2.8	0.4513		0.0676	(0.065)	-0.0031	-0.0015	-0.0004
3.0	0.2929	(0.281)		(0.046)	-0.0017	-0.0009	
3.2	0.1927		0.0313		-0.0010		
3.4	0.1290		0.0213		-0.0007		
3.6	0.0880						
3.8	0.0611						

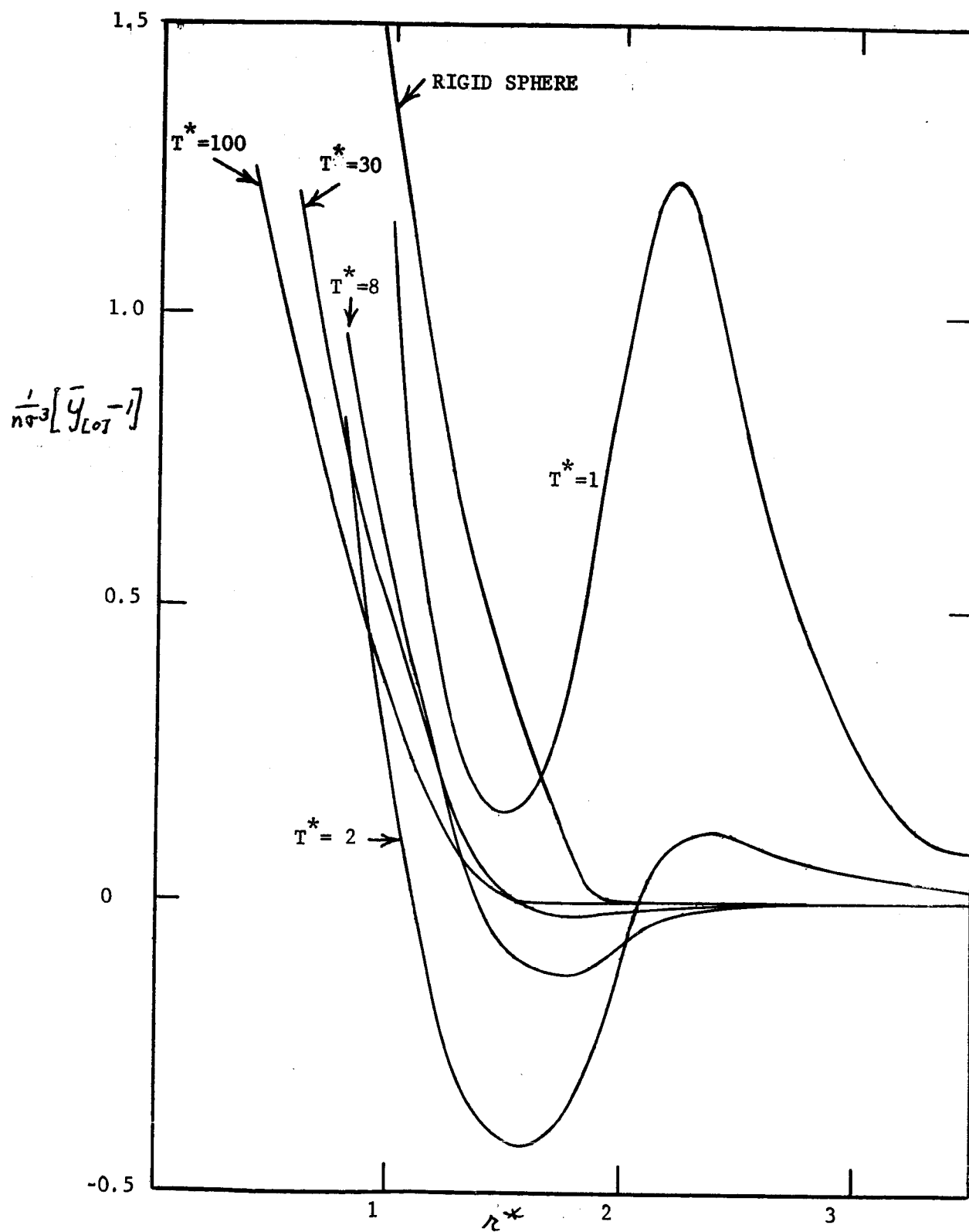


Fig. 5

The Function $\frac{1}{n\sigma^3} [\bar{y}_{L01} - 1]$ for Various Temperatures

there is a transition region which is highly dependent on temperature between the range of applicability of these two approximations.

This transition region is more important at low temperatures than at high temperatures; but even at low temperatures the contribution to $\mathcal{R}$ is small. The curve fitted approximations at the various temperatures are given in Table 2.

The numerical evaluation of the collisional contributions to the transport virial coefficient has been discussed in detail by Curtiss, McElroy, and Hoffman³⁶. The computational problems involved in evaluating the integral $\mathcal{R}$ are quite similar to those encountered in the earlier study.

Section 5.3 Numerical Values of the Reduced Transport Virial Coefficients.

From equations (4.2 - 21) and (4.2 - 22) we have

$$B_{\lambda}^* - (B_{\lambda}^*)_{s.c.} = B_{\eta}^* - (B_{\eta}^*)_{s.c.} = \frac{-\mathcal{R}}{8\pi^2\sigma^3\Omega^{(2,2)*}} \quad (5.3 - 1)$$

This quantity along with $(B_{\eta}^*)_{s.c.}$ and $(B_{\lambda}^*)_{s.c.}$ (as given by Curtiss, McElroy and Hoffman³⁶), and B_{η}^* and B_{λ}^* are given in Table 3. The values of $\Omega^{(2,2)*}$ are taken from Molecular Theory of Gases and Liquids by Hirschfelder, Curtiss and Bird³⁸.

The tabulated quantities are illustrated in Figs. 6 and 7.

Although Curtiss, McElroy and Hoffman considered rigorously only the collisional corrections to the transport virial coefficients, they corrected their results in an intuitive manner to account for three body interactions. The correction is based on a method

TABLE 2

ANALYTIC APPROXIMATIONS FOR $\frac{1}{n\sigma^2} [\bar{y}_{[0]} - 1]$

T^*	Range of r^*	Approximation
1	0 - 2.0	$11.657 - 17.603r^* + 8.1347r^{*2} - 1.0122r^{*3}$
	2.0 - 2.6	$-129.75 + 164.00r^* - 67.872r^{*2} + 9.2667r^{*3}$
	2.6 - ∞	$190.64\exp(-2.1594r^*)$
2	0 - 2.0	$5.1084 - 7.5927r^* + 2.9521r^{*2} - .22929r^{*3}$
	2.0 - ∞	$(11.864 + 8.2291 \frac{1}{(r^*-1.8)} - 6.2996 \frac{1}{(r^*-1.8)^2} + .79720 \frac{1}{(r^*-1.8)^3}) \exp(-1.9241r^*)$
8	0 - 1.8	$3.3345 - 3.5777r^* + .66075r^{*2} + .14427r^{*3}$
	1.8 - 2.0	$-.59320 + .26120r^*$
	2.0 - ∞	$-248.43\exp(-4.0816r^*)$
30	0 - 1.6	$2.5863 - 2.4615r^* + .14083r^{*2} + .23685r^{*3}$
	1.6 - 1.8	$.64644 - .93865r^* + .32867r^{*2}$
	1.8 - ∞	$-7.5857\exp(-3.0859r^*)$
100	0 - 1.5	$2.0038 - 1.9103r^* - .019016r^{*2} + .26942r^{*3}$
	1.5 - 1.8	$1.0899 - 1.2932r^* + .37987r^{*2}$
	1.8 - ∞	$-1.5087\exp(-2.9777r^*)$

TABLE 3

VALUES OF THE SECOND VIRIAL COEFFICIENTS FOR VISCOSITY
AND THERMAL CONDUCTIVITY

T^*	1	2	8	30	100
$(B_\eta^*)_{s.c.}$	-1.2129	0.6942	0.8991	0.6827	0.5156
$(B_\lambda^*)_{s.c.}$	4.6662	3.0513	1.6967	1.1169	0.8008
$\frac{-R}{8\pi^2\sigma^3\Omega(2p)^*}$	-1.226	-0.3512	-0.7737	-0.7804	-0.6487
B_η^*	-2.439	0.3430	0.1254	-0.0977	-0.1331
B_λ^*	3.440	2.7001	0.9230	0.3365	0.1521

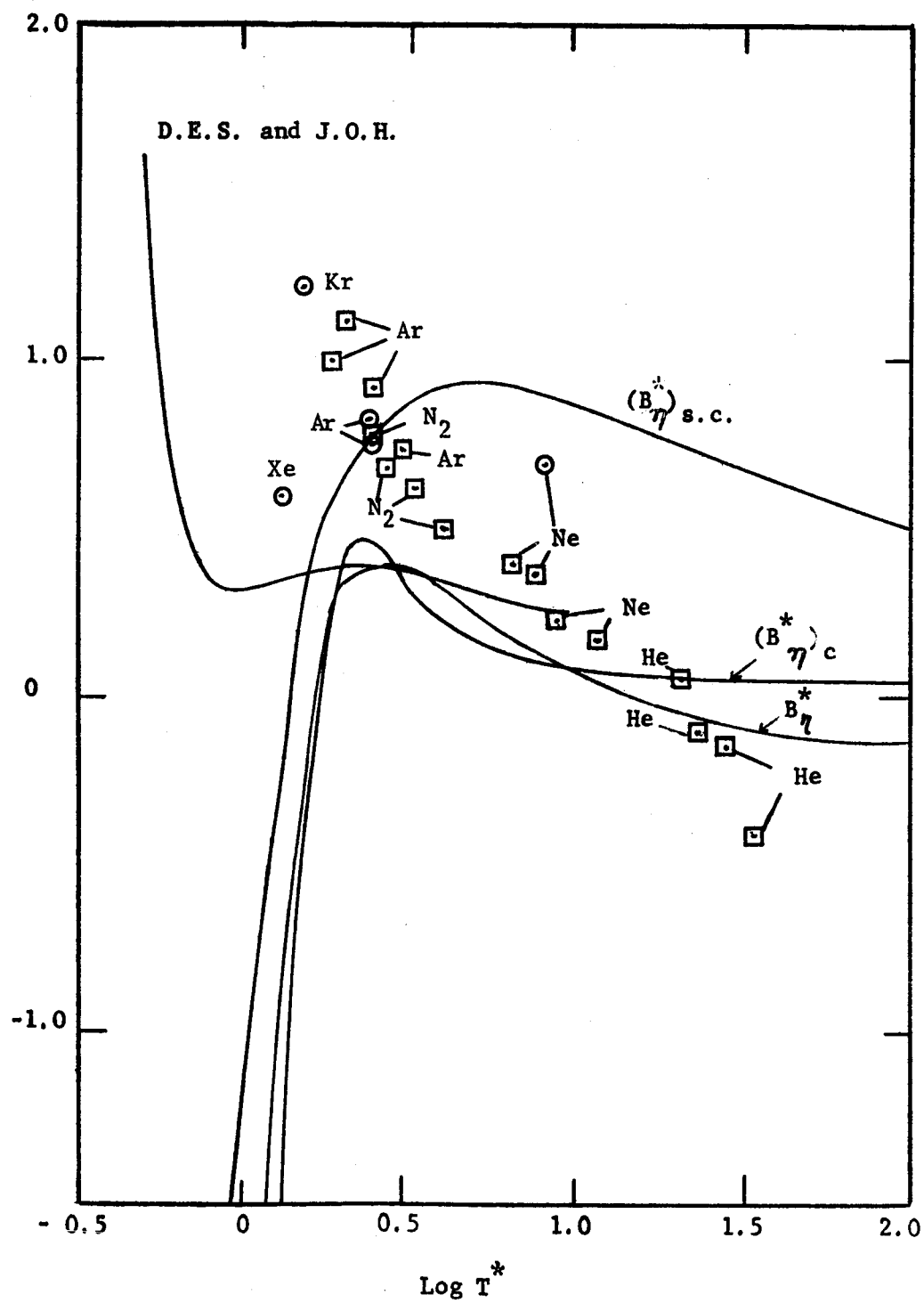
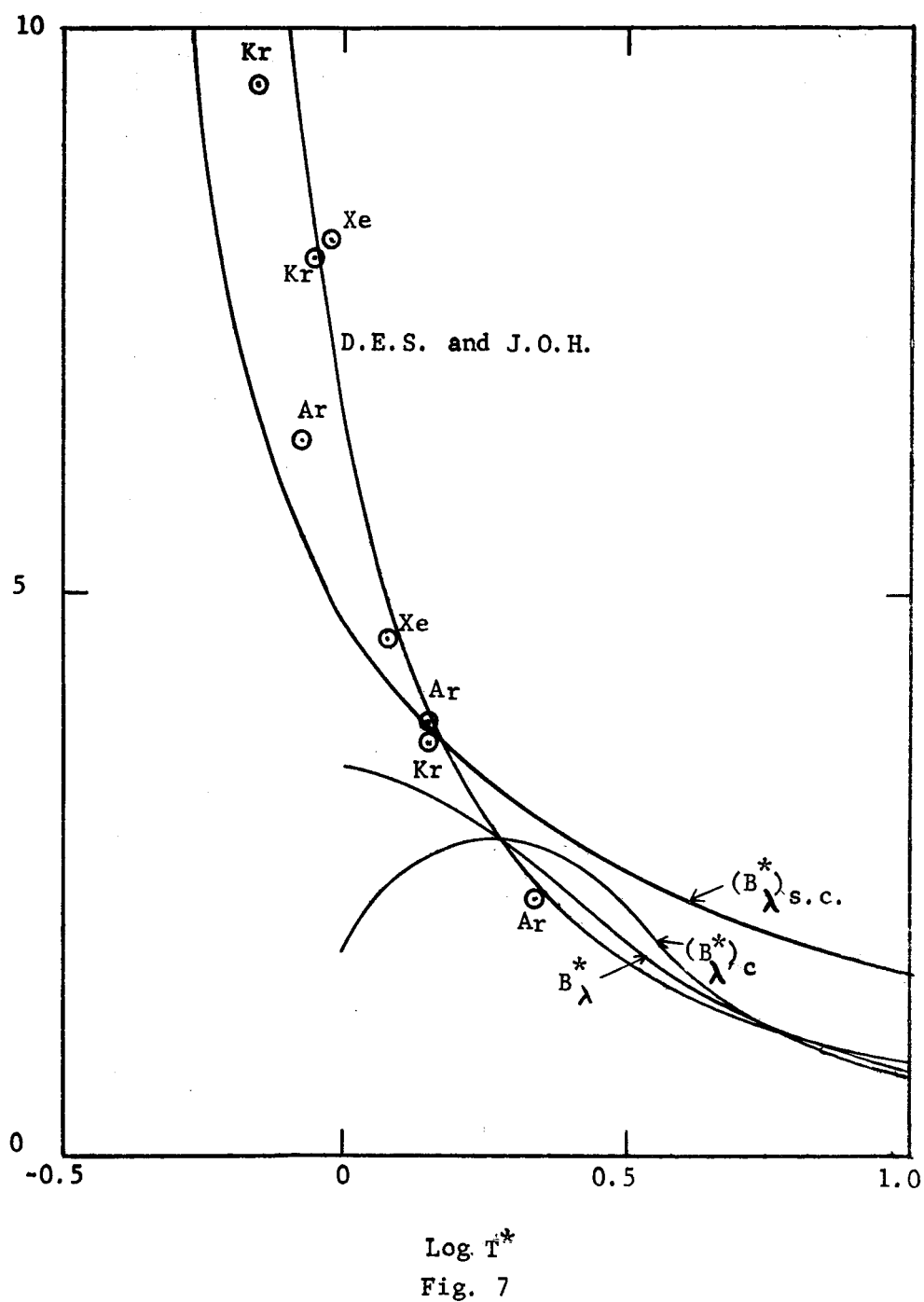


Fig. 6

The Viscosity Second Virial Coefficient



The Thermal Conductivity Second Virial Coefficient

suggested by Enskog for the approximate application of his work on the rigid sphere gas⁶ to a realistic system. Their corrected coefficients are included in the figures, and are labeled $(B_{\eta}^*)_c$ and $(B_{\lambda}^*)_c$. Also illustrated in the figures are the results of a theoretical study by Stogryn and Hirschfelder¹² on the effect of stable and metastable bound molecular pairs on the transport virial coefficients.

Experimental points from two sources are included in the figures. The circled points are taken from the paper by Stogryn and Hirschfelder. The viscosity points in squares are recent values given by Flynn, Hanks, Lemaire and Ross³⁹. The parameters used to reduce their values to corresponding states values are given by Curtiss, McElroy and Hoffman³⁶.

Experimentally, B_{η}^* as a function of T^* is large and positive at low T^* . As T^* is increased, the value decreases and becomes negative. The shape of the B_{λ}^* curve is similar at low temperatures; but, due to a lack of data, it can only be extrapolated at high temperatures.

Both theoretical curves fit the data reasonably well at high temperatures. In particular, B_{η}^* is negative at high temperatures and approaches zero asymptotically from below. This is in contrast with the intuitively obtained quantity $(B_{\eta}^*)_c$ which approaches zero from above. The deviation between theory and experiment at low temperatures is probably due to the effect of bound states which have not been treated in a satisfactory theoretical manner.

CHAPTER VI

SUMMARY

The purpose of this study is the investigation of the density expansions of the transport coefficients. We do this by formally considering the equations which govern the time evolution of the lower order distribution functions. This approach leads us to a derivation of a modified or generalized Boltzmann equation which includes the effect of three body interactions. From the solution of this equation, we obtain expressions for the transport coefficients.

In Chapter II we develop a factorization principle which is a generalization of the usual molecular chaos assumption. This principle is used to approximate the $(h+1)^{th}$ order distribution function in terms of the h lower order distribution functions. We truncate the B.B.G.K.Y. hierarchy by the use of this approximation. The truncation results in a closed but coupled system of equations for the h lower order distribution functions. We compare this set of equations with the formal expansion of the Boltzmann equation given by Hollinger and Curtiss¹⁰.

The Hollinger and Curtiss expansion of the Boltzmann equation is based on a formal solution for $f^{(2)}$ in terms of $f^{(1)}$. This expression for $f^{(2)}$, when substituted into the $f^{(1)}$ B.B.G.K.Y. equation, yields a Boltzmann equation whose collision integral is given as a series expansion. The first term in the expansion gives rise to the ordinary collision integral plus the collisional corrections suggested by Green⁷. The second term in the expansion of the collision integral describes three body collisional effects.

This term involves the dynamics of two and three body collisions in a very complex manner. We show explicitly that this three body term also arises when the B.B.G.K.Y. hierarchy is terminated by the use of the factorization principle for $f^{(3)}$.

Our approach differs from that of Hollinger and Curtiss, however, in that we do not formally solve the $f^{(2)}$ equation. Instead we consider the $f^{(1)}$ and $f^{(2)}$ equations simultaneously. We approximate the solution of the $f^{(2)}$ equation to derive a Boltzmann equation which takes into account three body interactions in an approximation. For the special case of rigid spheres, this equation reduces to the Enskog dense gas equation. The Boltzmann equation derived in this manner does not depend in detail on the dynamics of three body collisions. This equation is solved; and from the solution expressions for the transport coefficients are derived as density expansions. The linear terms in the density expansions contain separate collisional and three body contributions. The collisional contributions have been considered previously by Snider and Curtiss¹¹. The three body contributions are new to this work.

These results apply only to the non-bound state contributions to the transport coefficients. Bound states have not yet been handled properly in a theoretical manner; the application of the present formalism to this problem will be considered in a later study.

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Recently Curtiss, McElroy and Hoffman have calculated the collisional contributions to the transport coefficients of a gas of molecules, which interact according to a Lennard-Jones potential.

In Chapter V we complete these results by calculating the three body collisional contributions. The theoretical results are compared with experimental values.

APPENDIX A

Equation (2.4 - 7) gives the general expression for $f^{(s)}$ in any factorization region:

$$f^{(s)} = \frac{p_{s-1}^{(s)}(f^{(s-1)}) p_{s-3}^{(s)}(f^{(s-3)}) p_{s-5}^{(s)}(f^{(s-5)}) \dots}{p_{s-2}^{(s)}(f^{(s-2)}) p_{s-4}^{(s)}(f^{(s-4)}) p_{s-6}^{(s)}(f^{(s-6)}) \dots} \quad (\text{A} - 1)$$

We now establish the validity of this expression. It is sufficient to prove that this statement gives the correct factorization when the s particles are divided into two groups A and B containing a and b particles respectively. Any further factorization of the two groups is trivial. Thus we must show that

$$f^{(s)} = f_A^{(a)} f_B^{(b)} \quad (\text{A} - 2)$$

where $a + b = s$. The method of proof is to compute the power to which each term appears in the factored expression by computing the total contribution of each set of combinations to that term.

Let us first consider the term $f_A^{(a)}$. The set of combinations $p_{s-1}^{(s)}(f^{(s-1)})$ contributes to the numerator through such factorizations as

$$f_{A, B-1}^{(s-1)} = f_A^{(a)} f_{B-1}^{(b-1)} \quad (\text{A} - 3)$$

Since any of the b particles can be omitted in the set $B-1$, there are $\frac{b!}{(b-1)!} = b$ terms of this type. The term $f_A^{(a)}$ appears in the denominator through the factorization of the set of combinations

$\rho_{s-2}^{(s)} / f^{(s-2)}$. Such a factorization is

$$f_{A, B-2}^{(s-2)} = f_A^{(a)} f_{B-2}^{(b-2)} \quad (\text{A} - 4)$$

There are $\frac{b!}{(b-2)!2!} = \frac{b(b-1)}{2}$ different possible $f_{B-2}^{(b-2)}$.

By continuing this reasoning to show the successive contributions of

$\rho_{s-3}^{(s)} / f^{(s-3)}$, $\rho_{s-4}^{(s)} / f^{(s-4)}$, etc., we find the power, n_A , to which $f_A^{(a)}$ is raised in the factored expression is

$$n_A = \sum_{i=1}^b (-1)^{i+1} \frac{b!}{(b-i)!i!} \quad (\text{A} - 5)$$

But since

$$\sum_{i=0}^b (-1)^i \frac{b!}{(b-i)!i!} = (1-1)^b = 0 \quad (\text{A} - 6)$$

it follows that

$$n_A = 1 \quad (\text{A} - 7)$$

Similar reasoning shows that

$$n_B = 1 \quad (\text{A} - 8)$$

In a similar manner we find that any term of the type $f_{A-1}^{(a-1)}$ appears in the numerator $\frac{b!}{b!0!} = 1$ times from the factorization of the combination set $\rho_{s-1}^{(s)} / f^{(s-1)}$. The set $\rho_{s-2}^{(s)} / f^{(s-2)}$ contributes in the denominator $\frac{b!}{(b-1)!1!} = b$ times. Continuing this reasoning we find the power n_{A-1} to which any term of the

type $f_{A-1}^{(a-1)}$ is raised is

$$n_{A-1} = \sum_{i=0}^b (-1)^i \frac{b!}{(b-i)! i!} = 0 \quad (\text{A} - 9)$$

In an analogous manner we establish that for $j \neq 0$

$$n_{A-j} = n_{B-j} = 0 \quad (\text{A} - 10)$$

and, therefore,

$$f^{(s)} = f_A^{(a)} f_B^{(b)} \quad (\text{A} - 11)$$

APPENDIX B

In this appendix, we evaluate the integrals $\int (\underline{I} : \underline{U}) W_1^2 d\underline{W}_1$ and $\int (\underline{I} : \underline{U}) W_1^4 d\underline{W}_1$ which arise in the solution of the integral equations.

Let us consider the integral $\int (\underline{I} : \underline{U}) W_1^2 d\underline{W}_1$. From the definition of $\underline{I}$ given by equation (3.1-12), we have

$$\begin{aligned} & \int (\underline{I} : \underline{U}) W_1^2 d\underline{W}_1 \quad (\text{B - 1}) \\ &= \frac{2}{n^2 m} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{x} d\underline{r}' W_1^2 \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{x}} \right)_{\underline{r}'} \left(\underline{x}' \cdot \underline{r}' f_{1[0]}^{-''} f_{2[0]}^{-''} e^{-\frac{\phi^{(1,2)}}{k T}} \right) \\ &= \frac{2}{n^2 m} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \left[\int d\underline{r} d\underline{x} d\underline{r}' \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{x}} \right)_{\underline{r}'} \left[W_1^2 (\underline{x}' \cdot \underline{r}') f_{1[0]}^{-''} f_{2[0]}^{-''} e^{-\frac{\phi^{(1,2)}}{k T}} \right] \right. \\ & \quad \left. - \int d\underline{r} d\underline{x} d\underline{r}' \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{x}} W_1^2 \right)_{\underline{r}'} (\underline{x}' \cdot \underline{r}') f_{1[0]}^{-''} f_{2[0]}^{-''} e^{-\frac{\phi^{(1,2)}}{k T}} \right] \end{aligned}$$

where $\underline{x}$ and $\underline{r}$ are related to $\underline{W}_1$ and $\underline{W}_2$ by the equations

$$\underline{r} = \frac{1}{\sqrt{2}} (\underline{W}_1 + \underline{W}_2) \quad (\text{B - 2})$$

and

$$\underline{x} = \frac{1}{\sqrt{2}} (\underline{W}_2 - \underline{W}_1) \quad (\text{B - 3})$$

By Gauss theorem we have

$$\begin{aligned} & \int (\underline{I} : \underline{U}) W_1^2 d\underline{W}_1 \quad (\text{B - 4}) \\ &= -\frac{2}{m} \left(\frac{2 k T}{m} \right)^{\frac{3}{2}} \left(\frac{m}{2 \pi k T} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{x} d\underline{r}' \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \left(\frac{\partial}{\partial \underline{x}} W_1^2 \right)_{\underline{r}'} (\underline{x}' \cdot \underline{r}') e^{-\frac{\underline{x}^2}{2}} e^{-\frac{\underline{r}^2}{2}} e^{-\frac{\phi^{(1,2)}}{k T}} \end{aligned}$$

where we have made use of the relation

$$\bar{f}_{1[0]}^{(1)} \bar{f}_{2[0]}^{(1)} = n^2 \left(\frac{m}{2\pi kT} \right)^3 e^{-\gamma^2} e^{-r^2} \quad (\text{B - 5})$$

The quantity W_i^2 is given by

$$W_i^2 = \frac{1}{2} (r^2 - 2 \underline{\gamma} \cdot \underline{r} + \gamma^2) \quad (\text{B - 6})$$

We can integrate over $\underline{r}$ to yield

$$\begin{aligned} & \int (\underline{I} : \underline{U}) W_i^2 d\underline{W}_i \\ &= \frac{1}{m} \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{\gamma} \frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{\gamma}} (\gamma^2) \left\{ (\underline{\gamma}' \cdot \underline{r}') e^{-\gamma^2} e^{-\frac{\phi^{(1,2)}}{kT}} \right\} \end{aligned} \quad (\text{B - 7})$$

From the identity of equation (2.6 - 18) we have

$$\frac{\partial \phi^{(1,2)}}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{\gamma}} (\gamma^2) = -2kT \underline{\gamma}' \cdot \frac{\partial}{\partial \underline{r}'} (\gamma'^2) \quad (\text{B - 8})$$

Hence

$$\begin{aligned} & \int (\underline{I} : \underline{U}) W_i^2 d\underline{W}_i \\ &= \frac{2kT}{m} \left(\frac{m}{2\pi kT} \right)^{\frac{3}{2}} \int d\underline{r} d\underline{\gamma} \underline{\gamma}' \cdot \frac{\partial}{\partial \underline{r}'} (\gamma'^2) \left\{ (\underline{\gamma}' \cdot \underline{r}') e^{-\gamma'^2} \right\} \end{aligned} \quad (\text{B - 9})$$

or equivalently

$$\begin{aligned} & \int (\underline{I} : \underline{U}) W_i^2 d\underline{W}_i \\ &= \frac{1}{\pi^{\frac{3}{2}}} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left[\int d\underline{r} d\underline{\gamma} \underline{\gamma}' \cdot \frac{\partial}{\partial \underline{r}'} \left\{ \gamma'^2 (\underline{\gamma}' \cdot \underline{r}') e^{-\gamma'^2} \right\} \right. \\ & \quad \left. - \int d\underline{r} d\underline{\gamma} \gamma'^2 (\gamma')^2 e^{-\gamma'^2} \right] \quad (\text{B - 10}) \end{aligned}$$

In the first integral in equation (B - 10) we make the coordinate transformation $(\underline{x}, \underline{z}) \rightarrow (\underline{x}', \underline{z}')$ and write $\underline{z}'$ in the particular coordinate system discussed in Sec. 2.6. We then have

$$\begin{aligned}
 & \int (\underline{I} : \underline{U}) W_i^2 d\underline{W}_i \\
 &= \frac{1}{\pi^{\frac{3}{2}}} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left[\int d\underline{x}' \int d\underline{z} d\underline{b} d\underline{b} \, x' \frac{\underline{z}}{z^2} \left\{ x^2 (\underline{z}')^2 e^{-x'^2} \right\} \right. \\
 & \quad \left. - \int d\underline{z} d\underline{x} \, x^2 (\underline{z}')^2 e^{-x'^2} \right] \\
 &= \frac{1}{\pi^{\frac{3}{2}}} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left[\int d\underline{x}' \int d\underline{z} d\underline{b} d\underline{b} (\underline{z}')^4 e^{-x'^2} \right. \\
 & \quad \left. - \int d\underline{z} d\underline{x} \, x^2 (\underline{z}')^2 e^{-x'^2} \right] \\
 &= \frac{1}{\pi^{\frac{3}{2}}} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left\{ \int d\underline{z} d\underline{x} \left[(\underline{z}')^4 - x^2 (\underline{z}')^2 \right] e^{-x'^2} \right\} \\
 &= \frac{1}{\pi^{\frac{3}{2}}} \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left\{ \int d\underline{z} d\underline{x} \left[x^2 \frac{\phi^{(1,2)}}{kT} + \left(\frac{\phi^{(1,2)}}{kT} \right)^2 \right] e^{-x^2} e^{-\frac{\phi^{(1,2)}}{kT}} \right\}
 \end{aligned}$$

We can integrate over $\underline{x}$ to yield

$$\begin{aligned}
 & \int (\underline{I} : \underline{U}) W_i^2 d\underline{W}_i \\
 &= \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \int d\underline{z} \left[\frac{3}{2} \left(\frac{\phi^{(1,2)}}{kT} \right) + \left(\frac{\phi^{(1,2)}}{kT} \right)^2 \right] e^{-\frac{\phi^{(1,2)}}{kT}}
 \end{aligned}
 \tag{B - 12}$$

But

$$\frac{\phi^{(1,2)}}{kT} e^{-\frac{\phi^{(1,2)}}{kT}} = T \frac{\partial}{\partial T} \left(e^{-\frac{\phi^{(1,2)}}{kT}} - 1 \right) \quad (\text{B} - 13)$$

and

$$\left(\frac{\phi^{(1,2)}}{kT} \right)^2 e^{-\frac{\phi^{(1,2)}}{kT}} = \left[T^2 \frac{\partial^2}{\partial T^2} + 2T \frac{\partial}{\partial T} \right] \left(e^{-\frac{\phi^{(1,2)}}{kT}} - 1 \right) \quad (\text{B} - 14)$$

Hence

$$\int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i \quad (\text{B} - 15)$$

$$= \left(\frac{m}{2kT} \right)^{\frac{1}{2}} \left[\frac{\gamma}{2} T \frac{\partial}{\partial T} + T^2 \frac{\partial^2}{\partial T^2} \right] \int d\underline{R} \left[e^{-\frac{\phi^{(1,2)}}{kT}} - 1 \right]$$

The second virial coefficient, B , is given by

$$B = -\frac{1}{2} \int \left(e^{-\frac{\phi^{(1,2)}}{kT}} - 1 \right) d\underline{R} \quad (\text{B} - 16)$$

Thus, we have

$$\begin{aligned} & \int (\underline{I} : \underline{U}) w_i^2 d\underline{w}_i \\ &= - \left(\frac{2m}{kT} \right)^{\frac{1}{2}} \left[\frac{\gamma}{2} T \frac{\partial}{\partial T} B + T^2 \frac{\partial^2}{\partial T^2} B \right] \end{aligned} \quad (\text{B} - 17)$$

By an analogous integration procedure we find that

$$\begin{aligned} & \int (\underline{I} : \underline{U}) w_i^4 d\underline{w}_i \\ &= -\frac{1}{2} \left(\frac{2m}{kT} \right)^{\frac{1}{2}} \left[40 T \frac{\partial}{\partial T} B + \frac{31}{2} T^2 \frac{\partial^2}{\partial T^2} B + T^3 \frac{\partial^3}{\partial T^3} B \right] \end{aligned} \quad (\text{B} - 18)$$

and, thus, the integrals $\int (\underline{I} : \underline{U}) \underline{w}_i^2 d\underline{w}_i$ and $\int (\underline{I} : \underline{U}) \underline{w}_i^4 d\underline{w}_i$ can be written in terms of the second virial coefficient, B , and its temperature derivatives.

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