CALCULATION OF THE TRANSPORT COEFFICIENTS
FOR DILUTE GASES USING AN
ITERATIVE SOLUTION OF BOLTZMANN'S EQUATION

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Summary

The second approximation to Boltzmann's equation for dilute gases, in the Chapman-Enskog form, is solved for several different potential models by using an iterative procedure. This method is presented as an alternative to the standard one of Chapman and Cowling. The first order perturbation function, $ \phi$, to the local Maxwellian distribution, $f^{(0)}$, is obtained as an infinite series

$$\phi = \sum_{i=0}^{\infty} \phi^{(i)},$$

where the $\phi^{(i)}$'s are obtained by repeated iterations of the Boltzmann equation. The transport coefficients, such as thermal conductivity, $\lambda$, and viscosity, $\eta_s$, are obtained from $\phi$ as infinite series

$$\lambda = \sum_{i=0}^{\infty} \lambda^{(i)}; \quad \eta_s = \sum_{i=0}^{\infty} \eta_s^{(i)}.$$

In the case of the Maxwellian and Pseudo-Maxwellian potential models, for a single component gas, both the $\phi^{(i)}$'s and $\lambda^{(i)}$'s and $\eta_s^{(i)}$'s are found to follow exact geometrical progression which can be summed. The transport coefficient obtained by performing these sums are found to correspond to the analytical values obtained by the Chapman-Cowling method. For the rigid sphere model the $\lambda^{(i)}$'s still seem to approximate closely to a geometrical progression. On assuming an exact geometrical progression for the $\lambda^{(i)}$'s, one obtains a value for the thermal conductivity which is in close agreement with that obtained by Chapman-Cowling.
The iterative method is extended to deal with binary mixtures for the case of Maxwellian and Pseudo-Maxwellian potential models, where exact geometrical progressions are again exhibited, and values for the transport coefficients are found to correspond to those for the Chapman-Cowling method.

The significance of the form of the results obtained by the iterative procedure is discussed particularly with regard to the possibility of extending the method to deal with more general repulsive potentials and higher order mixtures.
To my Mother and Father.
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Introduction

We are interested in being able to calculate the transport coefficients for dilute gases and gas mixtures. These transport coefficients are obtained from the flux equations which involve the velocity distribution function(s), $f_i(r, v_i, t)$. The form of these distribution functions can be found by solving the Boltzmann equations which contain these functions. For a single gas the equation has the following form

$$\frac{\partial f}{\partial t} + v \cdot \frac{\partial f}{\partial v} + \frac{F}{m} \cdot \frac{\partial f}{\partial v} = \int \left\{ f(v') f(u') - f(v) f(u) \right\} g \text{ } b \text{ } db \text{ } de \text{ } du \quad (0.1)$$

On examining (0.1) we can see that the Boltzmann equation is an integro-differential equation which, in its present form, is exceedingly difficult to solve for $f$.

However, equation (0.1) can be simplified considerably if we remember that we are interested in gases which contain only small gradients in such macroscopic quantities as: temperature, $T$; density, $n$; and mass average velocity, $u_0$. This assumption was utilised by Chapman-Enskog in their standard method of solution of the Boltzmann equation, which involves expanding the distribution function, $f$, in the infinite series

$$f = f^{(0)} + f^{(1)} + ...$$

Using this standard method, the second approximation to the distribution function, $f^{(1)}$, from which we can obtain the transport coefficients, is written as
\[ f^{(1)} = f^{(o)}(1 + \phi) \]

where \( f^{(o)} \) is the local Maxwellian distribution function, whose form is known, and \( \phi \) is a perturbation function. Substituting this form of \( f^{(1)} \) into equation (0.1), we have, on eliminating the time variation by using the equations of change

\[
- (\vec{S} - \alpha \vec{V}^2) \vec{V} + 2\alpha \vec{V}^0 \vec{V} \cdot \vec{V} u_o
\]

\[
= \int f^{(o)}(U) \{ \phi(U') + \phi(V') - \phi(U) - \phi(V) \} g b \, db \, de \, du .
\]

(0.2)

This is the so-called second approximation to the Boltzmann equation.

The transport coefficients can be expressed in terms of integrals involving \( \phi \) namely

\[
\alpha^{[1]} = -\lambda \vec{V} \cdot \vec{T} = \int \frac{1}{2} m \vec{V}^2 \vec{V} f^{(o)} \phi \, dv , \quad (0.3)
\]

\[
\beta^{[1]} = -\eta_s \vec{V}^s : \vec{U}_0 = \int m \vec{V} \vec{V} f^{(o)} \phi \, dv , \quad (0.4)
\]

where

\[
\lambda \text{ is the coefficient of thermal conductivity ,}
\]

and

\[
\eta_s \text{ is the coefficient of viscosity .}
\]

On examining equations (0.2, 3 and 4) we can see that the evaluation of the transport coefficients involves solving equation (0.2) for \( \phi \).
In the standard method of solution developed by Chapman and Cowling, the perturbation function, \( \phi \), is expanded in two convergent series of Sonine polynomials

\[
\phi = -\frac{1}{n} \left( \frac{2kT}{m} \right)^\frac{1}{2} \sum_{n=0}^{\infty} A(V) V \cdot V \ln T - \frac{2}{n} B(V) V^o V : V u_\infty ,
\]  

(0.5)

where

\[
A(V) = \sum_{p=0}^{\infty} a_p S_{\frac{3}{2}}^{(p)}(aV^2)
\]

and

\[
B(V) = \sum_{p=0}^{\infty} b_p S_{\frac{5}{2}}^{(p-1)}(aV^2) .
\]

It can be shown that the thermal conductivity coefficient, \( \lambda \), depends only on the coefficient \( a_1 \) and the viscosity, \( \eta_s \), only on \( b_1 \) but the determination of these coefficients, \( a_1 \) and \( b_1 \), involves solving two infinite sets of equations. However, a method of successive approximations developed by Enskog is used to overcome this intractible problem. In most cases, the successive approximations to \( a_1 \) and \( b_1 \) and the corresponding transport coefficients \( \lambda \) and \( \eta_s \), namely

\[
[\lambda]_1 , \quad [\lambda]_2 \ldots ,
\]

converge so rapidly that the fourth degree of approximation, namely \( [\lambda]_4 \) and \( [\eta_s]_4 \), may be taken as correct to within one-tenth of one per cent.

A possible alternative method of attempting to find a solution to the Boltzmann equation, which is to be presented in this thesis,
is an iterative method. This method has already been used with some success in analogous problems in the field of transport phenomena of electrons in metals. A particular instance is the work of M.C. Jones\textsuperscript{(1,2)} on the calculation of an approximation expression for the Galvanomagnetic tensor using an iterative procedure.

This success prompted the idea that such a method might be used successfully in the field of transport phenomena in gases.

The present work, part of which has already been presented elsewhere\textsuperscript{(3,4,5)} is, therefore, concerned with applying an iterative method to the solution of the Boltzmann equation; firstly, in the case of pure gases using several different molecular models, and then to more general cases involving gas mixtures.

The essentials of the iterative method, together with the results obtained, are as follows. The second approximation to Boltzmann's equation, which we are interested in solving, is written

\[
- (S_2 - \alpha V^2) \nabla \cdot \frac{\nabla T}{T} + 2\alpha \nabla^o \nabla : \nabla u_o = - \phi(V) \int \! f^{(0)}(U) \, g \, d\beta \, d\varepsilon \\
+ \xi \int \! f^{(0)}(U) \{ \phi(U') + \phi(V') - \phi(U) \} \, g \, d\beta \, d\varepsilon \, d\mu ,
\]

(0.6)

where $\xi$ is an ordering parameter to be set equal to unity at the end of the calculations.

Equation (0.6) may be written schematically as

\[
X_{c, \eta} = - \phi_{c, \eta} L_0 + \xi L_1 \phi_{c, \eta} ,
\]

(0.7)

where $c$ and $\eta$ are alternative subscripts referring to the gradient terms in temperature and mass average velocity respectively.
In order to perform the iterative procedure we must first expand $\phi$ in the infinite series

$$\phi_{c,\eta}(V) = \sum_{n=0}^{\infty} \zeta^n \phi^{(n)}_{c,\eta}(V). \quad (0.8)$$

On substituting equation (0.8) into equation (0.7), and equating the coefficients of corresponding powers of $\zeta$, we obtain the following iterative relationships

$$X_{c,\eta} = -\phi^{(0)}_{c,\eta}(V) L, \quad \phi^{(n)}_{c,\eta}(V) L = L_{1} \phi^{(n-1)}_{c,\eta},$$

for $n > 1$. \quad (0.9)

Each $\phi^{(i)}_{c,\eta}(V)$ separately is required to satisfy the auxiliary conditions. This can be achieved by redefining $\phi^{(i)}_{c}(V)$ as follows

$$\phi^{(i)}_{c}(V) \frac{V}{T} = \phi^{(i)}_{c}(V) \frac{V}{T} + \alpha^{(i)} \cdot V, \quad (0.10)$$

where $\alpha^{(i)}$ is to be determined from the second auxiliary condition.

Since the transport coefficients are determined from the flux equation, (0.3 and 4), which contain $\phi$, they too can be expanded as infinite series

$$\lambda = \sum_{n=0}^{\infty} \zeta^n \lambda^{(n)} \quad \text{and} \quad \eta_s = \sum_{n=0}^{\infty} \zeta^n \eta^{(n)}_s. \quad (0.11)$$

The transport coefficients have been calculated for three different potential models, and the results obtained are as follows.

For the Maxwellian and Pseudo-Maxwellian models, the $\phi^{(i)}$'s, and hence the $\lambda^{(i)}$'s and $\eta^{(i)}_s$'s, form exact geometrical progres-
sions which can be summed and their analytical values, for the transport coefficients, are the same as those obtained by the standard Chapman-Cowling method. In the case of the rigid sphere model, the $\lambda^{(i)}$s seem to approximate closely to a geometrical progression. On assuming an exact geometrical progression based on $\lambda^{(0)}$ and $\lambda^{(1)}$ we obtain a value for the thermal conductivity which is about 95% of that obtained by Chapman and Cowling; and for one based on $\lambda^{(1)}$ and $\lambda^{(2)}$ we obtain a value as close as 99.3 ± 1.3%. In both cases here, we have used the fourth approximation in the Chapman-Cowling method, namely $[\lambda]^4$, as a reference.

A similar procedure is used to determine the transport coefficients for mixtures and a similar success to that obtained for the single component case is achieved.

The arrangement of the material in the thesis is as follows:

Chapter 1 is concerned with the derivation of the Boltzmann equation, the Chapman-Ensikog regime and the solution of the second approximation to Boltzmann's equation by the standard Chapman-Cowling method.

Chapter 2 outlines the iterative solution of the second approximation to the Boltzmann equation for both single and multi-component gas mixtures.

Chapter 3 deals with the calculation of the transport coefficients, using the iterative method, for a single component gas for Maxwellian and Pseudo-Maxwellian potential models.

In Chapter 4 the transport coefficients for the rigid sphere model are calculated for the single component case using the iterative method.
Chapter 5 deals with the calculation of the transport coefficients for a binary mixture, using the iterative method, for the case of Maxwellian and Pseudo-Maxwellian potential models.

Finally, in Chapter 6 we discuss the significance of the results obtained and compare them with those given by the standard Chapman-Cowling method. A brief discussion is given of the possible avenues for future work.
CHAPTER 1

Derivation of Boltzmann's Equation and the Chapman-Enskog Solution

Introduction

This chapter is concerned with the setting up of a description of a gas using the concept of ensembles. The derivation of Boltzmann's equation from Liouville's equation, together with a physical treatment, is described. The Chapman-Enskog solution of Boltzmann's equation is described along with the calculation of the transport coefficients by expanding the perturbation term, associated with the second approximation to the distribution function, in a convergent series of Sonine Polynomials. Finally, a brief discussion is given of the comparison of the iterative method with that of the Chapman-Cowling method for three different potential models which are being considered in the forthcoming chapters.

1.1 Outline of the Derivation of Boltzmann's Equation using Two Different Methods

In this section, we are concerned with the setting up of a description of a gas using the concept of ensembles due to Gibbs. The Liouville equation, which describes the evolution of the N particle distribution function, \( f^{[N]}(\mathbf{r}^N, \mathbf{p}^N, t) \) is introduced. The derivation of Boltzmann's equation from Liouville's equation, together with a physical treatment is described. An indication of the derivation of the BBGKY hierarchy of equation is given. Finally, the Maxwellian distribution for a gas in equilibrium is introduced.
Since this thesis is concerned with the calculation of the transport properties of dilute gases by solving Boltzmann’s equation, it is appropriate here to discuss the setting up of a possible description of a gas. A typical gas system contains of the order of $10^{23}$ molecules. It is clearly not feasible to specify the individual motion of each of these molecules in order to obtain a time-dependent description of the gas. Further, the properties of a gas are determined experimentally on a macroscopic level so that a complete description, on the microscopic level, is not necessary. One may use a statistical approach using the Gibbs ensembles. In this method one represents the system under consideration by means of an ensemble consisting of a large number of replicas of the system. The state of the ensemble is then described by a distribution function, $f[N]_{\vec{r}^N, \vec{p}^N, t}$ in the phase space of the single system which contains $N$ particles. This distribution function is chosen so that averages over the ensemble are in exact agreement with the macroscopic knowledge of the state of the system at some particular time.

The variation of the distribution function, $f[N]_{\vec{r}^N, \vec{p}^N, t}$ with time is described by the Liouville equation which is as follows

$$\frac{\partial f[N]}{\partial t} + \sum_{k=1}^{N} \left\{ \frac{1}{m_k} \left( \vec{p}_k \cdot \frac{\partial f[N]}{\partial \vec{r}_k} \right) + \left[ F_k + \vec{X}_k \right] \cdot \frac{\partial f[N]}{\partial \vec{p}_k} \right\} = 0$$

(1.1.1)

where $F_k$ is the force on molecule $k$ due to all other molecules and $\vec{X}_k$ is the external force on molecule $k$.

Equation (1.1.1) is difficult to solve since it involves $6N$ variables but, fortunately, we are interested in much lower order distribution functions. We can obtain equations containing these lower order functions, such as $f^{[s]}$, by integrating (1.1.1) over the co-ordinates of $(N-S)$ molecules. The set of equations we obtain for $s=1, 2, 3 ...$ are called the BBGKY hierarchy of equations.
The initials stand for the five people who originally and independently derived this equation: Bogoliubov, Born, H. S. Green, Kirkwood, and Yvon. We are interested in the lowest order distribution function, namely \( f^{[1]}(r, p, t) \), since for dilute gases we do not need information regarding the relative position of two or more molecules as given by the higher order functions. The equation which describes the variation of \( f^{[1]} \) is called the Boltzmann equation, whose solution we wish to determine.

Although the Liouville equation defines uniquely how \( f^{[N]} \) changes with time, this is not the case for the lower order distribution functions. The reason for this is essentially that the lower order distribution functions are obtained by integrating \( f^{[N]} \) over the co-ordinates of the molecules which are of no interest and, as a consequence, a given lower order distribution function, \( f^{[h]} \), is not uniquely associated with a given \( f^{[N]} \). This means that no unique integro-differential equation exists for \( f^{[1]} \). To remove this ambiguity, the condition of molecular chaos is introduced to restrict the possible functions \( f^{[N]} \). The condition of molecular chaos is such that the probabilities of finding any of the molecules of the system in a given state are independent, i.e.

\[
f^{[N]}(t, \Sigma_1, \ldots \Sigma_N; p_1, \ldots p_N) = f^{[1]}(t, \Sigma_1, p_1) f^{[1]}(t, \Sigma_2, p_2) \\
\ldots f^{[1]}(t, \Sigma_N, p_N).
\]

This condition is used in the derivation of Boltzmann's equation, which is to be described next.

We will consider two ways of arriving at an equation which describes \( f^{[1]} \). Firstly, we will consider a physical derivation and, secondly, a derivation using the Liouville equation.
(a) Physical derivation of Boltzmann's Equation

The treatment used here for the physical derivation follows very closely that given in Hirschfelder, Curtissand Bird: "Molecular Theory of Gases and Liquids" (see Chapter 7), (hereafter referred to as HCB).

From the preceding description of a gas, the distribution function, \( f_i^{[1]}(r, p_i, t) \), on using symmetry arguments with regard to the particles of each species being identical, may be defined such that the probable number of molecules of species \( i \) with position and momentum co-ordinates in the range \( dr \) about \( r \) and \( dp_i \) about \( p_i \) respectively is

\[
f_i^{[1]}(r, p_i, t) \, dr \, dp_i .
\]

In the absence of collisions in the gas, the molecules associated with these phase points move in such a way that at time \( t + dt \) we have

\[
f_i^{[1]}(r, p_i, t) \, dr \, dp_i = f_i^{[1]}(r + \frac{p_i}{m_i} \, dt, [p_i + X_i \, dt], [t + dt]) \, dr \, dp_i , \quad (1.1.2)
\]

where \( X_i \) is the external force on molecules of species \( i \).

However, if we consider collisions, then the actual phase points associated with \( f_i \) are changed with time so to take account of this we have, for equation (1.1.2)

\[
f_i^{[1]}(r + \frac{p_i}{m_i} \, dt, [p_i + X_i \, dt], [t + dt]) \, dr \, dp_i = f_i^{[1]}(r, p_i, t) \, dr \, dp_i + \sum_j (r_i^{(+)} - r_i^{(-)}) \, dr \, dp_i \, dt , \quad (1.1.3)
\]

where

\[
\sum_j r_i^{(+)} \, dr \, dp_i \, dt , \quad \sum_j r_i^{(-)} \, dr \, dp_i \, dt
\]
represent the number of molecules of \(i\)th species gained and lost respectively in the time interval \(dt\) by collisions.

On expanding the terms on the left-hand side of equation (1.1.3) in a Taylor series about the point \((r, p_i, t)\) and re-arranging, we have

\[
\frac{\partial f_i^{[1]}}{\partial t} + \frac{1}{m_i} \left( p_i \cdot \frac{\partial f_i^{[1]}}{\partial r} \right) + \left( X_i \cdot \frac{\partial f_i^{[1]}}{\partial p_i} \right) = \sum_j \left( \Gamma_{ij}^{(+)} - \Gamma_{ij}^{(-)} \right).
\]

(1.1.4)

We will now look at the quantities \(\sum_j \Gamma_{ij}^{(+)}\) and \(\sum_j \Gamma_{ij}^{(-)}\), which are called the collision integrals. \(\Gamma_{ij}^{(+)} dr dp_i dt\) represents the number of molecules of type \(i\) which are removed from the volume element \(dr dp_i\) by collisions with molecules of type \(j\) during an interval of time \(dt\). In other words, we first want to determine the probability that a molecule of type \(i\) with momentum \(p_i\) experiences a collision with a molecule of type \(j\) with momentum \(p_j\), in the time interval \(dt\) with the impact parameter in a range \(db\) about \(b\) (the concept of an impact parameter is explained in the appendix). The arrangement is shown diagrammatically in Figure (1). (Here \(Z\) is the intermolecular distance at which the potential begins to take effect.)

On considering Figure (1), then any molecule of type \(j\) within the shaded sector of the cylindrical shell will undergo a collision with molecule \(i\) during the time interval \(dt\) with the appropriate impact parameter and momentum. The probable number of molecules of type \(j\) within this sector is

\[
\Gamma_{ij} f_i^{[1]}(r, p_i, t) \ g_{ij} \ db \ dB \ dt,
\]
Any molecule of type $j$ situated within the shaded cylindrical shell will collide with a fixed molecule $i$ during the succeeding time interval $dt$. 

Fig. 1: Molecular collisions with impact parameter $b$. 

\[ \frac{P_j}{m_j} - \frac{P_i}{m_i} \ dt = g_{ij} \ dt \]
and the number characterised by all values of the parameters and
momentum is

\[ \frac{dt}{f_j^{[1]}(r, p_j, t)} g_{ij} \frac{db}{db} \frac{d\varepsilon}{d\varepsilon} dp_j. \]

Further, since the probable number of molecules of type \( i \) in
the volume element \( dr \) about \( r \) and momentum \( dp_j \), about \( p_j \)
is

\[ f_i^{[1]}(r, p_i, t) dr dp_i, \]

it follows that

\[ r_i^{(-)} dr dp_i dt = dr dp_i dt \int f_j^{[1]}(r, p_j, t) \]

\[ f_i^{[1]}(r, p_i, t) g_{ij} \frac{db}{db} \frac{d\varepsilon}{d\varepsilon} dp_j. \]

Hence

\[ r_i^{(-)} = \int f_i^{[1]} f_j^{[1]} g_{ij} \frac{db}{db} \frac{d\varepsilon}{d\varepsilon} dp_j. \]

We can determine \( r_i^{(+)} \) in a similar manner by invoking the concept
of inverse collisions for spherically symmetric potentials and
the conservation of extension in phase space we obtain

\[ r_i^{(+)} = \int f_i^{[1]} f_j^{[1]} g_{ij} \frac{db}{db} \frac{d\varepsilon}{d\varepsilon} dp_j, \]

where \( f_i^{[1]} \) represents \( f_i^{[1]}(r, p_i, t) \) and \( p_i \) is the momentum
of the molecules of type \( i \) associated with an inverse encounter.
(The relationships between the collision variables mentioned here
are described in the appendix.)
Substituting for $\Gamma_{ij}^{(-)}$ and $\Gamma_{ij}^{(+)}$ in equation (1.1.4), we obtain Boltzmann's equation

$$\frac{\partial f_i^{[1]}}{\partial t} + \frac{1}{m_i} \left( p_i \cdot \frac{\partial f_i^{[1]}}{\partial r_i} \right) + \left[ X_i \cdot \frac{\partial f_i^{[1]}}{\partial p_i} \right]$$

$$= \sum_j \int (f_i^{[1]} f_j^{[1]} - f_i^{[1]} f_j^{[1]}) g_{ij} \, db \, dr \, dp_j \ ,$$

(1.1.5)

whose solution we are interested in determining.

(b) Boltzmann Equation derived from the Liouville Equation

We will now consider the derivation of the Boltzmann equation by integrating Liouville's equation.

An equation for $f_i^{[1]}(r, p_i, t)$ can be obtained from the Liouville equation (1.1.1) by integrating over the co-ordinates of $(N-1)$ molecules

$$\frac{\partial f_i^{[1]}}{\partial t} + \frac{1}{m_i} \left( p_i \cdot \frac{\partial f_i^{[1]}}{\partial r} \right) + \left[ X_i \cdot \frac{\partial f_i^{[1]}}{\partial p_i} \right]$$

$$= - \frac{1}{(N-1)!} \int \int \left[ F_i \cdot \frac{\partial f^{[N]}}{\partial p_i} \right] \, dr^{N-1} \, dp^{N-1} \ ,$$

(1.1.6)

(for a fairly detailed derivation see S. J. Harris(7)).

On integrating (1.1.1) to obtain (1.1.6), we have lowered the level of description and, as mentioned earlier, we invoke the concept of molecular chaos in order to remove any ambiguity associated with the form of $f_i^{[1]}$. 
We will now consider, in outline only, the derivation of the Boltzmann equation from equation (1.1.6). We will assume that there are only two body forces between the molecules so that equation (1.1.6) reduces to

\[ \frac{\partial f_1}{\partial t} + \frac{1}{m} \left( \mathbf{p}_1 \cdot \frac{\partial f_1}{\partial \mathbf{r}} \right) + \left( \mathbf{x}_1 \cdot \frac{\partial f_1}{\partial \mathbf{p}_1} \right) \]

\[ = - \int \mathbf{F}_{12} \cdot \frac{\partial f_2}{\partial \mathbf{p}_1} \, d\mathbf{r}_2 \, d\mathbf{p}_2 \, , \quad (1.1.7) \]

for a single component gas.

The principle of molecular chaos assumes that

\[ f_{12}^[2] = f_{1}^[1] f_{2}^[1] \ . \quad (1.1.8) \]

During a collision, since the particles are correlated, we cannot write \( f_{12}^[2] \) as shown in equation (1.1.8). Nevertheless, if the collision time is such that \( f_{1}^[1] \) and \( f_{2}^[1] \) do not change appreciably, it can be shown that we can transform (1.1.7) into the following form

\[ \frac{\partial f(v)}{\partial t} + \left( \mathbf{v} \cdot \frac{\partial f(v)}{\partial \mathbf{r}} \right) + \frac{1}{m} \left( \mathbf{x} \cdot \frac{\partial f(v)}{\partial \mathbf{v}} \right) \]

\[ = \int (f'(v') f'(u') - f(v) f(u)) \, g \, db \, ds \, du \quad ; \quad (1.1.9) \]

and for a mixture
Here we have introduced a new distribution function, \( f(r, v, t) \), without the superscript \([1]\), which is a function of the velocity variable, \( v \), rather than momentum.

Before considering the solution of Boltzmann's equation (1.1.10), in general we will look at the equilibrium case. In equilibrium there are no spatial gradients or time dependencies in \( f_i \) so the left-hand side of equation (1.1.10) is zero, from which we obtain for \( f_i \)

\[
f_i = n_i \left( \frac{m_i}{2\pi kT} \right)^{3/2} \exp\left( -\frac{m_i v_i^2}{2kT} \right),
\]

which is the well-known Maxwellian distribution, where \( v_i = v_i - u_o \) is the peculiar velocity and \( u_o \) is the mass average velocity defined by equation (1.2.6).

There are a number of ways of solving Boltzmann's equation, but we are interested in the Chapman-Enskog solution which will now be outlined.

1.2 Chapman-Enskog Solution of the Boltzmann Equation and the Determination of the Transport Coefficients

The second approximation to the distribution function in the Chapman-Enskog regime is written as \( f = f^{(c)}[1 + \phi(v)] \), where \( \phi(v) \) is a perturbation term. This perturbation term is expressed...
in terms of convergent series of Sonine polynomials from which we obtain approximations to the transport coefficients.

The Boltzmann equation (1.1.10) is written

\[
\frac{\partial f_i}{\partial t} + v_i \cdot \frac{\partial f_i}{\partial x} + \frac{1}{n_i} \left[ x_i \cdot \frac{\partial f_i}{\partial v_i} \right] = \frac{1}{\xi} \sum J(f_i f_j),
\]

(1.2.1)

where \( J(f_i f_j) \) represents the collision integrals

\[
J(f_i f_j) = \int (f_i f_j - f_i f_j) g_{ij} b db \, dc \, dv_j;
\]

(1.2.2)

and \( \xi \) is a perturbation parameter which effectively orders the contribution to \( f_i \) from the different terms in equation (1.2.1). We can appreciate what \( \xi \) represents and its possible magnitude by comparing the relative size of the terms which appear in equation (1.2.1). We can associate a typical macroscopic length and time with the left-hand side terms, while the collision term is associated with a length and time namely the time between collisions and the mean free path. So \( \xi \) is a measure of the ratio of these length or time scales. In the regime to be considered here, we take the system to behave as a continuum where many collisions take place over a macroscopic length, so \( \xi \) is a small number.

The distribution function is expanded in the infinite series

\[
f_i = f_i^{(0)} + \xi f_i^{(1)} + \xi^2 f_i^{(2)} + \ldots,
\]

(1.2.3)

and then, on substituting into (1.2.1) and equating coefficients of corresponding powers of \( \xi \), we obtain the following set of
equations for the functions $f_i^{(0)}$, $f_i^{(1)}$, $f_i^{(2)}$ ...

\[ 0 = \sum_j J(f_i^{(0)}, f_j^{(0)}) , \]

\[ \frac{\partial f_i^{(0)}}{\partial t} + \left( v_i \cdot \frac{\partial f_i^{(0)}}{\partial r} \right) + \frac{1}{m_i} \left( \frac{\partial f_i^{(0)}}{\partial v_i} \right) = \sum_j [J(f_i^{(0)}, f_j^{(1)}) + J(f_i^{(1)}, f_j^{(0)})] , \]

\[ \frac{\partial f_i^{(1)}}{\partial t} + \left( v_i \cdot \frac{\partial f_i^{(1)}}{\partial r} \right) + \frac{1}{m_i} \left( \frac{\partial f_i^{(1)}}{\partial v_i} \right) \]

\[ = \sum_j [J(f_i^{(0)}, f_j^{(2)}) + J(f_i^{(1)}, f_j^{(2)}) + J(f_i^{(2)}, f_j^{(0)})] , \]

(1.2.4)

and so on.

On looking at the equilibrium case considered earlier, the most general solution of the first expression in (1.2.4) is of the Maxwellian form

\[ f_i^{(0)} = \left( \frac{m_i}{2\pi kT} \right)^{\frac{3}{2}} \exp\left\{ -\frac{m_i(v_i - u_0)^2}{2kT} \right\} . \]

For this particular method we arrange that the quantities

\[ n_i = n_i(r,t) ; \quad u_0 = u_0(r,t) ; \quad T = T(r,t) \]

represent the local values of the physical quantities, number density, mass average velocity, and temperature. Now by definition we have
\[ \int f_i \, d\nu_i = n_i \quad (1.2.5) \]
\[ \sum_i m_i \int \nu_i \, f_i \, d\nu_i = \rho \, u_c \quad (1.2.6) \]

where
\[ \rho = \sum_i m_i \, n_i \]

and
\[ \frac{1}{2} \sum_i m_i \int (\nu_i - u_c)^2 \, f_i \, d\nu_i = \frac{3}{2} \, n \, k \, T \quad (1.2.7) \]

So this requires that
\[ \int f_i^{(r)} \, d\nu_i = 0 \quad (1.2.8) \]
\[ \sum_i m_i \int f_i^{(r)} \nu_i \, d\nu_i = 0 \quad (1.2.9) \text{ for } r > 0 \]
\[ \frac{1}{2} \sum_i m_i \int (\nu_i - u_c)^2 f_i^{(r)} \, d\nu_i = 0 \quad (1.2.10) \]

in order for the above to be fulfilled.

Equations (1.2.8, 9 and 10) are the auxiliary conditions which will be referred to throughout this thesis. Equations (1.2.4) and (1.2.8, 9 and 10) specify uniquely a set of functions \( f_i^{(r)} \).

It is appropriate here to introduce the flux equations from which we obtain the transport coefficients we wish to determine. For the single component gas case we have:
(1) Heat flux, which involves the flux of kinetic energy (here we consider molecules without internal degrees of freedom)

\[
q = \sum_{r=0}^{\infty} \xi(r) \frac{q}{q(r)}
\]

\[
q(r) = \int \frac{1}{2} m V^2 V f(r)(v) \, dv
\]  
(1.2.11)

where \( q \) is the heat flux vector from which we obtain the thermal conductivity coefficient, \( \lambda \) (see (1.2.26)).

(2) Flux of momentum

\[
P = \sum_{r=0}^{\infty} \xi(r) \frac{p}{p(r)}
\]

\[
p(r) = \int m V V f(r)(v) \, dv
\]  
(1.2.12)

where \( p \) is the pressure tensor from which we obtain the coefficient of viscosity, \( \eta_s \) (see (1.2.23)).

We now have the problem of deciding what order of \( f \) to go to in order to calculate the transport coefficients. Now we have already seen that for the Chapman-Enskog method of solution a parameter \( \xi \) is introduced to order the contribution to \( f \) from the different terms in Boltzmann's equation. Here we are considering gases for which the mean collision interval is small compared with the time scale of variation of the macroscopic properties such as \( n, T, \) and \( u_0 \) and likewise for the length scale; namely a collision-dominated gas. For this case \( \xi \) is small and hence the Chapman-Enskog method is applicable. Since \( \xi \) is small, then it is likely that only a few terms of the series,
depicted in (1.2.3), are needed. In fact, using only $f^{(0)} + f^{(1)}$ turns out to be a sufficiently good approximation to the distribution function, $f$, for most purposes. With regard to the higher order terms, it is at present unclear whether they are generally physically relevant.

On the basis of the above analysis, we will consider only $f^{(0)}$ and $f^{(1)}$. We write

$$f_i^{(1)} = f_i^{(0)} \phi_i (x, y, t) \quad (1.2.13)$$

where $\phi_i$ is a perturbation function and $f_i^{(0)}$ is the local Maxwellian distribution function. We will now consider the determination of $\phi$ which leads to $q_i^{(1)}$ and $p_i^{(1)}$ from which we obtain expressions for the coefficients of thermal conductivity, $\lambda$, and viscosity, $\eta$, respectively. (See (1.2.26) and (1.2.23).)

If we substitute (1.2.13) into the second equation in (1.2.4), we obtain

$$\frac{\partial f_i^{(0)}}{\partial t} + \left( v_i \cdot \frac{\partial f_i^{(0)}}{\partial x} \right) + \frac{1}{m_i} \left( \lambda_i \cdot \frac{\partial f_i^{(0)}}{\partial y_i} \right) = \sum_j \left[ f_i^{(0)} f_j^{(0)} (\phi_i^{(0)} + \phi_j^{(0)} - \phi_i^{(0)} - \phi_j^{(0)}) g_{ij} \right] \frac{db}{db} \frac{d\theta}{d\theta_j} \quad (1.2.14)$$

The differentiation of $f_i^{(0)}$ indicated in (1.2.14), results in space and time derivatives of $n$, $u$, and $T$ for which the time derivatives are eliminated by using the equation of change. (These equations are obtained by multiplying both sides of BE equation (1.1.10) by $m_i$, $m_i v_i$ and $\frac{1}{2} m_i v_i^2$ respectively, and integrating
wrt to \( v_i \). Further, it is consistent with this approximation to replace \( f_i \) by \( f_i^{(o)} \) in the integrals for the flux vectors occurring in the equations of change. On using the above we obtain for (1.2.14)

\[
f_i^{(o)} \left\{ \left( \frac{n_i}{n} (v_i \cdot d_i) + \left[ b_i : \frac{3}{\partial r} u_o \right] - (\delta_2 - \alpha V^2) v_i \cdot \frac{\partial ln T}{\partial r} \right) \right\} = \sum_j \int f_i^{(o)} f_j^{(o)} (\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} b db \, dv_{ij} \, dc ,
\]

where \( d_i \) and \( b_i \) are defined by

\[
d_i = \frac{3}{\partial r} \left( \frac{n_i}{n} \right) + \left( \frac{n_i}{n} - \frac{n_i}{\rho} \right) \frac{\partial \ln p}{\partial r} - \left( \frac{n_i}{\rho} \right) \left( \frac{p}{m_i} v_i \cdot \sum_j n_j v_j \right) ,
\]

\[
b_i = 2 \alpha_i [V_i \cdot v_i - \frac{1}{3} V^2 u] = 2 \alpha_i \frac{v_i^0}{v_i} v_i .
\]

On examining (1.2.15), it is clear that the perturbation function \( \phi_i(v_i) \) is of the following form

\[
\phi_i(v_i) = \left( A_i(v_i) \cdot \frac{\partial ln T}{\partial r} \right) - \left( \delta^{B}_{i} (v_i) \cdot \frac{3}{\partial r} u_o \right) + n \sum_j \left( c^{(j)}_{i} (v_i) \cdot d_j \right) .
\]

Or for the single gas case, which we will consider here, we have

\[
\phi = - \left( A \cdot \frac{\partial ln T}{\partial r} \right) - \left( \delta^{B} \cdot \frac{3}{\partial r} u_o \right) ,
\]

Substitution of \( \phi \) in equation (1.2.15) leads to

\[
I(A) = - f^{(o)} [\delta_2 - \alpha V^2] v ,
\]

\[
I(B) = - \alpha f^{(o)} v^0 v ,
\]
where

\[ I(A) = \int \int f^{(o)}(v) f^{(o)}(u) \left[ A(V') + A(U') - A(V) - A(U) \right] \, \text{d}v \, \text{d}u \, . \]  

(1.2.21)

In terms of \( \Phi \), we have

\[ P^{(1)} = \int m V \, V \, f^{(o)} \, \Phi \, \text{d}v \]  

(1.2.22)

\[ = - 2n_s \, \bar{V}^s \, u_o \]  

(1.2.23)

where \( \bar{V}^s \, u_o \) is a symmetric non-divergent tensor and \( n_s \) is the shear viscosity coefficient. From equations (1.2.20, 22, 23) we have

\[ \eta_s = \frac{2}{3} kT \int B : I(B) \, \text{d}v \]  

(1.2.24)

\[ = \frac{2}{3} kT \left[ B, B \right] \]  

(1.2.25)

This serves to define the bracket notation, as used by Chapman and Cowling, which will be used frequently in the remaining part of this section. Similarly

\[ q^{(1)} = \int \frac{1}{2} m V^2 \, V \, f^{[c]} \, \Phi \, \text{d}v = - \lambda \, \bar{V} \, T \]  

(1.2.26)

where

\[ \lambda = \frac{k}{3} \int I(A) \cdot A \, \text{d}v \]  

(1.2.27)

\[ = \frac{k}{3} [A, A] \]  

(1.2.28)

is the thermal conductivity coefficient. In order to calculate \( \eta_s \) and \( \lambda \) we have to solve equations (1.2.19 and 20). Here we
will discuss the solution due to Chapman and Cowling, which involves expanding the $A$'s and the $B$'s in terms of an infinite convergent series of Sonine Polynomials. The following treatment is based on that given in Chapman and Cowling: The Mathematical Theory of Non-Uniform Gases (Chapter 7) [hereafter referred to as C-C].

**Formal Evaluation of Transport Coefficients**

This method essentially involves expanding $A(V)$ in a convergent series of Sonine Polynomials, $S_m^{(n)}(x)$

$$A(V) = \sum_{p=0}^{\infty} a_{p} S_{2}^{(p)}(aV^2) V,$$  \hspace{1cm} (1.2.29)

where the coefficients $a_p$ are independent of $V$. Using the auxiliary conditions and the properties of the polynomials, we find $a_0$ is zero, so we have

$$A(V) = \sum_{p=1}^{\infty} a_{p} \frac{a^{(p)}}{p}$$ \hspace{1cm} (1.2.30)

where

$$\frac{a^{(p)}}{p} = S_{2}^{(p)}(aV^2) V.$$

On noting the form of $S_{2}^{(1)}(aV^2)$, equation (1.2.19) can be written

On noting the form of $S_{2}^{(1)}(aV^2)$, equation (1.2.19) can be written as follows

$$I(A) = - \int \frac{a}{V} S_{2}^{(1)}(aV^2) \, dV$$ \hspace{1cm} (1.2.31)

which on multiplying by $\frac{a^{(q)}}{q} = S_{2}^{(q)}(aV^2) V$ and integrating wrt $V$ we obtain
where
\[ a_q = -\frac{15}{4} \text{ (q=1)} \]
\[ = 0 \quad \text{q \neq 1} . \]

If we let
\[ a_{pq} = [a(p), a(q)] \quad (1.2.33) \]
then (1.2.32) becomes
\[ \sum_{p=1}^{\infty} a_p a_{pq} = a_q \quad (q = 1, 2 \ldots \infty) . \quad (1.2.34) \]

Since we have defined \( a(p) \) and thus we know \( a_{pq} \), equation (1.2.33), then equation (1.2.34) represents an infinite set of equations to determine the infinite set of coefficients \( a_p \).

Instead of considering the intractible infinite set of equations to determine \( A \) a method of successive approximations to \( A \) will be used. (Curtis and Hirschfelder\(^9\) expanded \( A(V) \), \( B(V) \) and \( C_i(j)(V) \) in a series of Sonine polynomials and used a variational method to determine the coefficients associated with the polynomials.)

Enskog assumed that \( A(m) \), given by
\[ A(m) = \sum_{p=1}^{m} a_{p} a^{(m)}(p) \quad (1.2.35) \]

where
\[ \sum_{p=1}^{m} a^{(m)}(m) a_{pq} = a q \quad (q = 1, 2 \ldots m) \quad (1.2.36) \]
can be taken to be an $m^{th}$ approximation to $A$.

The thermal conductivity $\lambda$ depends only on the coefficient $a_1$, i.e.

$$\lambda = \frac{k}{3} [A, A] = \frac{k}{3} \sum_{p=1}^{\infty} a_p \langle a(p), A \rangle$$

which by (1.2.32) becomes

$$\lambda = -\frac{5}{4} k a_1 \quad (1.2.37)$$

From equations (1.2.35 and 36) we can obtain approximations to $a_1$, namely $a_1^{(m)}$. After a good deal of manipulation (see C-C, p129), we obtain for $a_1$, and hence $\lambda$, the following approximations

$$[\lambda]_1 = -\frac{5}{4} k a_1^{(1)} = \frac{25 c_v}{8} \frac{1}{a_{11}} \quad (1.2.38)$$

$$[\lambda]_2 = -\frac{5}{4} k a_1^{(2)} = \frac{25 c_v}{8} \frac{a_{22}}{a_{11} a_{22} - a_{12}^2} \quad (1.2.39)$$

and so on for higher approximations.

However, it turns out that $[\lambda]_1$ and $[\lambda]_2$ are the only terms that contribute significantly to $\lambda$, so we will consider only these two terms in detail. On looking at equations (1.2.38 and 39) we can see that we have factors of the type $a_{pq}$ to consider.

These are defined by equation (1.2.33), and after further lengthy manipulation we obtain, see C-C, Chapter 9, pp149-158

$$a_{11} = [a^{(1)}_1, a^{(1)}_1] = 4 \Omega_1^{(2)}(2) \quad (1.2.40)$$

$$a_{12} = [a^{(2)}_1, a^{(2)}_1] = 7 \Omega_1^{(2)}(2) - 2 \Omega_1^{(2)}(3) \quad (1.2.41)$$
where, for a single gas

$$\frac{a_{22}}{(2, a_{(2)})} = \frac{77}{4} \Omega_1^{(2)}(2) - 7 \Omega_1^{(2)}(3) + \Omega_1^{(2)}(4)$$

(1.2.42)

The evaluation of the relevant functions indicated in equations (1.2.40, 41 and 42) requires a knowledge of the particular potential models under consideration. The relationships between the integrating variables for the respective potential models, necessary to evaluate the functions, are given in the appendix.

Having evaluated the functions we can determine the approximation to the transport coefficients, namely for the thermal conductivity coefficient, \(\lambda\), we have

$$\lambda : [\lambda]_1 , [\lambda]_2 , \ldots$$

and for viscosity, \(\eta_s\)

$$\eta_s : [\eta_s]_1 , [\eta_s]_2 , \ldots$$

We have not considered the viscosity case separately, since it is obtained in a similar manner to \(\lambda\) by expanding \(B\) in Sonine polynomials and then following as for \(\Lambda\), but using the pressure tensor.
The convergences of the series for $\lambda$ and $\eta_s$ are very rapid and a very good result for the transport coefficients is obtained by considering only the second or third term, for instance $[\lambda]_2$ or $[\lambda]_3$, in the respective series.

1.3 Comparisons to be drawn between the two methods

An indication of the comparisons to be drawn between the results obtained using the two methods for three different potential models is discussed in this final section, along with the reasons for choosing these particular potential models.

Having outlined the Chapman-Cowling method of solution of the second approximation to Boltzmann's equation within the Enskog regime, we are now in a position to consider our method of solution with which most of this thesis is concerned. However, before going into detail, a few words concerning the approach to the analysis of our method are appropriate here. Throughout the thesis we will be comparing our results for the distribution function and the transport coefficients with those resulting from using the standard Chapman-Cowling method for three different potential models. The three different potential models used are: the Maxwellian, Pseudo-Maxwellian (soft sphere), and the rigid sphere. (A description of these models is given in the appendix and in the appropriate chapters.)

These particular models are chosen because they are well documented in the standard text books, such as C-C, and produce the most direct way of assessing the feasibility and accuracy of our method. Further, for the Chapman-Cowling method, the Maxwellian and the rigid sphere potential models produce the two
extremes of convergence of the series associated with the transport coefficients and thus makes the comparison with our results a more searching test.

The comparison with our results from this standpoint, together with other points arising from our method, will be analysed in Chapter 6.
CHAPTER 2

Mathematical Outline of the Iterative Method
and the Determination of the Transport Coefficients

Introduction

In this chapter, we are concerned with the basic mathematics associated with the iterative solution of Boltzmann's equation for dilute gases and the determination of the transport coefficients. In section 1 we deal with the single component case and obtain formal expressions for the transport coefficients in terms of the infinite series expansion of the appropriate perturbation term. In section 2 we deal with the binary mixture case and for completeness we deal briefly with the multi-component case in section 3. Finally, in section 4, we investigate the possible ways of determining the infinite sums associated with the transport coefficients.

2.1 Single Component Gas

In this section we will be considering the solution of Boltzmann's equation and the determination of the transport coefficients for a gas containing only one species of molecule.

(a) Iterative Method and Auxiliary Conditions

The second approximation to Boltzmann's equation, in the Chapman-Enskog regime, for a single component gas is as follows (see Chapter 1 for details of derivation)
\[ f^{(o)}(V) \left\{ (\alpha V^2 - 2\phi) V \cdot \nabla + T + 2\alpha \nabla^2 V : \nabla U_c \right\} = \int f^{(o)}(V) f^{(o)}(U) \left\{ \phi(U') + \phi(V') - \phi(V) - \phi(U) \right\} g b \, db \, de \, du \]  

(2.1.1)

Since the left-hand side of (2.1.1) contains linear gradients terms we write \( \phi \) in the following way

\[ \phi = \phi_c(V) \cdot \nabla \ln T + \phi_\eta(V) : \nabla U_c , \]

or

\[ = \phi_c(V) \cdot \nabla \ln T + \phi_\eta(V) \nabla^2 V : \nabla U_c . \]  

(2.1.2)

Then, on substituting (2.1.2) into (2.1.1) and equating like gradients, we have the following two equations to solve

\[ (\alpha V^2 - 2\phi) V = \int f^{(o)}(U) \left\{ \phi_c(U') + \phi_c(U') - \phi_c(V) 
\]  

\[ - \phi_c(U) \right\} g b \, db \, de \, du , \]  

(2.1.3)

\[ 2\alpha \nabla^2 V = \int f^{(o)}(U) \left\{ \phi_\eta(U') + \phi_\eta(U') - \phi_\eta(V) 
\]  

\[ - \phi_\eta(U) \right\} g b \, db \, de \, du . \]  

(2.1.4)

Using the fact that \( \phi_c(V) \) and \( \phi_\eta(V) \) are independent of the integrating variables in equations (2.1.3-4), we can re-arrange these equations into the following form

\[ (\alpha V^2 - 2\phi) V = - \phi_c(V) \int f^{(o)}(U) g b \, db \, de \, du 
\]  

\[ + \int f^{(o)}(U) \left\{ \phi_c(U') + \phi_c(U') - \phi_c(U) \right\} g b \, db \, du \, de , \]  

(2.1.5)
and
\[ 2\alpha V^0 = - \phi_n(V) \int f^{(o)}(U) g b \, db \, du \, d\varepsilon \]
\[ + \int f^{(o)}(U) g \left\{ \phi_n(V') + \phi_n(U') - \phi_n(U) \right\} b \, db \, du \, d\varepsilon \]
(2.1.6)

or for convenience we can write (2.1.5-6) in the following form

\[ X_0 = - \phi_c(V) L_0 + L_1 \phi_c \]
(2.1.7)
\[ X_n = - \phi_n(V) L_0 + L_1 \phi_n \]
(2.1.8)

where
\[ X_0 = (\alpha V^2 - \frac{5}{2}) V \]
and \[ X_n = 2\alpha V^0 V \].

Both equations (2.1.7) and (2.1.8) are of the general form

\[ X = - \phi(V) L_0 + L_1 \phi \]
(2.1.9)

The integral operators \( L_0 \) and \( L_1 \) are given by

\[ L_0 = \int f^{(o)}(U) g b \, db \, du \, d\varepsilon \]
(2.1.10)

and

\[ L_1 \phi = \int f^{(o)}(U) g \left\{ \phi(U') + \phi(V') - \phi(U) \right\} b \, db \, du \, d\varepsilon \]
(2.1.11)

To perform the iterations we expand \( \phi(V) \) in the infinite series

\[ \phi(V) = \sum_{n=0}^{\infty} \xi^n \phi^{(n)}(V) \]
(2.1.12)

where \( \phi(V) \) is either of the functions \( \phi_c(V) \), \( \phi_n(V) \); and rewrite (2.1.9) as follows
\[ X = - \phi(V) L_0 + \zeta L_1 \phi, \]  

(2.1.13)

where we have introduced \( \zeta \) in (2.1.12,13) as an ordering parameter which will eventually be set equal to unity.

If we now substitute (2.1.12) into (2.1.13) and equate coefficients of corresponding powers of \( \zeta \) we obtain the following relationships

\[ X = - \phi^{(0)}(V) L_0 \ldots 0^{th} \text{ iteration}, \]  

(2.1.14)

\[ \phi^{(1)}(V) L_0 = L_1 \phi^{(0)} \ldots 1^{st} \text{ iteration}, \]  

(2.1.15)

\[ \vdots \]

\[ \phi^{(h)}(V) L_0 = L_1 \phi^{(h-1)} \ldots h^{th} \text{ iteration}. \]  

(2.1.16)

From equations (2.1.14,16) we can obtain all the \( \phi^{(h)} \)'s. Now there are auxiliary conditions that must be placed upon \( \phi \) to ensure correct definitions of \( n, u_0, \) and \( T \); namely

\[ \int f^{(0)}(V) \phi(V) dV = 0, \]  

(2.1.17)

\[ m \int f^{(0)}(V) \phi(V) V dV = 0, \]  

(2.1.18)

\[ \frac{1}{2} m \int f^{(0)}(V) \phi(V) V^2 dV = 0. \]  

(2.1.19)

In our case we have expanded \( \phi \) into two infinite series so that we have to make sure that each of the \( \phi_{\alpha_1}^{(h)} \) separately satisfy equations (2.1.17,18,19). To do this, we substitute from equation (2.1.12) into the auxiliary conditions and we find that the individual \( \phi_{\alpha_1}^{(h)} \) automatically satisfy equations (2.1.17) and (2.1.19) and in fact all the \( \phi_{\alpha_1}^{(h)} \)'s also satisfy equations (2.1.18) as well; so we are left with the following equation to satisfy for all \( h \)
We can satisfy the second auxiliary condition equation (2.1.20) for all \( h \) by redefining the perturbation term to include a collision invariant quantity which does not affect the solution of the Boltzmann equation but does enable us to satisfy all the auxiliary conditions. We therefore define

\[
\bar{\phi}_c^{(h)}(v) \cdot \nabla \ln T = \phi_c^{(h)}(v) \cdot \nabla \ln T + \alpha_c^{(h)} \cdot m_v ,
\]

for \( h > 0 \)  \hspace{1cm} (2.1.21)

where \( \alpha_c^{(h)} \) is a constant and does not affect the other two auxiliary conditions and \( m_v \) is a collision invariant quantity.

On substituting (2.1.21) into (2.1.20) we have for all \( h \)

\[
\int f^{(c)} m_v \phi_c^{(h)}(v) \cdot \nabla \ln T \, dv + \int f^{(c)} m_v \alpha_c^{(h)} \cdot m_v \, dv = 0 ,
\]

\hspace{1cm} (2.1.22)

from which we can obtain \( \alpha_c^{(h)} \) and hence \( \bar{\phi}_c^{(h)}(v) \cdot \nabla \ln T \) for all \( h \).

We are now in a position to be able to obtain expressions for the transport coefficients for a single component gas.

(b) **Transport Coefficients**

(i) **Thermal Conductivity**

The thermal conductivity coefficient, \( \lambda \), is determined from the heat flux equation

\[
g = -\lambda \nabla T = \frac{1}{2} m \int v^2 v \cdot f^{(c)} \phi(v) \, dv \, , \hspace{1cm} (2.1.23)
\]
where \( \mathbf{q} \) is the heat flux vector.

Then, on using equations (2.1.2 and 12), taking into account the auxiliary conditions and noting that integration of odd functions of \( V \) vanish, equation (2.1.23) becomes

\[
\mathbf{q} = -\lambda \, \nabla T = \frac{1}{2} \, m \int V^2 \, f^{(o)} \sum_{n=0}^{\infty} \zeta^n \\
[\phi_c^{(n)}(V) \, \nabla \cdot (\nabla \ln T + \alpha_c^{(n)} \cdot m \, V) \, dV].
\] (2.1.24)

From (2.1.24), we note that \( \lambda \) can be written in the form

\[
\lambda = \sum_{n=0}^{\infty} \zeta^n \lambda^{(n)} \), (2.1.25)
\]

where \( \zeta \) is the same ordering parameter introduced in (2.1.12), and the \( \lambda^{(n)} \)'s obey the equations

\[
-\lambda^{(o)} \, \nabla T = \frac{1}{2} \, m \int V^2 \, f^{(o)} [\phi_c^{(o)}(V) \, \nabla \cdot (\nabla \ln T \\
+ \alpha_c^{(o)} \cdot m \, V) \, dV],
\] (2.1.26)

and

\[
-\lambda^{(n)} \, \nabla T = \frac{1}{2} \, m \int V^2 \, f^{(o)} [\phi_c^{(n)}(V) \, \nabla \cdot (\nabla \ln T \\
+ \alpha_c^{(n)} \cdot m \, V) \, dV].
\] (2.1.27)

On using equation (2.1.22) we can rewrite equations (2.1.26,27) in the following way

\[
-\lambda^{(h)} \, \nabla T = -k \int f^{(c)} (\frac{5}{2} - \alpha V^2) \, \phi_c^{(h)}(V) \, \nabla \cdot (\nabla T) \, dV
\]

for all \( h \). (2.1.28)
(ii) **Viscosity**

The coefficient of shear viscosity $\eta_s$ is determined from the pressure tensor, which is given by

$$p = m \int (f^{(0)} + f^{(1)} \phi) V V \, dV,$$

(2.1.29)

from which we have

$$p^{(1)} = -2\eta_s v^s u_\infty = m \int f^{(0)} \phi V V \, dV,$$

(2.1.30)

where $p^{(1)}$ is the correction to the pressure tensor and $v^s u_\infty$, the shear viscosity tensor, is a symmetric non-divergent tensor formed from the components of $V u_\infty$. Then on using equations (2.1.2 and 12) and discarding integrals of odd functions of $V$

equation (2.1.30) becomes

$$p^{(1)} = -2\eta_s v^s u_\infty = \frac{2}{15} m \int f^{(0)} \sum_{n=0}^{\infty} \zeta^n \phi^{(n)} (v) v^4 v^s u_\infty \, dV.$$

(2.1.31)

On putting

$$\eta_s = \sum_{n=0}^{\infty} \zeta^n \eta_s^{(n)},$$

(2.1.32)

and equating coefficients of the corresponding powers of $\zeta$ in (2.1.31) we obtain the following relationships

$$-2\eta_s^{(h)} v^s u_\infty = \frac{2}{15} m \int f^{(0)} \phi^{(h)} (v) v^4 v^s u_\infty \, dV$$

for all $h$.

(2.1.33)

On considering equations (2.1.25) and (2.1.32) it is evident that to calculate the transport coefficients we will have to perform the sums
indicated in those equations. The determination of these sums is
discussed in general in the last section of this chapter, and in
specific for some particular potential models, in Chapters 3 and 4
of the thesis.

2.2 Binary Gas Mixtures

In this section we will be considering the solution of Boltzmann's
equation and the determination of the transport coefficients for a gas
containing two species of molecules.

(a) Iterative Method and Auxiliary Conditions

The second approximation to Boltzmann's equation for a binary
mixture is as follows (see Chapter 1, equation (1.2.15)).

\[
\begin{align*}
\phi_i (V_i) & = \phi_{ic} (V_i) \cdot \nabla \ln T + \phi_{in} (V_i) : \nabla u_0 \\
& + \phi_{id} (V_i) \cdot d_i \\ 
\text{or} \\
& = \phi_{ic} (V_i) \cdot \nabla \ln T + \phi_{in} (V_i) \cdot V_i \cdot V_i : \nabla u_0 \\
& + \phi_{id} (V_i) \cdot V_i \cdot d_i .
\end{align*}
\]

for \( i, j = 1, 2 \).
Then, on substituting (2.2.2) into (2.2.1), and equating like gradients, we have the following equations to solve

\[
(a_i V_i^2 - s_2) V_i = \sum_j \int f_j^{(o)} (U_j) \left\{ \Phi_{ic} (V_i) + \Phi_{jc} (U_i) \right\} g_{ij} b \, db \, d u_j \, d\varepsilon ,
\]

\[ - \Phi_{ic} (V_i) - \Phi_{jc} (U_i) \} g_{ij} b \, db \, d u_j \, d\varepsilon , \tag{2.2.3} \]

\[
2a_i V_i^2 V_i = \sum_j \int f_j^{(o)} (U_j) \left\{ \Phi_{in} (V_i) + \Phi_{jn} (U_i) \right\}
- \Phi_{in} (V_i) - \Phi_{jn} (U_i) \} g_{ij} b \, db \, d u_j \, d\varepsilon , \tag{2.2.4} \]

\[
\frac{n}{n_i} V_i = \sum_j \int f_j^{(o)} (U_j) \left\{ \Phi_{id} (V_i) + \Phi_{jd} (U_i) \right\} (-)^{i+j}
- \Phi_{id} (V_i) - \Phi_{jd} (U_i) \} g_{ij} b \, db \, d u_j \, d\varepsilon , \tag{2.2.5} \]

for \( i, j = 1, 2 \) throughout.

In equation (2.2.5) we have introduced the additional factor \((-1)^{i+j}\) since \( d_i = - d_j \) for \( i \neq j \) (for a binary mixture only). Using the fact that \( \Phi_{ic} (V_i) \), \( \Phi_{in} (V_i) \) and \( \Phi_{id} (V_i) \) are independent of the integrating variables in equations (2.2.3, 4 and 5) we can re-arrange these equations into the following form

\[
(a_i V_i^2 - s_2) V_i = - \Phi_{ic} (V_i) \sum_j \int f_j^{(o)} (U_j) g_{ij} b \, db \, d u_j \, d\varepsilon 
+ \int f_i^{(o)} (U_i) \left\{ \Phi_{ic} (V_i) + \Phi_{ic} (U_i) - \Phi_{ic} (U_i) \right\} g_{ij} b \, db \, d u_j \, d\varepsilon 
+ \sum_{i \neq j} \int f_j^{(o)} (U_j) \Phi_{ic} (V_i) g_{ij} b \, db \, d u_j \, d\varepsilon 
+ \sum_{i \neq j} \int f_j^{(o)} (U_j) \left\{ \Phi_{jc} (U_j) - \Phi_{jc} (U_j) \right\} g_{ij} b \, db \, d u_j \, d\varepsilon , \tag{2.2.6} \]

for \( i, j = 1, 2 \).
and similarly for \( \phi_{ic} \) and \( \phi_{id} \).

For convenience we can write (2.2.6) and the associated equations in the following way

\[
\begin{align*}
X_{ic} &= -\phi_{ic}(V_i) P_i + Q_i \phi_{ic} + \sum_{j \neq i} R_{ij} \phi_{jc}, \\
X_{in} &= -\phi_{in}(V_i) P_i + Q_i \phi_{in} + \sum_{j \neq i} R_{ij} \phi_{jn},
\end{align*}
\]

and

\[
\begin{align*}
X_{id} &= -\phi_{id}(V_i) P_i + Q_i \phi_{id} + \sum_{j \neq i} R_{ij} \phi_{jd},
\end{align*}
\]

for \( i,j = 1,2 \) \hspace{1cm} (2.2.7)

where

\[
\begin{align*}
X_{ic} &= (a_i V_i^2 - \frac{5}{2}) V_i, \\
X_{in} &= 2a_i V_i^2 V_i,
\end{align*}
\]

and

\[
X_{id} = \frac{n_i}{n} V_i.
\]

The integral operators are defined as follows

\[
P_i = \sum_j \int f_j^{(0)}(U_j) g_{ij} b \, db \, d u_j \, d\varepsilon, \quad (2.2.8)
\]

\[
Q_i \phi_i = \int f_i^{(0)}(U_i) \{ \phi_i(V_i) + \phi_i(U_i) - \phi_i(U_i) \} g_{ii} b \, db \, d u_i \, d\varepsilon
\]

\[
+ \sum_{j \neq i} \int f_j^{(0)}(U_j) \phi_i(V_j) g_{ij} b \, db \, d u_j \, d\varepsilon, \quad (2.2.9)
\]
As for the single gas case, to perform the iterations we expand \( \phi_{ic} \), \( \phi_{in} \) and \( \phi_{id} \) in infinite series as follows

\[
\phi(V) = \sum_{n=0}^{\infty} \xi^n \phi^{(n)}(V), \quad (2.2.11)
\]

where \( \phi(V) \) is any of the functions

\[
\phi_{ic}(V_i), \quad \phi_{in}(V_i), \quad \phi_{id}(V_i), \quad \text{for } i = 1, 2;
\]

and rewrite (2.2.7) as follows

\[
X = -\phi P + \xi Q \phi + \xi R \phi, \quad (2.2.12)
\]

where \( X \) and \( \phi \) are appropriate column vectors and \( P, Q, R, \)
are appropriate matrices. Here we have introduced, as in the
single gas case, \( \xi \) as an ordering parameter which will
eventually be set equal to unity.

Substituting (2.2.11) into (2.2.12) and equating coefficients of
corresponding powers of \( \xi \) we obtain the following relationships

\[
X = -\phi^{(0)} P \ldots \text{Oth iteration}, \quad (2.2.13)
\]

\[
\phi^{(1)} P = Q \phi^{(0)} + R \phi^{(0)} \ldots \text{1st iteration}, \quad (2.2.14)
\]

\[
\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots \}
\]

\[
\phi^{(h)} P = Q \phi^{(h-1)} + R \phi^{(h-1)} \ldots \text{hth iteration} \quad (2.2.15)
\]

\[
\vdots \quad \vdots \quad \vdots \quad \vdots \]

From equations (2.2.13, 15) we can obtain all the $\tilde{\phi}^{(h)}_i$.

As for the single gas case, there are auxiliary conditions that must be placed upon $\phi_i$ to ensure correct definitions of $n_i$, $\bar{u_i}$, and $T_i$; namely

$$\int f_i^{(0)}(v_i) \phi_i(v_i) \, dv_i = 0 \quad (2.2.16)$$

$$\sum m_i \int f_i^{(0)}(v_i) \phi_i(v_i) v_i \, dv_i = 0 \quad (2.2.17)$$

$$\sum \frac{1}{2} m_i \int f_i^{(0)}(v_i) \phi_i(v_i) v_i^2 \, dv_i = 0 \quad (2.2.18)$$

for $i = 1, 2$.

Substituting from equations (2.2.2) and (2.2.11) into the auxiliary conditions we find, as for the single gas case, only the second auxiliary condition, equation (2.2.17) is not automatically satisfied. Then, on considering the different gradient terms in (2.2.2), we have the following equations to satisfy for all $p$

$$\sum m_i \int f_i^{(0)}(v_i) \phi^{(p)}_{ic}(v_i) \, dv_i = 0 \quad (2.2.19)$$

$$\sum m_i \int f_i^{(0)}(v_i) \phi^{(p)}_{ld}(v_i) \, dv_i = 0 \quad (2.2.19)$$

As for the single gas case, we can satisfy equations (2.2.19) by redefining the perturbation terms to include collision invariant quantities which do not affect the solution of the Boltzmann equation, but enable us to satisfy all the auxiliary conditions.

We therefore define
\[ \phi_{ic}(V_i) V_i \cdot \nabla \ln T = \phi_{ic}(V_i) V_i \cdot \nabla \ln T + \frac{a_{ic}^{(h)}}{c} m_i V_i, \]

(2.2.20)

and

\[ \phi_{id}(V_i) V_i \cdot d_i = \phi_{id}(V_i) V_i \cdot d_i + \frac{a_{id}^{(h)}}{d} m_i V_i, \]

(2.2.21)

for all \( h \).

where \( a_{id}^{(h)} \) is a constant and \( m_i V_i \) is a collision invariant quantity.

On substituting (2.2.20, 21) into (2.2.19), we have, for all \( h \)

\[ \sum_i \left[ \int f_i^{(o)} m_i V_i \phi_{ic}(V_i) V_i \cdot \nabla \ln T \, d V_i + \right. \]

\[ \left. \int f_i^{(o)} m_i V_i a_{ic}^{(h)} m_i V_i \, d V_i \right] = 0, \]

(2.2.22)

and

\[ \sum_i \left[ \int f_i^{(o)} m_i V_i \phi_{id}(V_i) V_i \cdot d_i \, d V_i \right. \]

\[ \left. + \int f_i^{(o)} m_i V_i a_{id}^{(h)} m_i V_i \, d V_i \right] = 0. \]

(2.2.23)

Using these values in equations (2.2.20, 21) and (2.2.13-15), we obtain the complete \( \Phi \) and from this the transport coefficients.

(b) Transport Coefficients

(i) Diffusion and Thermal Diffusion

The diffusion coefficients are obtained from the following equation

for the difference in the mean velocities
\[ \overrightarrow{V}_1 - \overrightarrow{V}_2 = \frac{1}{n_1} \int f_1 \overrightarrow{V}_1 \, d\overrightarrow{V}_1 - \frac{1}{n_2} \int f_2 \overrightarrow{V}_2 \, d\overrightarrow{V}_2 \]  

(2.2.24)

On using equations (2.2.2, 11), taking into account the auxiliary conditions, and discarding integrands which contain odd functions of \( \overrightarrow{V}_i \), equation (2.2.24) becomes

\[
\overrightarrow{V}_1 - \overrightarrow{V}_2 = \sum h \left[ \frac{1}{n_1} \int f_1^{(o)} \left\{ \phi_{1d}^{(h)}(\overrightarrow{V}_1) \, \overrightarrow{V}_1 \cdot d_1 + \alpha_d^{(h)} \cdot m_1 \, \overrightarrow{V}_1 \right\} \, d\overrightarrow{V}_1 

- \frac{1}{n_2} \int f_2^{(o)} \left\{ \phi_{2d}^{(h)}(\overrightarrow{V}_2) \, \overrightarrow{V}_2 \cdot d_2 + \alpha_d^{(h)} \cdot m_2 \, \overrightarrow{V}_2 \right\} \, d\overrightarrow{V}_2 

+ \frac{1}{n_1} \int f_1 \left\{ \phi_{1c}^{(h)}(\overrightarrow{V}_1) \, \overrightarrow{V}_1 \cdot \mathbf{V} \ln T + \alpha_c^{(h)} \cdot m_1 \, \overrightarrow{V}_1 \right\} \, d\overrightarrow{V}_1 

- \frac{1}{n_2} \int f_2 \left\{ \phi_{2c}^{(h)}(\overrightarrow{V}_2) \, \overrightarrow{V}_2 \cdot \mathbf{V} \ln T + \alpha_c^{(h)} \cdot m_2 \, \overrightarrow{V}_2 \right\} \, d\overrightarrow{V}_2 \right] .
\]

(2.2.25)

From \( C \) and \( C[1] \) equation (8.4,1) we have

\[
\overrightarrow{V}_1 - \overrightarrow{V}_2 = - \left[ D_{12} \frac{n_2}{n_1 n_2} \, d_1 + \frac{n_2}{n_1 n_2} D_T \, \mathbf{V} \ln T \right] , \quad (2.2.26)
\]

where \( D_{12} \) is the coefficient of diffusion and \( D_T \) is the coefficient of thermal diffusion.

From equation (2.2.25), using the auxiliary conditions, \( \alpha_d^{(h)} \) can be written in terms of integrals containing \( \sum \phi_{i d}^{(h)}(\overrightarrow{V}_i) \, \overrightarrow{V}_i \cdot d_i \) and \( \alpha_c^{(h)} \) in terms of \( \sum \phi_{i c}^{(h)}(\overrightarrow{V}_i) \, \overrightarrow{V}_i \cdot \mathbf{V} \ln T \). Hence we can obtain \( D_{12} \) and \( D_T \) from equations (2.2.25, 26) by considering the terms associated with the respective gradients.
(ii) Thermal Conductivity

The thermal conductivity coefficient, $\lambda$, is obtained from the thermal flow equation

$$ q = \int f_1 \frac{1}{2} m_1 v_1^2 v_1 d v_1 + \int f_2 \frac{1}{2} m_2 v_2^2 v_2 d v_2. $$

(2.2.27)

Following Chapman and Cowling (Chapter 8, section 41), we have

$$ \frac{q}{kT} - \frac{5}{2}(n_1 \overline{v}_1 + n_2 \overline{v}_2) = \int f_1 (\alpha_1 v_1^2 - \frac{5}{2}) \overline{v}_1 d \overline{v}_1 $$

$$ + \int f_2 (\alpha_2 v_2^2 - \frac{5}{2}) \overline{v}_2 d \overline{v}_2, $$

(2.2.28)

where we have used

$$ \overline{v}_i = \frac{1}{n_i} \int f_i v_i d v_i \quad \text{for } i = 1, 2. $$

On using equations (2.2.2, 11), taking into account the auxiliary conditions, and again discarding odd functions of $v_i$, then the right-hand side of equation (2.2.28) becomes

$$ \sum \xi^h \left[ \int f_1^{(o)} (\alpha_1 v_1^2 - \frac{5}{2}) \overline{v}_1 \{ \phi_1^{(h)}(v_1) \overline{v}_1 \cdot \overline{v} \ln T + a_c^{(h)} \cdot m_1 \overline{v}_1 \} d \overline{v}_1 $$

$$ + \int f_2^{(o)} (\alpha_2 v_2^2 - \frac{5}{2}) \overline{v}_2 \{ \phi_2^{(h)}(v_2) \overline{v}_2 \cdot \overline{v} \ln T + a_c^{(h)} \cdot m_2 \overline{v}_2 \} d \overline{v}_2 $$

$$ + \int f_1^{(o)} (\alpha_1 v_1^2 - \frac{5}{2}) \overline{v}_1 \{ \phi_1^{(h)}(v_1) \overline{v}_1 \cdot d_1 + a_d^{(h)} \cdot m_1 \overline{v}_1 \} d \overline{v}_1 $$

$$ + \int f_2^{(o)} (\alpha_2 v_2^2 - \frac{5}{2}) \overline{v}_2 \{ \phi_2^{(h)}(v_2) \overline{v}_2 \cdot d_2 + a_d^{(h)} \cdot m_2 \overline{v}_2 \} d \overline{v}_2 \right]. $$

Since the $a_{c,d}^{(h)}$ terms do not contribute to these integrals and, since for a binary mixture, we have $d_1 = -d_2$, then, on performing the inte-
grations in the above, the right-hand side of equation (2.2.28) becomes

\[ \sum_h \xi \left[ \int f_1^{(o)}(a_1 V_1^2 - s_2) V_1 \phi_{1c}^{(h)}(V_1) V_1 \cdot V \ln T \, d V_1 \\
+ \int f_2^{(o)}(a_2 V_2^2 - s_2) V_2 \phi_{2c}^{(h)}(V_2) V_2 \cdot V \ln T \, d V_2 \\
+ \int f_1^{(o)}(a_1 V_1^2 - s_2) V_1 \phi_{1d}^{(h)}(V_1) V_1 \, d V_1 \\
- \int f_2^{(o)}(a_2 V_2^2 - s_2) V_2 \phi_{2d}^{(h)}(V_2) V_2 \, d V_2 \right] \].

Now we can substitute for \( d_1 \) from equation (2.2.26), i.e.

\[ - \left[ \overline{V_1} - \overline{V_2} + \frac{n_1^2}{n_1n_2} D_T V \ln T \int \frac{n_1n_2}{D_{12} n^2} = d_1 \right] . \]  

On using (2.2.29), the heat flux equation becomes

\[ q = \frac{s_2}{2} kT(n_1 \overline{V_1} + n_2 \overline{V_2}) + kT \sum_h \xi \left[ \int f_1^{(o)}(a_1 V_1^2 - s_2) \\
\phi_{1c}^{(h)}(V_1) V_1 \cdot V \ln T \, d V_1 \\
+ \int f_2^{(o)}(a_2 V_2^2 - s_2) V_2 \phi_{2c}^{(h)}(V_2) V_2 \cdot V \ln T \, d V_2 \\
- \int f_1^{(o)}(a_1 V_1^2 - s_2) V_1 \phi_{1d}^{(h)}(V_1) V_1 \, d V_1 \\
- \int f_2^{(o)}(a_2 V_2^2 - s_2) V_2 \phi_{2d}^{(h)}(V_2) V_2 \, d V_2 \right] \\
\left[ \overline{V_1} - \overline{V_2} + \frac{n^2}{n_1n_2} D_T V \ln T \int \frac{n_1n_2}{D_{12} n^2} \right] . \]  

(2.2.30)
On combining the $V \ln T$ terms together, then we can write equation (2.2.30) in the following way

\[
\frac{q}{\lambda} = -\lambda \frac{V}{T} + \frac{5}{2} kT n_1 \bar{V}_1 + n_2 \bar{V}_2 - kT \sum_h \zeta^h
\]

\[
\left\{ \int f^{(o)}_1 (\alpha_1 \bar{V}_1^2 - \frac{5}{2}) \phi^{(h)}_{1d} (V_1) \frac{V_1}{\bar{V}_1} d V_1 - \int f^{(o)}_2 (\alpha_2 \bar{V}_2^2 - \frac{5}{2}) \phi^{(h)}_{2d} (V_2) \frac{V_2}{\bar{V}_2} d V_2 \right\} \left( \bar{V}_1 - \bar{V}_2 \right) \frac{n_1 n_2}{p_{12} n_2} ,
\]

(2.2.31)

where

\[
\lambda = -k \sum_h \zeta^h \left\{ \int f^{(o)}_1 (\alpha_1 \bar{V}_1^2 - \frac{5}{2}) \phi^{(h)}_{1d} (V_1) \frac{V_1}{\bar{V}_1} d V_1 + \int f^{(o)}_2 (\alpha_2 \bar{V}_2^2 - \frac{5}{2}) \phi^{(h)}_{2c} (V_2) \frac{V_2}{\bar{V}_2} d V_2 \right\}
\]

\[
+ k \sum_h \zeta^h \left\{ \int f^{(o)}_1 (\alpha_1 \bar{V}_1^2 - \frac{5}{2}) \phi^{(h)}_{1d} (V_1) \frac{V_1}{\bar{V}_1} d V_1 - \int f^{(o)}_2 (\alpha_2 \bar{V}_2^2 - \frac{5}{2}) \phi^{(h)}_{2d} (V_2) \frac{V_2}{\bar{V}_2} d V_2 \right\} \frac{D_T}{D_{12}} .
\]

(2.2.32)

Note $\lambda$ reduces to the single gas expression if we put $\phi^{(h)}_{1d}$ to zero and put $f^{(o)}_1 = f^{(o)}$ and $f^{(o)}_2$ to zero.

(iii) Viscosity

As in the single gas case, the coefficient of shear viscosity, $\eta_s$, is obtained from the pressure tensor, $p_z$, which is given by

\[
p_z = \sum_{i=1}^2 m_i \int \left( f^{(o)}_i + f^{(o)} \phi_i \right) \frac{V_i}{\bar{V}_i} d V_i ,
\]

(2.2.33)
from which we have

\[
p^{(1)} = -2n_s \frac{v^s}{u_o} = \sum_{i=1}^{2} m_i \int f_i^{(o)} \phi_i \frac{v_i}{v} \frac{d v_i}{v_i} ,
\]

(2.2.34)

where \( p^{(1)} \) is the correction to the pressure tensor.

On using equations (2.2.2, 11) and discarding odd functions of \( V_i \), then equation (2.2.34) becomes for \( p^{(1)} \)

\[
p^{(1)} = -2n_s \frac{v^s}{u_o} = \sum_{i=1}^{2} m_i \int f_i^{(o)} \sum_{h} \gamma h \phi_{ih}^{(h)}(V_i) \frac{V_i}{v} \frac{d v_i}{v_i}
\]

\[
= \left[ \frac{2}{15} \sum_{i=1}^{2} m_i \int f_i^{(o)} \sum_{h} \gamma h \phi_{ih}^{(h)}(V_i) \frac{V_i}{v} \frac{d v_i}{v_i} \right] \frac{v^s}{u_o}
\]

(2.2.35)

so that

\[
\eta_s = -\frac{1}{15} \sum_{i=1}^{2} m_i \int f_i^{(o)} \sum_{h} \gamma h \phi_{ih}^{(h)}(V_i) \frac{V_i}{v} \frac{d v_i}{v_i} .
\]

(2.2.36)

We saw that, for the single gas case, the transport coefficients are obtained as the sum of an infinite set of integrals. Here too, we can write the transport coefficients as the sum of infinite series

\[
y = \sum_{h} \gamma h y(h) ,
\]

where

\[
y = \lambda , \quad D_{12} , \quad D^T \quad \text{or} \quad \eta_s .
\]

(2.2.37)
On equating powers of $\xi$ we have expressions for $y^{(h)}$ in terms of integrals involving $\phi_{ic,d,n}^{(h)}$.

In order to obtain the total transport coefficients, we have to perform the sums indicated in (2.2.37). The determination of these sums is discussed in general at the end of Chapter 1, and in specific in Chapter 5.

Finally in this chapter, for completeness, we will consider briefly the multicomponent gas case.

2.3 Multi-Component Gas Mixture

(a) Iterative Method and Auxiliary Conditions

For a gas containing $N$ components we have $N$ equations for the 2nd approximation to Boltzmann's equation of the following form (see Chapter 1 for details)

$$f_i^{(0)}\left[\frac{n_i}{n_1} (v_{i1} \cdot d_{i1}) + 2 a_i v_{i1} \cdot \frac{\partial}{\partial v_{i1}} \left( v u_0 - (\xi^2 - a_i v_{i1}^2) v_{i1} \cdot v \ln T \right) \right]$$

$$= \sum_{j=1}^{N} \left[ f_i^{(0)}(v_j) f_i^{(0)}(u_j) \right] \left\{ \phi_i(v_j) + \phi_j(u_j) \right\}$$

$$- \phi_i(v_j) - \phi_j(u_j) \right\} d_i g_{ij} b \, db \, d\xi \, d \xi$$

for $i = 1, 2, \ldots, N$ \hspace{1cm} (2.3.1)

As for the single and binary gas cases, we can write

$$\phi_i^{(1)}(v_i) = \phi_{ic} \cdot v \ln T + \phi_{i0} : v u_0 + \phi_{id} \cdot d_i$$

or
\[ \begin{align*}
= \phi_{ic}(V_i) \frac{V_i}{V_1} \cdot \nabla \ln T + \phi_{in}(V_i) \frac{V_i}{V_1} \cdot \nabla u_0 \\
+ \phi_{id}(V_i) \frac{V_i}{V_1} \cdot d_i \\
\text{for } i = 1 \ldots N. 
\end{align*} \tag{2.3.2} \]

Then, on substituting (2.3.2) into (2.3.1) and equating like gradients we have 3N equations to solve of the form

\[ \begin{align*}
(a_i V_i^2 - s_i) V_i &= \sum_{j=1}^{N} \int_{f_j}^{(s)}(U_j) \left\{ \phi_{ic}(V_i) + \phi_{jc}(U_j) \right\} \\
&- \phi_{ic}(V_i) - \phi_{jc}(U_j) \right\} g_{ij} \text{ b } \text{ d b } u_j \text{ d } v_j, \\
\tag{2.3.3} \end{align*} \]

\[ \begin{align*}
2a_i V_i^2 V_i &= \sum_{j=1}^{N} \int_{f_j}^{(s)}(U_j) \left\{ \phi_{in}(V_i) + \phi_{jn}(U_j) \right\} \\
&- \phi_{in}(V_i) - \phi_{jn}(U_j) \right\} g_{ij} \text{ b } \text{ d b } u_j \text{ d } v_j, \\
\tag{2.3.4} \end{align*} \]

\[ \begin{align*}
\frac{\n_i}{n_i} V_i \cdot d_i &= \sum_{j=1}^{N} \int_{f_j}^{(s)}(U_j) \left\{ \phi_{id}(V_i) \cdot d_i + \phi_{jd}(U_j) \cdot d_j \right\} \\
&- \phi_{id}(V_i) \cdot d_i - \phi_{jd}(U_j) \cdot d_j \right\} g_{ij} \text{ b } \text{ d b } u_j \text{ d } v_j, \\
\tag{2.3.5} \end{align*} \]

For convenience we can write equation (2.3.3, 4, 5) in a more compact form as follows

\[ \begin{align*}
X_{ic} &= - \phi_{ic}(V_i) P_i + Q_i \phi_{ic} + \sum_{j \neq i} R_{ij} \phi_{jc}, \\
X_{in} &= - \phi_{in}(V_i) P_i + Q_i \phi_{in} + \sum_{j \neq i} R_{ij} \phi_{jn}, \\
\text{and} \\
X_{id} \cdot d_i &= - \phi_{id} \cdot d_i P_i + Q_i \phi_{id} \cdot d_i + \sum_{j \neq i} R_{ij} \phi_{jd} \cdot d_j, \\
\text{for } i, j = 1, 2 \ldots N. \tag{2.3.6} \end{align*} \]
or generally

\[ X = - \phi P + Q \phi + R \phi, \quad (2.3.7) \]

where we have made use of the fact that the functions \( \phi(V) \) are independent of the integrating variables in the collision operator.

The operators \( P_i, Q_i, \) and \( R_i \) are defined as follows

\[ P_i = \sum_{j=1}^{N} \int f_j^{(o)}(U_j) g_{ij} b \, db \, dU_j \, d\varepsilon \quad (2.3.8) \]

\[ Q_i \phi_i = \int f_i^{(o)}(U_i) \left\{ \phi_i(V_i') + \phi_i(U_i') - \phi_i(U_i) \right\} g_{ii} b \, db \, dU_i \, d\varepsilon \]

\[ + \sum_{j=1}^{N} \int f_j^{(o)}(U_j) \phi_j(V_i') g_{ij} b \, db \, dU_j \, d\varepsilon \quad (2.3.9) \]

\[ \sum_{j \neq i}^{N} R_{ij} \phi_j = \sum_{j=1}^{N} \int f_j^{(o)}(U_j) \left\{ \phi_j(U_i') - \phi_j(U_j) \right\} g_{ij} b \, db \, dU_j \, d\varepsilon \quad (2.3.10) \]

These operators are similar to those for the binary case, except that here the summations are from 1 to \( N \).

As in the previous cases, to perform the iterations we expand the \( \phi \)'s in infinite series as follows

\[ \phi = \sum_{h=0}^{\infty} \zeta^h \phi^{(h)}, \quad (2.3.11) \]

where \( \phi \) is any of the functions \( \phi_{ic}, \phi_{in}, \phi_{id}, d_i \), and rewrite equation (2.3.7) as follows

\[ X = - \phi P + \zeta Q \phi + \zeta R \phi, \quad (2.3.12) \]
where $\zeta$ in both equations is an ordering parameter which will eventually be set equal to unity.

Then, on substituting equation (2.3.11) into (2.3.12), and equating coefficients of corresponding powers of $\zeta$ we obtain the following relationships

$$X = -\phi P \quad \text{zeroth iteration}, \quad (2.3.13)$$

$$\phi^{(1)} P = Q \phi^{(0)} + R \phi^{(0)} \quad \text{1st iteration}, \quad (2.3.14)$$

$$\vdots \quad \vdots \quad \vdots$$

$$\phi^{(h)} P = Q \phi^{(h-1)} + R \phi^{(h-1)} \quad \text{hth iteration}, \quad (2.3.15)$$

from which we can obtain all the $\phi^{(h)}$s.

As for the other cases, there are auxiliary conditions that must be placed upon $\phi_1$ to ensure correct definition of $n_1$, $u_0$, and $T$, namely

$$\int f_i^{(o)}(V_i) \phi_i(V_i) d\tilde{V}_i = 0, \quad \text{for } i = 1,2 \ldots N \quad (2.3.16)$$

$$\sum_{i=1}^{N} \int f_i^{(o)}(V_i) m_{\tilde{V}_i} \phi_i(V_i) d\tilde{V}_i = 0 \quad (2.3.17)$$

$$\sum_{i=1}^{N} \int f_i^{(o)}(V_i) \tilde{V}_i m_{\tilde{V}_i} \phi_i(V_i) d\tilde{V}_i = 0 \quad (2.3.18)$$

Using the form of $\phi$ given by equations (2.3.2 and 11) we find the only condition not automatically satisfied is that given by equation (2.3.17). On considering the different gradient terms given by
equation (2.3.11), we have the following equations, from (2.3.17),
to satisfy

\[
\sum_{i=1}^{N} \int f_i^{(o)}(V_i) m_i V_i \phi_i^{(h)}(V_i) V_i \cdot \frac{\partial}{\partial V_i} \ln T d V_i = 0 ,
\]

(2.3.19)

\[
\sum_{i=1}^{N} \int f_i^{(o)}(V_i) m_i V_i \phi_i^{(h)}(V_i) V_i \cdot \frac{d i}{d V_i} d V_i = 0 .
\]

(2.3.20)

for all \( h \).

As for the other cases, we can satisfy equations (2.3.19, 20) by
redefining the perturbation function to include invariant quantities
which do not affect the solution of the Boltzmann equation, but
enable us to satisfy all the auxiliary conditions.

On satisfying the auxiliary conditions, the transport coefficients
can be obtained by using the flux equations in a similar way to the
binary gas case, but the coefficients turn out to be somewhat more
involved, as indicated by the expressions given in H.C.B.\(^{(6)}\) (Chapter 7, §4).

2.4 Determination of the Infinite Sums Associated with
the Transport Coefficients

This section is concerned with investigating the possible ways
of determining the infinite sums associated with the transport coeffi­
cients.

In order to obtain the transport coefficients we have to sum
the infinite series given by equations (2.1.25, 32) and (2.2.37).
In the case of the Maxwellian and Pseudo-Maxwellian potential models,
we will find that the \( \varphi^{(i)} \)'s and hence \( \lambda^{(i)} \)'s and \( \eta^{(i)} \)'s are
described by geometrical progressions which can, of course, be summed easily to give expressions which are the same as those obtained by the Chapman-Cowling method. In the case of the Rigid Sphere model, it will be found that the $\lambda^{(i)}$'s closely approximate a geometrical progression and, on assuming this, the result so obtained is very close to that by the Chapman-Cowling method.

We can throw more light on the geometrical progression concept by using an alternative procedure for obtaining the coefficient of thermal conductivity, $\lambda$. If we represent the appropriate approximation to Boltzmann's equation in the following way

\[ L \phi_c = \lambda \phi_c \]  \hspace{1cm} (2.4.1)

then

\[ \frac{\langle \phi_c, L \phi_c \rangle}{k \langle \phi_c, \phi_c \rangle^2} = \frac{1}{\lambda} \phi \]  \hspace{1cm} (2.4.2)

where

\[ \lambda = \lambda \phi \]  \hspace{1cm} (2.4.3)

Here we have used the facts that

\[ \langle \phi_c, \phi_c \rangle = \frac{q}{(V \ln T) kT} = \frac{\lambda}{k} \]  \hspace{1cm} (2.4.4)

\[ \langle \phi_c, L \phi_c \rangle = \langle \phi_c, \phi_c \rangle \]  \hspace{1cm} (2.4.5)

and for any $\Psi$

\[ \langle \Psi \rangle = \int \Psi(y) f^{(0)}(y) dy \]  \hspace{1cm} (2.4.5)
If
\[ \langle \psi, L \psi \rangle = \langle \psi, X_c \rangle , \]  
(2.4.5)

\[ L \psi \neq X_c , \]  
(2.4.7)

we have
\[ \frac{\langle \psi, L \psi \rangle}{k \langle \psi, X_c \rangle^2} = \frac{1}{\lambda_\psi} , \]  
(2.4.8)

where \( \lambda_\psi < \lambda \) (this is a consequence of the variational principle, which states that of all the functions which satisfy (2.4.6), the solution of the integral equation (2.4.1) gives \( \phi_c, L \phi_c \) its maximum value. For more detail see Ziman's 'Electrons and Phonons' p.278-279(10).

By using the variational principle, one can try to match \( \phi_c \) with \( \phi_c \) and minimise (2.4.8) to force \( \lambda_\psi \) towards \( \lambda \).

In our case, we are iterating equation (2.4.1). Following the mathematics in section 1 of this chapter, we write equation (2.4.1) as
\[ (-L_0 + L_1) \phi_c = X_c . \]  
(2.4.9)

On iterating equation (2.4.9), we have
\[ \phi_c^{(o)} = -\frac{X_c}{\lambda_0} , \]  
(2.4.10)

\[ \phi_c^{(1)} L_0 = L_1 \phi_c^{(o)} , \]  
(2.4.11)

and
\[ \phi_c^{(n)} L_0 = L_1 \phi_c^{(n-1)} . \]  
(2.4.12)
So we can write

$$\varphi_c = \varphi_c^{(0)} + \varphi_c^{(1)} + \varphi_c^{(2)} + \ldots$$ \hspace{1cm} (2.4.13)

and in a corresponding manner

$$\lambda = \lambda^{(0)} + \lambda^{(1)} + \lambda^{(2)} + \ldots$$ \hspace{1cm} (2.4.14)

Using equations (2.4.2, 13), we have

$$\frac{\langle \phi_i^{(o)} + \phi_i^{(1)} + \ldots \rangle, L \langle \phi_c^{(o)} + \phi_c^{(1)} + \ldots \rangle}{k \langle \phi_c^{(o)} + \phi_c^{(1)} + \ldots \rangle X_c^2} = \frac{1}{\lambda} \hspace{1cm} (2.4.15)$$

In our case, if we put $\varphi = \varphi_c^{(o)}$ in (2.4.15), then we have

$$\frac{\langle \phi_c^{(o)} \rangle, L \phi_c^{(o)} \rangle}{k \langle \phi_c^{(0)} \rangle, X_c^2} = \frac{1}{\lambda^o} \hspace{1cm} (2.4.16)$$

where $\lambda^o$ is that approximation to the thermal conductivity coefficient, $\lambda$, which one obtains by using $\varphi_c^{(o)}$ as a trial function in equation (2.4.8).

On expanding $L$, as shown in equation (2.4.9), in the left-hand side of equation (2.4.16), we have

$$\frac{\langle \phi_c^{(o)} \rangle, -L_0 \phi_c^{(o)} \rangle + \langle \phi_c^{(o)} \rangle, L_1 \phi_c^{(o)} \rangle}{k \langle \phi_c^{(0)} \rangle, X_c^2} \hspace{1cm} (2.4.17)$$

which becomes, on using the iterative relationships

$$- \frac{\langle \phi_c^{(o)} \rangle, X_c^2}{k \langle \phi_c^{(0)} \rangle, X_c^2} + \frac{\langle X_c, \phi_c^{(1)} \rangle}{k \langle \phi_c^{(0)} \rangle, X_c^2} \hspace{1cm} (2.4.18)$$
From equation (2.4.3) we can write

$$\langle \phi_c, x_c \rangle = \frac{\lambda^{(n)}}{k}, \quad (2.4.19)$$

so that, on using equations (2.4.18, 19), we have, for (2.4.16)

$$\frac{1}{\lambda(o)} - \frac{\lambda(1)}{\lambda(o)^2} = \frac{1}{\lambda_o}. \quad (2.4.20)$$

On re-arranging (2.4.20), we obtain

$$\frac{\lambda(o)}{1 - \frac{\lambda(1)}{\lambda(o)}} = \lambda_o, \quad (2.4.21)$$

which represents a geometrical progression.

Expanding the left-hand side of equation (2.4.21), assuming $\lambda(1) < \lambda(o)$, we have

$$\lambda_o = \lambda(o) + \lambda(o) \left( \frac{\lambda(1)}{\lambda(o)} \right) + \lambda(o) \left( \frac{\lambda(1)}{\lambda(o)} \right)^2 + \ldots, \quad (2.4.22)$$

compared with actual series for $\lambda$, equation (2.4.14)

$$\lambda = \lambda(o) + \lambda(1) + \lambda(2) + \ldots. \quad (2.4.14)$$

If we calculate $\lambda_o$ we find $\lambda_o \leq \lambda$ for the different potential models (see Chapters 3 and 4). In the case of two of the models, $\lambda(o), \lambda(1), \lambda(2) \ldots$ do form an exact geometrical progression and we have $\lambda = \lambda_o$. The other model gives results which numerically approximate very closely to a geometrical progression and in this case we have $\lambda = \lambda_o$. Now if $\phi_c^{(1)}(y)$ can, in fact, be described
by a geometrical progression, as in the Maxwellian and Pseudo-
Maxwellian cases, then we can write

\[ \phi_c^{(0)}(v) = a \phi_c(v) , \]  

(2.4.23)

where \( a \) is a constant.

On putting (2.4.23) into (2.4.16), we have

\[ \frac{\phi_c^{(0)} \cdot L \phi_c^{(0)}}{k \phi_c^{(0)} \cdot X_c^2} = \frac{a^2 \phi_c \cdot L \phi_c}{a^2 \phi_c \cdot X_c^2 k} , \]  

(2.4.24)

where replacing \( \phi_c^{(0)} \) with \( \phi_c^{(0)} \) does not affect (2.4.24). The implication of equation (2.4.24) is that \( \lambda = \lambda_0 \) in the geometrical progression case, so that the series representing \( \lambda \), (2.4.14), can be replaced by that representing \( \lambda_0 \), (2.4.22). For the case when we cannot assume equation (2.4.23) but we do find that \( \lambda^{(0)}, \lambda^{(1)} \) and \( \lambda^{(2)} \) follow an approximate geometrical progression, and that \( \lambda_0 = \lambda \) it seems a reasonable guess to use the series representing \( \lambda_0 \) instead of \( \lambda \).

Further, on considering the iterative procedure, this geometrical progression representation is not so surprising, since when we iterate Boltzmann's equation (2.4.2), it is effectively a repeated operation on the function

\[ \phi_c^{(0)} = - \frac{X_c}{L_0} ; \]

Namely

\[ \phi_c^{(1)} = \frac{1}{L_0} L_1 \phi_c^{(0)} , \]
\[ \phi^{(2)}_c = \frac{1}{L_0} L_1 \phi^{(1)}_c = \frac{1}{L_0} L_1 \frac{1}{L_0} L_1 \phi^{(o)}_c, \]

\[ = \left( \frac{L_1}{L_0} \right)^2 \phi^{(o)}_c, \]

and so on such that for \( \phi^{(n)}_c \) we have

\[ \phi^{(n)}_c(V) = \left( \frac{L_1}{L_0} \right)^n \phi^{(o)}_c. \]

In the case of the Maxwellian and Pseudo-Maxwellian potential models
the 'operator' \( L_0 \) is not a function of the velocity variable, \( V \),
(see appendix and Chapter 3), so we have

\[ \phi^{(1)}_c(V) = \frac{1}{L_0} L_1 \phi^{(o)}_c, \]

\[ \phi^{(2)}_c(V) = \frac{1}{L_0^2} L_1^2 \phi^{(o)}_c, \]

\[ \vdots \]

\[ \phi^{(n)}_c(V) = \frac{1}{L_0^n} L_1^n \phi^{(o)}_c. \]

For

\[ \dot{\phi}_c = \dot{\phi}^{(o)}_c + \dot{\phi}^{(1)}_c + \cdots + \dot{\phi}^{(n)}_c + \cdots, \]

we have

\[ \dot{\phi}_c = \dot{\phi}^{(o)}_c + \frac{1}{L_0} L_1 \dot{\phi}^{(o)}_c + \frac{1}{L_0^2} L_1^2 \dot{\phi}^{(o)}_c + \cdots + \frac{1}{L_0^n} L_1^n \dot{\phi}^{(o)}_c + \cdots. \] (2.4.25)

We find in Chapter 3 that
\[ L_1 \hat{\phi}_c^{(o)} = \hat{\phi}_c^{(o)} \left\{ \int F(x) \right\}, \quad (2.4.26) \]

and

\[ L_0 = \int G(x), \quad (2.4.27) \]

\( \chi \) is the scattering angle in the case of these two particular potential models. Hence we have an exact geometrical progression whose sum is

\[ \hat{\phi}_c = \frac{\hat{\phi}_c^{(o)}}{1 - \left( \frac{L_1}{L_0} \right)} = - \frac{X_c}{G(x)} \cdot \int G(x) = - \int H(x), \quad (2.4.28) \]

where we have put \( \int G(x) - \int F(x) = \int H(x). \)

In the rigid sphere case, \( L_0 \) is a function of \( \nu \), since

\[ L_0 = \left( \int e^{-u^2} (u^2 + v^2 - 2uv \cos \theta)^{\frac{1}{2}} du \right) \cdot \int H(x) = L_0(\nu), \quad (2.4.29) \]

(see Chapter 4) and we have, effectively,

\[ \hat{\phi}_c^{(o)}(\nu) = - \frac{X_c(\nu)}{L_0(\nu)}, \]

\[ \hat{\phi}_c^{(1)}(\nu) = \frac{1}{L_0(\nu)} L_1 \hat{\phi}_c^{(o)}(s), \]

\[ \hat{\phi}_c^{(2)}(\nu) = \frac{1}{L_0(\nu)} L_1 \hat{\phi}_c^{(1)}(s) = \frac{1}{L_0(\nu)} L_1 \frac{1}{L_0(s)} L_1 \hat{\phi}_c^{(o)}(t), \]

where \( s \) and \( t \) are dummy variables and \( L_0(\nu) \) can only be determined numerically.
Here, as in the Maxwellian and Pseudo-Maxwellian cases, we have a repeated operation, but since the operator, $L_\phi$, is now a function of the velocity variable, its effect is not so clear. However, I feel, even in this case, that it re-inforces, to some degree at least, the concept of an approximate geometrical progression being exhibited.

A similar analysis can, of course, be carried out for $\phi_\eta$ and hence for the viscosity coefficient, $\eta$, but since it closely parallels the thermal conductivity case we have confined ourselves to discussing the latter in this section.

A further discussion of the basic properties of the perturbation term, $\phi$, arising from the iterative method, together with possible implications, will be presented in Chapter 6.

On the basis of this analysis, we will henceforth look for solutions of $\lambda$ and the other transport coefficients in the form of (exact or approximate) geometrical progressions.

Having covered the general outline of the iterative method, we will now proceed to consider the calculating of the transport coefficient for specific potential models in forthcoming chapters.
Calculation of the Coefficients of Thermal Conductivity and Viscosity of a Simple Gas for Maxwellian and Pseudo-Maxwellian Molecules

Introduction

In this chapter we will be considering the calculation of the two transport coefficients of a simple gas containing (a) Maxwellian molecules, and (b) Pseudo-Maxwellian molecules.

It should be noted that for the molecular models being considered in this chapter there is no \( g \) dependence in the collision operator, so that the mathematical treatment will be identical up to the stage when the actual calculation of the coefficients for the respective molecular models are performed. We will also leave the differential cross-section, until the respective models are considered, in the following form

\[
\text{differential cross section} = [g \, b \, db].
\]

3.1 Thermal Conductivity

In this section we will be dealing with the calculation of the coefficient of thermal conductivity.

(a) Boltzmann's Equation and Iterative Relations

From the zeroth iteration of the second approximation to Boltzmann's equation, equation (2.1.14), we obtain an expression for \( \phi_c^{(o)} \) given by
\[ \phi_{c}^{(0)}(V) V \cdot V T = \frac{(\frac{5}{2} - \alpha V^2) V \cdot V T}{L_0}, \]  

(3.1.1)  

where \( L_0 \) does not depend on \( V \) for the particular molecular models we are considering.

Let us write

\[ \phi_{c}^{(0)}(V) = A^{(o)} + B^{(o)} \alpha V^2, \]  

(3.1.2)

where \( A^{(o)} \) and \( B^{(o)} \) do not depend on \( V \).

We wish to show that \( \phi_{c}^{(i)}(V) \) can be written in the form

\[ \phi_{c}^{(i)}(V) = A^{(i)} + B^{(i)} \alpha V^2, \]  

(3.1.3)

with a view to summing the \( \phi_{c}^{(i)} \)'s.

To establish this, we will determine \( \phi_{c}^{(0)} \) and \( \phi_{c}^{(1)} \) and then generalise.

Performing the first iteration equation (2.1.15) using \( \phi_{c}^{(0)} \) in the form of equation (3.1.2), we get for \( \phi_{c}^{(1)} \)

\[ \phi_{c}^{(1)}(V) V L_0 = \int f^{(o)}(U) \left\{ (A^{(o)} + B^{(o)} \alpha U^2) U \right\} \right. \]

\[ + \left. (A^{(o)} + B^{(o)} \alpha V^2) V - (A^{(o)} + B^{(o)} \alpha U^2) U \right\} [g b \, db] \, de \, du, \]

(3.1.4)

and thus

\[ \phi_{c}^{(1)}(V) V^2 L_0 = \int f^{(o)}(U) \left\{ (A^{(o)} + B^{(o)} \alpha U^2) U' \cdot V \right\} \right. \]

\[ + \left. (A^{(o)} + B^{(o)} \alpha V^2) V' \cdot V - (A^{(o)} + B^{(o)} \alpha U^2) U \cdot V \right\} \]

\[ [g b \, db] \, de \, du. \]  

(3.1.5)
The expression containing \((U \cdot V)\) in equation (3.1.5) does not contribute to the integration, since the collision operator is \(g\) independent in the cases being considered here, so equation (3.1.5) becomes

\[
\begin{align*}
\phi_{c}^{(1)}(V) V^{2} L_{o} &= \int f^{(o)}(U) \{ (A^{(o)} + B^{(o)} a U^{12}) U' \cdot V \\
&+ (A^{(o)} + B^{(o)} a V^{12}) V' \cdot V \} [g b db] de du .
\end{align*}
\tag{3.1.6}
\]

Separating out the terms into factors of \(A^{(o)}\) and \(B^{(o)}\) in equation (3.1.6), we have

\[
\begin{align*}
\phi_{c}^{(1)}(V) V^{2} L_{o} &= A^{(o)} \int f^{(o)}(U) (U' \cdot V + V' \cdot V) [g b db] de du \\
&+ a B^{(o)} \int f^{(o)}(U) (U^{12} U' \cdot V + V^{12} V' \cdot V) [g b db] de du .
\end{align*}
\tag{3.1.7}
\]

For a single component gas from conservation of momentum we have

\[
V + U = V' + U' .
\tag{3.1.8}
\]

So that the integral involved with \(A^{(o)}\) can be transformed using equation (3.1.8) to become

\[
A^{(o)} \int f^{(o)}(U) (V + U) \cdot V [g b db] de du .
\tag{3.1.9}
\]

As mentioned earlier the \((U \cdot V)\) term does not contribute, so we are left with a straightforward integral of similar form to \(L_{o}\), namely

\[
A^{(o)} V^{2} \int f^{(o)}(U) [g b db] de du .
\tag{3.1.10}
\]
Having dealt with the $A^{(o)}$ term, we will now consider the $B^{(o)}$ term, which is

$$a B^{(o)} \int f^{(o)}(U) (U'^2 \mathbf{V} + \mathbf{V}'^2 \mathbf{V}' \cdot \mathbf{V}) [g \ b \ db] \ d^2 \mathbf{u} \cdot \mathbf{u}.$$  

(3.1.11)

To perform the $\mathbf{u}$ integration in equation (3.1.11), we must extract the $\mathbf{u}$ dependence from the term $(U'^2 \mathbf{V} + \mathbf{V}'^2 \mathbf{V}' \cdot \mathbf{V})$. This is done in the following way. On using the conservation laws, we can write

$$(U'^2 \mathbf{V} + \mathbf{V}'^2 \mathbf{V}' \cdot \mathbf{V}) = U'^2 \left(\mathbf{U} + \mathbf{V} - \mathbf{V}'\right) \cdot \mathbf{V} + (U'^2 + V'^2 - U'^2) \mathbf{V}' \cdot \mathbf{V}.$$  

(3.1.12)

On re-arranging, we have, for the right-hand side

$$U'^2 \mathbf{V} + \mathbf{V}'^2 \mathbf{V}' - 2U'^2 \mathbf{V} \cdot \mathbf{V}' + U'^2 \mathbf{V}' \cdot \mathbf{V} + V'^2 \mathbf{V}' \cdot \mathbf{V}.$$  

(3.1.13)

From the appendix we obtain for $U'^2$ and $\mathbf{V}' \cdot \mathbf{V}$ the following relationships

$$U'^2 = \frac{1}{2} \left\{2 \mathbf{V}^2 (1 - \cos \chi) + \mathbf{U}^2 (2 + 2 \cos \chi)\right\} + |\mathbf{V} \cdot \mathbf{U}| \sin \chi \cos \chi ;$$

$$\mathbf{V}' \cdot \mathbf{V} = \frac{1}{2} \left\{\left(1 + \cos \chi\right) \mathbf{V}^2 + (1 - \cos \chi) \mathbf{V} \cdot \mathbf{U}\right\} - \frac{1}{2} |\mathbf{V} \cdot \mathbf{U}| \sin \chi \cos \chi .$$

Before substituting for $U'^2$ and $\mathbf{V}' \cdot \mathbf{V}$ in equation (3.1.13), and performing the integration indicated in equation (3.1.11), we can achieve a degree of simplification by noting that on performing the $\mathbf{u}$
integration terms linear in $\cos \theta$ do not contribute. Similarly, we can obtain further simplification if, on performing the angular part of the $\underline{U}$ integration we define $\cos \theta = \underline{U} \cdot \underline{V} / ||\underline{U}|| ||\underline{V}|$; then the linear terms in $(\underline{U} \cdot \underline{V})$ do not contribute. On taking advantage of the above simplifications when performing the appropriate angular integrations, the expression (3.1.11) becomes, after first substituting for $\underline{U}^{'2}$ and $\underline{V}' \cdot \underline{V}$

$$\alpha B^{(o)} 4\pi^2 \int f^{(o)}(U) \left[ v^4 (1 + \cos^2 \chi) + \frac{5}{3} v^2 u^2 (1 - \cos^2 \chi) \right]$$

$$[g \ b \ \text{db}] U^2 \ du \ .$$  \hspace{1cm} (3.1.14)

Finally, on performing the $||\underline{U}||$ integration, equation (3.1.14) becomes

$$\alpha B^{(o)} v^4 \pi n \int [g \ b \ \text{db}] (1 + \cos^2 \chi) + \frac{5}{2} B^{(o)} v^2 \pi n \int [g \ b \ \text{db}]$$

$$(1 - \cos^2 \chi) \ .$$ \hspace{1cm} (3.1.15)

For the $A^{(o)}$ term, expression (3.1.10), on performing the $\underline{U}$ integration, we have

$$2 A^{(o)} \pi v^2 n \int [g \ b \ \text{db}] \ .$$ \hspace{1cm} (3.1.16)

So far we have determined the form of the right-hand side of equation (3.1.6). For the left-hand side, we have (see equation (2.1.15))

$$\phi^{(1)}_c (V) v^2 \int f^{(o)}(U) [g \ b \ \text{db}] \ de \ du \ ,$$ \hspace{1cm} (3.1.17)

which, on performing the $e$ and $u$ integration, becomes

$$\phi^{(1)}_c (V) v^2 n 2\pi \int [g \ b \ \text{db}] \ .$$ \hspace{1cm} (3.1.18)
Equating the left-hand side and right-hand side of equation (3.1.6), using equations (3.1.15, 16 and 18) and cancelling common terms, we obtain the following relationship

\[ \phi_c^{(1)} \int [g \ b \ db] = \{ \mathfrak{B}_4 B^{(o)} \int (1 - \cos^2 x) [g \ b \ db] + A^{(o)} \int [g \ b \ db] \} + \{ \frac{B^{(o)}}{2} \int (1 + \cos^2 x) [g \ b \ db] \} \alpha V^2. \]  

(3.1.19)

From equation (3.1.19) we can write \( \phi_c^{(1)} \) in the form

\[ \phi_c^{(1)} = A^{(1)} + B^{(1)} \alpha V^2. \]  

(3.1.20)

It thus follows that, in general

\[ \phi_c^{(i)} = A^{(i)} + B^{(i)} \alpha V^2, \]  

(3.1.21)

so that from equations (3.1.19, 20 and 21) we can obtain a relationship between the \( A^{(i+1)} \) and \( B^{(i+1)} \) terms and the \( A^{(i)} \) and \( B^{(i)} \) terms.

Before we obtain relationships between the \( i \)th and \( (i+1) \)th terms, we must make sure that each of the \( \phi_c^{(i)} \)'s individually satisfy the auxiliary conditions.

(b) Auxiliary Conditions and Summation of Perturbation Terms

The only condition that is not automatically satisfied is the second one (see Chapter 2, equation (2.1.18)). In order to satisfy this condition a term, \( \alpha^{(i)} \cdot V \) is added to \( \phi_c^{(i)} \), the coefficient, \( \alpha^{(i)} \), of which can be determined from satisfying the second auxiliary condition.
So the total functional representation of the \( i \)th approximation to the perturbation term, \( \overline{\phi}_c \), is given by

\[
\overline{\phi}_c^{(i)} V \cdot \frac{V_T}{T} = \phi_c^{(i)} V \cdot \frac{V_T}{T} + \alpha^{(i)} \cdot V ,
\]  

(3.1.22)

where \( \phi_c^{(i)} \) is defined in equation (3.1.22).

If we place equation (3.1.22) into the second auxiliary conditions, we get

\[
\int \phi^{(o)}(V) \overline{\phi}_c^{(i)} V \cdot \frac{V_T}{T} dV + \int \phi^{(o)}(V) \alpha^{(i)} \cdot V dV = 0 .
\]  

(3.1.23)

On putting in the form given in equation (3.1.21), and cancelling common terms, equation (3.1.23) becomes

\[
\frac{V_T}{T} \int e^{-\alpha V^2} V \phi^{(i)}(V) (A^{(i)} + \alpha B^{(i)} V^2) dV + \alpha^{(i)} \int e^{-\alpha V^2} V dV = 0 ,
\]  

(3.1.24)

from which we obtain

\[
\alpha^{(i)} = - (A^{(i)} + s^2 B^{(i)}) \frac{V_T}{T} .
\]  

(3.1.25)

Substituting for \( \alpha^{(i)} \) in equation (3.1.22), and putting \( \phi^{(i)}_c \) in the form indicated in equation (3.1.21), we get for \( \overline{\phi}_c^{(i)} \)

\[
\overline{\phi}_c^{(i)} V \cdot \frac{V_T}{T} = (A^{(i)} + \alpha B^{(i)} V^2) V \cdot \frac{V_T}{T} - (A^{(i)} + s^2 B^{(i)}) V \cdot \frac{V_T}{T} \\
= (\alpha V^2 - s^2) B^{(i)} V \cdot \frac{V_T}{T} ;
\]  

(3.1.26)
and similarly

$$\frac{\phi_c}{V} \cdot \frac{V_T}{T} = (\alpha \nu^2 - \frac{\gamma}{2}) B(i+1) \cdot \frac{V}{T}. \quad (3.1.27)$$

We see that summing the \( \phi_c \)'s essentially involves summing the \( B(i) \)'s; hence we need to find a relationship between the \( B(i) \)'s in order to perform the sum. We can obtain a relationship between the \( B(i) \)'s by considering equations (3.1.19, 20 and 21), namely

$$B(i+1) = B(i) \cdot \frac{1 + \cos^2 \chi}{[g b \, db]} . \quad (3.1.28)$$

Thus we have a straightforward geometrical progression type relationship, whose sum is given by

$$\sum B(i) = B = \frac{B(0)}{1 - \frac{B(1)}{B(0)}} . \quad (3.1.29)$$

From equations (3.1.1, 2) it can be seen that

$$B(0) = -\frac{1}{L_c} = -\frac{1}{\int f(u) \, [g b \, db] \, de \, du} . \quad (3.1.30)$$

and, using expressions (3.1.17 and 18), (3.1.30) becomes

$$B(0) = -\frac{1}{2\pi n \int [g b \, db]} . \quad (3.1.31)$$

On using equations (3.1.31) and (3.1.28), equation (3.1.29) becomes

$$B = -\frac{1}{2\pi n \cdot \left\{ \int (1 - \cos^2 \chi) \, [g b \, db] \right\}} . \quad (3.1.32)$$

Having found an expression for \( B \) we can write
by using (3.1.26) and (3.1.29).

Having obtained $\bar{\phi}_c$ in explicit form, by performing the corresponding infinite sum, we can now determine the coefficient of thermal conductivity.

(c) Thermal Conductivity Coefficient

The coefficient of thermal conductivity can be obtained from the heat flux equation

$$q = -\lambda \nabla T = \int \frac{1}{2m} V^2 \nu f^{(0)}(V) \bar{\phi}_c(V) \nu \cdot \frac{V}{T} dV,$$

(3.1.34)

where $\lambda$ is the coefficient of thermal conductivity.

On substituting for $\bar{\phi}_c$ from (3.1.33) into (3.1.34), we get

$$q = -\lambda \nabla T = B \int \frac{1}{2m} V^2 \nu f^{(0)}(V) (\alpha V^2 - \frac{\gamma}{2}) \nu \cdot \frac{V}{T} dV.$$

(3.1.35)

Performing the integration, we obtain

$$q = -\lambda \nabla T = 5B \frac{k^2 T}{m} \nabla T,$$

(3.1.36)

from which we obtain

$$\lambda = -5B \frac{k^2 T}{m}.$$

(3.1.37)

Finally, we have to consider the form of B for the respective models.
(i) Maxwellian Model

Our B is given by

\[ B = - \frac{1}{2n \pi \{f(1 - \cos^2 \chi) [g b db]\}} \]  

(3.1.32)

In the case of the Maxwellian model, we can write

\[ [g b db] = \left( \frac{2K}{m} \right)^{1/2} \nu_o d \nu_o \]  

(3.1.38)

and further that

\[ \int (1 - \cos^2 \chi) \nu_o d \nu_o = A_2 (5) \]  

(3.1.39)

(For more details concerning equations (3.1.38 and 39) see appendix.)

Substituting (3.1.38 and 39) into (3.1.32), the expression for B becomes

\[ B = - \frac{1}{2n \pi A_2 (5)} \left( \frac{M}{2K} \right)^{1/2} \]  

(3.1.40)

Using equations (3.1.37) and (3.1.40), the final form for the coefficient of thermal conductivity, \( \lambda \), for Maxwellian molecules is given by

\[ \lambda = \frac{5}{A_2 (5)} \frac{k^2 T}{m^{1/2}} \cdot \frac{1}{2\pi} \cdot \frac{1}{(2K)^{1/2}} \]  

(3.1.41)

(ii) Pseudo-Maxwellian or Soft Sphere Model

Here we can write

\[ [g b db] = g^* \frac{g^2}{4} \sin \chi \, d\chi \]  

(3.1.42)
where $g^*$ and $\sigma$ are constants (see appendix for details). Then, the expression for $B$ in equation (3.1.32) becomes

$$B = \frac{3}{2n \pi \sigma^2 \ g^*}, \quad (3.1.43)$$

so that equation (3.1.37) gives for $\lambda$

$$\lambda = \frac{15 \ k^2 \ T}{2\pi \ m \ \sigma^2 \ g^*}, \quad (3.1.44)$$

which represents the final form for the thermal conductivity coefficient for Pseudo-Maxwellian molecules.

3.2 Viscosity

In this section we will be dealing with the calculation of the coefficient of shear viscosity.

(a) Boltzmann's Equation and Iterative Relations

From the zeroth iteration of the second approximation to Boltzmann's equation, (2.1.16), we obtain an expression for $\phi^{(o)}_{\eta}$ given by

$$\phi^{(o)}_{\eta} \ V^o \ V : \ V u_\circ = - \frac{2 \ a \ V^o \ V : \ V u_\circ}{L_\circ} . \quad (3.2.1)$$

For convenience, we will write

$$\phi^{(o)}_{\eta} \ V^o \ V : \ V u_\circ = D^{(o)} \ V^o \ V : \ V u_\circ , \quad (3.2.2)$$

and, as for the conductivity case, we expect a generalisation of the form

$$\phi^{(i)}_{\eta} \ V^o \ V : \ V u_\circ = D^{(i)} \ V^o \ V : \ V u_\circ , \quad (3.2.3)$$
where $D^{(i)}$ does not depend on $V$.

To establish this, we will determine the relationship between $\phi^{(1)}_n$ and $\phi^{(1)}_n$ and then generalise.

Performing the first iteration, equation (2.1.17), using $\phi^{(1)}_n$ in the form (3.2.2), we get for $\phi^{(1)}_n$

$$\phi^{(1)}_n \ V \ V : V \ u_0 \ L_0 = \int f^{(1)}(U) [g \ b \ db] \left\{ D^{(1)}_n \ V \ V : V \ u_0 \right\}$$

$$+ D^{(1)}_n \ u_0 \ u' : V \ u_0 \ - D^{(1)}_n \ u_0 \ u : V \ u_0 \} \, d\, u \, d\epsilon,$$

and thence

$$\phi^{(1)}_n \ V \ V : V \ V \ L_0 = \int f^{(1)}(U) [g \ b \ db] \left\{ D^{(1)}_n \ V \ V : V \ V \right\}$$

$$+ D^{(1)}_n \ u_0 \ u' : V \ V \ - D^{(1)}_n \ u_0 \ u : V \ V \} \, d\, u \, d\epsilon.$$  

(3.2.4)

If we use the identity

$$C_1 C_2 : C_1 C_2 = (C_1 \cdot C_2)^2 - \frac{1}{2} C_1^2 C_2^2,$$

then equation (3.2.5) can be simplified somewhat. On simplifying and neglecting terms which do not contribute to the $U$ integration, we are left with the following expressions for the curly bracket part of the integrand in (3.2.5)

$$\left\{ \frac{1}{2} V^b + 2(V_1 \cdot V)^2 - 2(U_1 \cdot V)(V_1 \cdot V) - 2V^2(V_1 \cdot V) \right\}.$$

From the appendix, equation (A1.6), we have

$$V_1 \cdot V = \frac{1}{2} \left\{ (1 + \cos x)V^2 + (1 - \cos x) V \cdot U \right\}$$

$$- \frac{1}{2} |V \cdot U| \sin x \cos \epsilon,$$
so that we can now perform the integration indicated in (3.2.5).

It is worth noting that linear terms in \((V \cdot U)\) and in \(\cos \theta\) do not contribute. On performing the integration, the right-hand side of (3.2.5) becomes

\[
\nu_3 \pi n \nu^4 D^{(o)} \left\{ [g \ b \ db] \ (1 + 3 \cos^2 \chi) \right\},
\]

and the left-hand side of (3.2.5) becomes, on substituting for \(L_0\)

\[
\phi_{\eta}^{(1)} \nu_3 \pi n \nu^4 \left\{ [g \ b \ db] \right\}.
\]

On equating the two sides of (3.2.5), we have

\[
\phi_{\eta}^{(1)} \int [g \ b \ db] = \nu_4 D^{(o)} \int [g \ b \ db] \ (1 + 3 \cos^2 \chi),
\]

but we also have, from (3.2.3), that

\[
\phi_{\eta}^{(1)} \nu^0 \nu : \nu \ U = D^{(1)} \nu^0 \nu : \nu \ U; \quad (3.2.7)
\]

thus, comparing (3.2.6) with (3.2.7), we have

\[
D^{(1)} = \nu_4 \frac{\int [g \ b \ db] \ (1 + 3 \cos^2 \chi)}{\int [g \ b \ db]} D^{(o)} \quad (3.2.8)
\]

It follows that, in general

\[
D^{(i+1)} = \nu_4 \frac{\int [g \ b \ db] \ (1 + 3 \cos^2 \chi)}{\int [g \ b \ db]} D^{(i)} \quad (3.2.9)
\]

Using equations (3.2.2) and (3.2.6-9), we can now sum the \(\phi_{\eta}^{(i)}\)'s
\[
\phi \varepsilon \varepsilon \varepsilon \varepsilon ; \varepsilon \varepsilon \varepsilon \varepsilon = \sum_{i=0}^{\infty} \phi^{(i)} \varepsilon \varepsilon \varepsilon \varepsilon ; \varepsilon \varepsilon \varepsilon \varepsilon = \sum_{i=0}^{\infty} D^{(i)} \varepsilon \varepsilon \varepsilon \varepsilon ; \varepsilon \varepsilon \varepsilon \varepsilon .
\]

(3.2.10)

(b) Auxiliary Conditions and Summation of Perturbation Terms

The individual \( \phi^{(i)} \) 's satisfy the auxiliary conditions (see
(2.1.17 -19) so we can obtain the viscosity coefficient directly from \( \phi \). But first we must perform the sum indicated in (3.2.10).

From equations (3.2.8) and (3.2.9), it is clear that a geometrical progression is exhibited by the \( D^{(i)} \) 's, so their sum is easily written as

\[
\sum_{i=0}^{\infty} D^{(i)} = D = \frac{D^{(0)}}{1 - \frac{D^{(1)}}{D^{(0)}}}.
\]

(3.2.11)

On substituting for \( D^{(1)} \) from (3.2.8), we have

\[
\sum_{i=0}^{\infty} D^{(i)} = D = \frac{D^{(0)}}{\frac{4a}{3\pi n} \int \left[ gb \right] (1 - \cos^2 \chi)}.
\]

(3.2.12)

and from equations (3.2.1) and (3.2.2), after substituting for \( L \), \( D^{(0)} \) is given by

\[
D^{(0)} = \frac{a}{\pi n \int \left[ gb \right]};
\]

(3.2.13)

so (3.2.12) becomes

\[
D = -\frac{4a}{3\pi n \int \left[ gb \right] (1 - \cos^2 \chi)}.
\]

(3.2.14)

From (3.2.10) we have

\[
\phi \varepsilon \varepsilon \varepsilon \varepsilon ; \varepsilon \varepsilon \varepsilon \varepsilon = D \varepsilon \varepsilon \varepsilon \varepsilon ; \varepsilon \varepsilon \varepsilon \varepsilon .
\]

(3.2.15)
Having determined $D$ and hence an explicit form for $\phi_n$ we can now calculate the shear viscosity coefficient, $\eta_s$.

(c) Shear Viscosity Coefficient

The shear viscosity coefficient is obtained from the pressure tensor in the following way.

The pressure tensor, $P$, is given by

$$P = m \int (f^{(o)} + f^{(c)} \phi_n V^o V : \nu u_o V V d V) ; \quad (3.2.16)$$

from which we have

$$P^{(1)} = m \int f^{(c)} \phi_n V^o V : \nu u_o V V d V, \quad (3.2.17)$$

where $P^{(1)}$ is the first order correction to the zero order pressure tensor. On using equation (3.2.15), we have

$$P^{(1)} = D m \int f^{(c)} V^o V : \nu u_o V V d V. \quad (3.2.18)$$

Equation (3.2.18) can be re-arranged into a more convenient form as follows

$$P^{(1)} = D \frac{2}{15} m \int f^{(c)}(V) V^4 d V \nu V^S u_o, \quad (3.2.19)$$

where $\nu V^S u_o$, the shear viscosity tensor, is a symmetric non-divergent tensor formed from $\nu u_o$. Then, making use of the fact that

$$P^{(1)} = -2\eta_s \nu V^S u_o \quad (3.2.20)$$

defines the coefficient of shear viscosity, $\eta_s$, we obtain from
equations (3.2.19 and 20) that

$$\eta_s = - \frac{1}{15} D m \int f^{(o)}(V) V^4 \, dV . \quad (3.2.21)$$

On performing the $V$ integration in (3.2.21), we obtain

$$\eta_s = - D \frac{n K^2 T^2}{m} . \quad (3.2.22)$$

Finally, we have to consider the form of $D$ for the respective models.

(i) **Maxwellian Model**

We have seen that $D$ is given by

$$D = - \frac{4\alpha}{3\pi n \int \left[ g \, b \, db \right] (1 - \cos^2 \chi)} . \quad (3.2.14)$$

In the case of the Maxwellian model we can write

$$\left[ g \, b \, db \right] = \left( \frac{2 K}{m} \right)^{\frac{1}{2}} v_o \, d v_o ; \quad (3.1.38)$$

and further that

$$\int (1 - \cos^2 \chi) v_o \, d v_o = A_2 (5) . \quad (3.1.39)$$

On substituting equations (3.1.38 and 39) into (3.2.14), the expression for $D$ becomes

$$D = - \frac{4\alpha}{3\pi n A_2 (5) \left( \frac{m}{2 K} \right)^{\frac{1}{2}}} . \quad (3.2.23)$$

Thus, using equations (3.2.22 and 23), $\eta_s$ is given by
\[ \eta_s = \frac{1}{3} \left( \frac{2m}{K} \right)^{\frac{3}{2}} \cdot \frac{kT}{\pi A_2} \left(5\right), \]  

which represents the final form for the viscosity coefficient, \( \eta_s \), for Maxwellian molecules.

(ii) **Pseudo-Maxwellian or Soft Sphere model**

Here we can write

\[ [g b db] = g^* \frac{\alpha^2}{4} \sin x \, dx, \quad (3.1.42) \]

where \( g^* \) and \( \alpha \) are constants.

Then, the expression for \( D \) in (3.2.14) becomes

\[
D = -\frac{4\alpha}{3\pi n \frac{\sigma^2}{4} g^*} \int (1 - \cos^2 \chi) \sin \chi \, d\chi
\]

\[ = -\frac{4\alpha}{\pi n \sigma^2 g^*}. \quad (3.2.25) \]

Thus, on using equation (3.2.22), we obtain for the coefficient of shear viscosity, in the case of Pseudo-Maxwellian molecules

\[ \eta_s = \frac{2 \frac{K}{\pi}}{\sigma^2} \frac{T}{g^*}. \quad (3.2.26) \]

3.3 **Concluding Remarks**

It should be noted that the results, which we have obtained here by the iterative method, are the same as those obtained by the standard Chapman and Cowling approach. Further, it can be seen that using this method we have quickly and easily obtained explicit forms both for the perturbation terms, \( \phi_c \) and \( \phi_\eta \) and for the corresponding transport coefficients.
CHAPTER 4

Calculation of the Transport Properties for
a Simple Gas of Rigid Spheres

4.1 Introduction

This chapter is mainly concerned with the calculation of the coefficient of thermal conductivity for a simple gas of rigid spheres. However, in the last section, a brief outline of how to calculate the coefficient of viscosity is given.

4.2 Basic Iterative Relationships

Following the procedure given in Chapter 2 section 1, we obtain the following relationships (see equations (2.1.14, 16))

\[
\left( \frac{5}{2} - \alpha v^2 \right) \frac{\nabla T}{T} = \phi_{c}\left(0\right) \left| \hat{V} \right| \frac{\nabla T}{T} \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) g b \, db \, d\epsilon \, du,
\]

\[\phi_{c}\left(0\right) \left| \hat{V} \right| \frac{\nabla T}{T} \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) g b \, db \, d\epsilon \, du = \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) \left\{ \phi_{c}\left(V'\right) \left| V' \right| \frac{\nabla T}{T} \right\} g b \, db \, d\epsilon \, du,
\]

\[+ \phi_{c}\left(0\right) \left| U' \right| \hat{U}' \cdot \frac{\nabla T}{T} - \phi_{c}\left(0\right) \left| U \right| \hat{U} \cdot \frac{\nabla T}{T} \right\} g b \, db \, d\epsilon \, du,
\]

\[\vdots
\]

\[\phi_{c}\left(n\right) \left| \hat{V} \right| \frac{\nabla T}{T} \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) g b \, db \, d\epsilon \, du = \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) \left\{ \phi_{c}\left(n-1\right) \left( V' \right) \left| V' \right| \frac{\nabla T}{T} \right\} g b \, db \, d\epsilon \, du,
\]

\[+ \phi_{c}\left(n-1\right) \left| U' \right| \hat{U}' \cdot \frac{\nabla T}{T} - \phi_{c}\left(n-1\right) \left( U \right) \left| U \right| \hat{U} \cdot \frac{\nabla T}{T} \right\} g b \, db \, d\epsilon \, du,
\]

\[\vdots
\]

\[\phi_{c}\left(0\right) \left| \hat{V} \right| \frac{\nabla T}{T} \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) g b \, db \, d\epsilon \, du,
\]

\[\vdots
\]

\[\phi_{c}\left(n\right) \left| \hat{V} \right| \frac{\nabla T}{T} \int n \left[ \frac{\alpha}{\pi} \right] \exp\left(- \alpha U^2 \right) g b \, db \, d\epsilon \, du,
\]

\[\vdots
\]
where
\[ \hat{U} = \frac{U}{|U|}. \]

As in Chapter 3, for the Maxwellian and Pseudo-Maxwellian potential model, we have the \( \phi_c^{(i)} \)'s to sum in order to determine the thermal conductivity coefficient. We will in like manner determine \( \phi_c^{(o)} \) and \( \phi_c^{(1)} \) first, and then use these to try to perform the infinite sum to obtain the transport coefficient. The relationships, in a more convenient form, containing \( \phi_c^{(o)} \) and \( \phi_c^{(1)} \) are as follows

\[
\left( \frac{5}{2} - \alpha v^2 \right) |V| = \phi_c^{(o)}(V) |V| \int n \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \exp(-\alpha U^2) \frac{g b \, d\theta \, d\phi \, du}{g b \, d\theta \, d\phi \, du}, \quad (4.2.4)
\]

\[
\phi_c^{(1)}(V) |V| \int n \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \exp(-\alpha U^2) \frac{g b \, d\theta \, d\phi \, du}{g b \, d\theta \, d\phi \, du} = \int n \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \exp(-\alpha U^2) \frac{g b \, d\theta \, d\phi \, du}{g b \, d\theta \, d\phi \, du}, \quad (4.2.5)
\]

and similarly for (4.2.3).

So, from equations (4.2.4, 5), we have three different types of integrals to consider, namely

\[
\int \exp(-\alpha U^2) g b \, d\theta \, d\phi \, du, \quad (I)
\]

\[
\int \exp(-\alpha U^2) \phi_c^{(o)}(U) |U| \hat{U} \cdot \hat{V} g b \, d\theta \, d\phi \, du, \quad (II)
\]

and

\[
\int \exp(-\alpha U^2) \phi_c^{(o)}(U') |U'| \hat{U}' \cdot \hat{V} g b \, d\theta \, d\phi \, du. \quad (III)
\]
At this point, I think it appropriate to introduce the details of the rigid sphere model so that the integrals mentioned above can be determined.

4.3 Rigid Sphere Model and the Manipulation of the Corresponding Iterative Relationships (into a more convenient form for computation)

Figure (2) shows the relationship between the variables involved in a collision between two rigid spheres of diameter \( \sigma_1 \) and \( \sigma_2 \) respectively.

The angle between \( \mathbf{g} \) and \( \mathbf{g}' \) is \( \chi \) which is the scattering angle; \( b \) is the impact parameter and the unit vector, \( \mathbf{a} \) is that joining the two centres at the instant of collision.

On considering the geometry, for like spheres, in Figure (2) we can write

\[
\pi \sigma^2 \int n \left( \frac{a}{\pi} \right)^{3/2} \exp(-\alpha U^2) g \, du , \quad (I)
\]

and

\[
\pi \sigma^2 \int n \left( \frac{a}{\pi} \right)^{3/2} \exp(-\alpha U^2) \phi_c^{(o)}(U) \, |U| \, \phi \, g \, du . \quad (II)
\]

In order to perform the \( U \) integration in (I) and (II) we can make
use of the Legendre polynomial properties in the following way.

First of all, \( g \) can be written in terms of the variables \( U \) and \( V \) as follows

\[
g = (U^2 + V^2 - 2 U \cdot V)^{1/2}.
\]

If we define \( U \cdot V = X = P_1(X) \) and \( P_0(X) = 1 \), where \( P_n \) is the Legendre polynomial of order \( n \) and use the identity

\[
g = (1 + \frac{U^2}{V^2} - 2 \frac{U}{V} X)^{1/2} = 1 - \sum_{n=0}^{\infty} \frac{(U/V)^{n+1}}{2n+1} \{P_{n+1}(X) - P_{n-1}(X)\}
\]

for \( U < V \), then integrals of type (I) and (II) can be determined.

This identity can be shown to be true in the following way.

Put \( \frac{U}{V} = h \), then the above identity becomes

\[
(1 + h^2 - 2hX)^{1/2} = 1 - \sum_{n=0}^{\infty} \frac{h^{n+1}}{2n+1} \{P_{n+1}(X) - P_{n-1}(X)\}.
\]

On differentiating, wrt \( X \), both sides of above, we have

\[
\frac{h}{(1 + h^2 - 2hX)^{3/2}} = \sum_{n=0}^{\infty} \frac{h^{n+1}}{2n+1} \frac{P_{n+1}'(X) - P_{n-1}'(X)}{2n+1},
\]

which, on making use of the Legendre polynomial properties, becomes

\[
\frac{1}{(1 + h^2 - 2hX)^{3/2}} = \sum_{n}^{} h^n P_n(X),
\]

which is a well-known generating function for \( P_n(X) \).
On making use of the orthogonality properties of the Legendre polynomials, (I) becomes

\[
4\pi^2 \sigma^2 n \left(\frac{\alpha}{\pi}\right)^{3/2} \int_0^V U^2 \exp(-\alpha U^2) \left[\frac{1}{3} \frac{U^3 + UV^2}{UV}\right] dU
\]

and (II) becomes

\[
4\pi^2 \sigma^2 n \left(\frac{\alpha}{\pi}\right)^{3/2} \int_0^V U^2 \exp(-\alpha U^2) \left[\frac{1}{3} \frac{V^3 + U^2 V}{UV}\right] dU
\]

The \(|U|\) integration in (I) and (II) can be performed numerically but we still have the type (III) integral to consider. The evaluation of type (III) is a little more difficult but it will be achieved in the following way. Firstly, using \(\hat{U}' \cdot \hat{V} = P_1(\hat{U}' \cdot \hat{V})\), then (III) can be written as

\[
\int \exp(-\alpha U^2) \left|U'\right| P_1(\hat{U}' \cdot \hat{V}) \sin\theta d\theta d\phi d\epsilon
\]

As mentioned previously, \(b \, db \, d\varepsilon = \frac{\sigma^2}{4} \sin\theta d\theta d\phi d\varepsilon\), for the rigid sphere model.

Now, for a rigid sphere model
\[
\begin{align*}
\sigma^2 \int \frac{1}{2} \delta(g'^2 - g^2) \, dg' &= \sigma^2 \iint \frac{1}{4} \delta(g'^2 - g^2) \, g' \, dg' \sin \theta \, d\theta \, d\phi \\
&= \sigma^2 \iint \sin \theta \, d\theta \, d\phi \, \frac{1}{4} \delta(g'^2 - g^2) \\
&= \sigma^2 \iint \sin \theta \, d\theta \, d\phi \, \frac{g}{4} \\
&= \int g \, dB \, d\phi \, d\theta,
\end{align*}
\]

where we have made use of the fact that \( |g| = |g'| \) during a collision between rigid spheres. So that equation (4.3.3) can be written as

\[
\sigma^2 \int \exp(-a \, U^2) \, \phi^0(U') \, |U'| \, P_1(\hat{U}' \cdot \hat{V}) \, \frac{1}{2} \delta(g'^2 - g^2) \, dg' \, dU.'
\]

(4.3.4)

On using

\[
g' = 2U' - U - V,
\]

(4.3.4) becomes

\[
\sigma^2 \int \delta \{U \cdot (V - U') - U' \cdot (V - U')\} \phi^0(U') \, |U'| \exp(-a \, U^2) \, P_1(\hat{U}' \cdot \hat{V}) \, du' \, du.
\]

(4.3.5)

Let

\[
\hat{W} = U - U',
\]

then the expression (4.3.5) becomes

\[
\sigma^2 \iint \delta(\hat{W} \cdot (V - U')) \exp(-a(U' + \hat{W})^2) \phi^0(U') \, |U'| \\
P_1(\hat{U}' \cdot \hat{V}) \, d\hat{W} \, du'.
\]

(4.3.6)
Consider the $W$ integration, then the relevant part of the integrand of (4.3.6) is

$$
\int \delta (W \cdot (V \cdot U')) \exp \left\{ - \alpha (U' + W)^2 \right\} \, dW . \quad (4.3.7)
$$

Choose $(V - U')$ to lie along the $W_z$ axis as shown in Figure (3).

Further, choose $U'$ and hence $V$ to be in the $X-Z$ plane. Since $(V - U')$ lies along the $z$ axis, it only has a $z$ component in the $W$ co-ordinate system so that

$$W \cdot (V - U') = W_z (V - U') ;$$

$$\therefore \delta (W \cdot (V - U')) = \delta (W_z (V - U'))$$

$$= \frac{1}{|V - U'|} \delta (W_z) . \quad (4.3.7)$$

Putting this into the integral being considered, and remembering that $U' \cdot W$ only has $x$ and $z$ components, we have

$$\int \frac{dW}{dW} \int \frac{dW}{dW} \int \frac{dW}{dW} \exp \left\{ - \alpha \{U'^2 + W^2 + 2W_x U'_x + 2W_z U'_z \} \right\} \delta (W_z)$$

The effect of $\delta (W_z)$ is to put $W_z$ to zero on integrating w.r.t. $W_z$; so we have

$$\int \frac{dW}{dW_x} \int \frac{dW}{dW_y} \frac{1}{|V - U'|} \exp \left\{ - \alpha \{U'^2 + W^2 + 2W_x U'_x \} \right\}$$

$$= \frac{\exp \left\{ - \alpha U'^2 \right\}}{|V - U'|} \int \frac{dW}{dW} \exp \left\{ - \alpha W^2 \right\} \int \frac{dW}{dW} \exp \left\{ - \alpha \{W_x^2 + 2W_x U'_x \} \right\} .$$

After performing the $W_y$ and $W_x$ integrations we obtain
fig [3]
\[
\frac{\pi \exp(-\alpha U'_{x}^2)}{a \frac{\exp(\alpha U'_{x}^2)}{|V - U'|}}
\]  

(4.3.8)

where we have completed the square of the exponential factor in order to perform the \(W_x\) integration.

Looking at Figure (3), it can be seen that

\[
U'_x = |U'| \sin \gamma ,
\]

so that

\[
U'_{x}^2 - U^2 = U'^2(\sin^2 \gamma - 1)
\]

\[
= - U'^2 \cos^2 \gamma .
\]

(4.3.9)

Now

\[
\cos \gamma = \frac{U' \cdot (V - U')}{|U'| |V - U'|},
\]

(4.3.10)

so that

\[
U'^2 \cos^2 \gamma = \frac{[U' \cdot (V - U')]^2}{|V - U'|^2} .
\]

(4.3.11)

On substituting (4.3.9) and (4.3.11) into (4.3.8), we have

\[
\frac{\pi \exp(- \alpha [U' \cdot (V - U')]^2/[|V - U'|^2])}{a \frac{\exp(\alpha [U' \cdot (V - U')]^2)}{|V - U'|}}
\]

(4.3.12)

so that (4.3.6) becomes, on substituting (4.3.12)

\[
\frac{\pi}{a \sigma^2} \int \frac{\phi_c(U')}{|V - U'|} P_1(U' \cdot \hat{V}) \exp(- \alpha [U' \cdot (V - U')]^2/[|V - U'|^2]) \, du' .
\]

(4.3.13)
The manipulation of (III) can be done with \( V' \) instead of \( U' \) and the expression obtained would be identical with (4.3.13), except that \( V' \) would be in the place of \( U' \) throughout.

The replacement of \( U' \) with \( V' \) leading to the equivalent expression will be exploited later.

Further manipulation of (4.3.13) is required before we are in a position to be able to perform the \( |U'| \) integration numerically.

Firstly, for convenience, we change the variable \( U' \), which is a dummy variable in (4.3.13), to \( U \) and then (4.3.13) becomes

\[
\frac{\pi}{a} \int \frac{\phi^{(o)}(U)}{|V - U|} P_1(U \cdot \hat{V}) \exp[-a(U \cdot (V - \hat{U}))^2] \, du.
\]

(4.3.14)

Then, on putting \( U \cdot \hat{V} = X \) and using spherical polars, (4.3.14) becomes

\[
\frac{4\pi^2}{a} \int_0^\infty \phi^{(o)}(U) \, |U| \, u^2 \, du \cdot \frac{1}{2} \int_{-1}^1 \frac{P_1(X) \exp[-a(U \cdot (U - V))^2]}{|U - V|} \, dx.
\]

(4.3.15)

Since the integral in (4.3.15) involves \( |U - V| \), we must split the range (as for type (I) and (II)) of integration over \( U \) into \( U < V \) and \( U > V \).

First consider \( U < V \) contribution, so the integral to be evaluated is

\[
\frac{4\pi^2}{a} \int_0^V \phi^{(o)}(U) \, |U| \, u^2 \, du \cdot \frac{1}{2} \int_{-1}^1 \frac{P_1(X) \exp[-a(U \cdot (U - V))^2]}{|U - V|} \, dx.
\]

(4.3.16)
Now put
\[ y = \frac{U \cdot (U - V)}{|U - V|} = \frac{U^2 - UVX}{(U^2 + V^2 - 2UVX)^{\frac{3}{2}}} \tag{4.3.17} \]
so we have

for \( x = -1 \), \( y = U \);
and \( x = +1 \), \( y = -U \).

On differentiating (4.3.17) w.r.t. \( x \) we obtain the relationship between \( dx \) and \( dy \) which is as follows
\[ dx = \frac{(U^2 + V^2 - 2UVX)^{\frac{3}{2}}}{UV(UVX - V^2)} \, dy \tag{4.3.18} \]
so that
\[ \frac{dx}{|U - V|} = \frac{(U^2 + V^2 - 2UVX)}{UV(UVX - V^2)} \, dy \tag{4.3.19} \]

On substituting (4.3.17) and (4.3.19) into (4.3.16), with the appropriate limits, we have
\[ \frac{4\pi^2}{\alpha} \int_0^V \phi_c(U) |U| U^2 \, dU \, \frac{1}{2} \int_U^U P_1(X) \, e^{-\alpha} y^2 \left[ \frac{U^2 + V^2 - 2UVX}{UV(UVX - V^2)} \right] \, dy \tag{4.3.20} \]

We next re-arrange the square bracket expression in (4.3.20) into a more convenient form, for use later, namely
\[ -\frac{1}{UV} \left[ 1 + \frac{(U^2 - UVX)}{(V^2 - UVX)} \right] \tag{4.3.21} \]
Now we need to express $X$ in terms of $y$, going back to (4.3.17) we have

$$y = \frac{U^2 - U V X}{(U^2 + V^2 - 2 U V X)^{\frac{3}{2}}}.$$  \hspace{1cm} (4.3.17)

If we square both sides of (4.3.17), and re-arrange, we get a quadratic equation for $X$; which can be solved by the usual method, to obtain

$$X = (-y^2 + u^2 \pm \sqrt{y^2 + v^2 - u^2})/UV .$$  \hspace{1cm} (4.3.22)

The negative sign is taken in (4.3.22), since this sign satisfies the limits for $X$ and $y$, so we have

$$U V = -y^2 + u^2 - \sqrt{y^2 + v^2 - u^2} .$$  \hspace{1cm} (4.3.23)

Putting (4.3.23) into (4.3.21), and simplifying, we obtain

$$-\frac{1}{UV} \left[ \frac{y}{\sqrt{a}} + 1 \right] .$$  \hspace{1cm} (4.3.24)

where

$$a = y^2 + v^2 - u^2 .$$

Then, on putting (4.3.24) into (4.3.20), we have

$$\frac{4 \pi^2}{\alpha} \int_0^N \phi_c^{(o)}(U) \left| U \right| U^2 dU \int_0^U P_1(X) \exp(-\alpha y^2) \frac{-1}{UV} \left[ 1 + \frac{y}{\sqrt{a}} \right] dy$$  \hspace{1cm} (4.3.25)

Now, putting $P_1(X) = X$, using (4.3.24), and neglecting terms in (4.3.25) which do not contribute on performing the $y$ integration, we have
\[
\frac{4\pi^2}{a} \int_0^N \phi_c^{(o)}(U) |U| U^2 \, dU \int_{-U}^U \exp\left(-a y^2\right) \frac{\left[-2y^2 + U^2\right]}{U^2V^2} \, dy.
\]

(4.3.26)

and since we have symmetric limits about zero, we can write (4.3.26) as follows

\[
\frac{4\pi^2}{a} \int_0^N \phi_c^{(o)}(U) |U| U^2 \int_0^U \exp\left(-a y^2\right) \frac{U^2 - 2y^2}{U^2V^2} \, dy \, dU.
\]

(4.3.27)

Now to consider the other part of the range of integration of \( U \), i.e. for \( U > V \).

So the integral to be evaluated in this case is as follows

\[
\frac{4\pi^2}{a} \int_V^\infty \phi_c^{(o)}(U) |U| U^2 \int_0^U \exp\left(-a y^2\right) \frac{U^2 - 2y^2}{U^2V^2} \, dy \, dU.
\]

(4.3.28)

First of all we will rewrite the factor in the exponential of (4.3.28) as follows

\[
\left[\frac{U \cdot (U - V)}{|U - V|}\right]^2 = \left[\frac{V \cdot (V - U)}{|U - V|}\right]^2 - (V^2 - U^2).
\]

(4.3.29)

Then, on continuing in a similar way as for the \( U < V \) case, we put

\[
y = \frac{V \cdot (V - U)}{|V - U|}
\]

and arrive at the following result for the integral (4.3.28)
So, combining (4.3.27) and (4.3.30), we obtain finally for the type (III) integral the following

\[ \frac{4\pi^2}{a} \int_{V}^{\infty} \phi^{(c)}(U) \cdot |U| \cdot U^2 \int_{0}^{V} \exp(-a\{U^2 - V^2\}) \cdot \exp(-a\,y^2) \times \frac{[V^2 - 2y^2]}{U^2y^2} \, dy \, dU. \]  

(4.3.30)

The manipulation of the integrals of type (I), (II), and (III) is similar to that used by Brooker and Green.

The final integrable forms for the type (I), (II), and (III) integrals are given by equations (4.3.1, 2 and 31) respectively. Notice that, unlike for the soft sphere and Maxwellian models, the integrals for the rigid sphere model will have to be evaluated numerically.

4.4 Auxiliary Conditions and Integral Form for the Coefficient of Thermal Conductivity, $\lambda$

As mentioned before, we have auxiliary conditions to satisfy (see Chapter 2, end of section 1(a)). Complying with the auxiliary conditions results in an additional factor $a^{(i)} \cdot Y$ being added to each of the $\phi^{(i)}(V)$, such that
\[
\int n \left( \frac{a}{\pi} \right)^{3/2} \exp(-aV^2) V \phi_c^{(i)}(V) |V| \hat{\nabla} \cdot \frac{V}{T} \, dV
\]
\[+ a^{(i)} \int n \left( \frac{a}{\pi} \right)^{3/2} \exp(-aV^2) VV \, dV = 0 \]
(4.4.1)

so that
\[
a^{(i)} = -\frac{\int \exp(-aV^2) V \phi_c^{(i)}(V) |V| \hat{\nabla} \cdot \frac{V}{T} \, dV}{\int \exp(-aV^2) VV \, dV} \] (4.4.2)

We define the perturbation function that satisfies the auxiliary condition, as well as Boltzmann's equation, by
\[
\phi_c^{(i)}(V) |V| \hat{\nabla} \cdot \frac{V}{T} = \phi_c^{(i)}(V) |V| \hat{\nabla} \cdot \frac{V}{T} + a^{(i)} \cdot V . \]
(4.4.3)

We are now in a position to calculate the coefficient of thermal conductivity, \( \lambda \), for the rigid sphere model. Just as we have expanded \( \phi_c(V) \) in an infinite series, then similarly for \( \lambda \) we have
\[
\lambda = \lambda^{(0)} + \zeta \lambda^{(1)} + \zeta^2 \lambda^{(2)} ... , \]
(4.4.4)

where, from the heat flux vector, \( q \)
\[
q = -\sum_{i=0}^{\infty} \zeta^i \lambda^{(i)} V \cdot \frac{V}{T} = -\sum_{i=0}^{\infty} \zeta^i \int \frac{m}{2a} (\mathcal{F}_2 - aV^2) n \left( \frac{a}{\pi} \right)^{3/2} \exp(-aV^2) \phi_c^{(i)}(V) |V| \hat{\nabla} \cdot \frac{V}{T} \, dV . \]
(4.4.6)
4.5 **Determination of Coefficient of Thermal Conductivity**

by Numerical Means

If we look at the relationships between the $\phi_c^{(i)}$'s, see equations (4.2.1, 5), then since the integrals involve types (I), (II), and (III), which are all numerical, it is only feasible to work out $\phi_c^{(0)}$, $\phi_c^{(1)}$ and $\phi_c^{(2)}$ and the corresponding $\lambda$ terms: $\lambda^{(0)}$, $\lambda^{(1)}$ and $\lambda^{(2)}$. This fact can be appreciated if we remember that, for each iteration, the order of the multi-fold integrations we have to perform increase by three, for this particular potential model.

Since, for the soft sphere model and the Maxwellian model, the $\phi_c^{(i)}$'s and the $\lambda^{(i)}$'s form geometrical progressions, then the $\lambda^{(i)}$'s may well approximately form a geometrical progression in the rigid sphere model case. In order to investigate this possibility we will first of all determine $\lambda^{(0)}$ and $\lambda^{(1)}$ for the rigid sphere model.

The calculation of $\lambda^{(0)}$ involves putting $i = 0$ in (4.4.6). Now $\phi_c^{(0)}$ is defined in (4.2.1) and (4.2.4), so we have

$$\phi_c^{(0)}(V) = \frac{\left(\frac{5}{2} - \alpha V^2\right)}{\int n \left(\frac{\alpha}{n}\right)^{3/2} \exp(-\alpha U^2) \, dt \, db \, de \, du} \cdot (4.5.1)$$

Now the integral in (4.5.1) involves a type (I), whose final form is given by (4.3.1). On substituting, (4.5.1) becomes

$$\phi_c^{(0)}(V) = \left(\frac{5}{2} - \alpha V^2\right) \left[4\pi^2 \, c^2 \, n \left(\frac{\alpha}{n}\right)^{3/2} \left\{ \int_0^V U^2 \exp(-\alpha U^2) \right. \right.$$}

$$\left. \left. \left[\frac{1}{3} U^3 + UV^2\right] \frac{1}{UV} \, du \right. \right.$$}

$$\left. \left. \left. + \int_V^\infty U^2 \exp(-\alpha U^2) \left[\frac{1}{3} V^3 + UV^2\right] \frac{1}{UV} \, du \right] \right}^{-1} \cdot (4.5.2)$$
so that we obtain $\lambda^{(0)}$ from

$$
- \lambda^{(0)} \nabla T = \int -\frac{m}{2a} (\frac{a}{V^2} - \alpha V^2) \ n \left( \frac{a}{V} \right) \ \hat{\phi}^{(0)}(V) \ \frac{V}{T} \ dV,
$$

(4.5.3)

where $\hat{\phi}^{(0)}(V)$ is given by (4.5.2).

The angular part of the $V$ integration in (4.5.3) can be performed analytically so that we are left with a double integration over $|U|$ and $|V|$. After changing to reduced variables the integration is performed numerically by Simpson's Rule on the computer with an accuracy of $\pm 10^{-4}$. The final result for $\lambda^{(0)}$ is put in a form similar to that in Chapman and Cowling for ease of comparison, namely

$$
\lambda^{(0)} = \frac{.2660}{\sigma^2} \left( \frac{k^3 T}{\pi m} \right)^{\frac{1}{2}} \left[ 1.8301 \pm 10^{-4} \right],
$$

(4.5.4)

where (.2660) comes from a $\left( \frac{2}{\pi} \right)^{\frac{3}{2}} \cdot \frac{1}{3}$ factor; and the square bracket term is the value of the double integration.

Chapman and Cowling get

$$
\lambda = \frac{75}{64} \cdot \frac{1}{\sigma^2} \cdot \left( \frac{k^3 T}{\pi m} \right)^{\frac{1}{2}} \cdot 1.02522
$$

$$
= 1.2014 \cdot \frac{1}{\sigma^2} \left( \frac{k^3 T}{\pi m} \right)^{\frac{1}{2}},
$$

(4.5.5)

or

$$
\lambda = \frac{.2660}{\sigma^2} \left( \frac{k^3 T}{\pi m} \right)^{\frac{1}{2}} \{4.5165\},
$$

to enable direct comparison with (4.5.4). Here the value for $\lambda$,
by the Chapman and Cowling method, is taken to be the fifth approximation, namely \([\lambda]_5\).

On comparing \(\lambda^{(0)}\) with \(\lambda\), the value of \(\lambda^{(0)}\) is about 39% of the value of \(\lambda\).

Now to calculate \(\lambda^{(1)}\). Here we need \(\phi^{(1)}(V)\) which is given by (see (4.3.2) and (4.3.5))

\[
\phi^{(1)}(V) \mid V \mid \int \exp(-a U^2) g b db d\epsilon du = \int \exp(-a U^2)
\]

\[
\left[\phi^{(0)}(U') \mid U' \mid (\hat{U}' \cdot \hat{V}) + \phi^{(0)}(V') \mid V' \mid \hat{V}' \cdot \hat{V}\right]
\]

\[
- \phi^{(0)}(U) \mid U \mid (\hat{U} \cdot \hat{V})\ g b db d\epsilon du . \tag{4.5.6}
\]

In (4.5.6) all three types of integrals are featured. Taking each term in turn, for the right-hand side; firstly, we have

\[
\int \exp(-a U^2) \phi^{(0)}(U') \mid U' \mid (\hat{U}' \cdot \hat{V}) g b db d\epsilon du ,
\]

which can be written in the form

\[
\int \exp(-a U^2) \phi^{(0)}(U') \mid U' \mid P_1(\hat{U}' \cdot \hat{V}) g b db d\epsilon du .
\]

Now this integral is of type (III) and its final integrable form is given by the expression (4.3.31).

Secondly, we have

\[
\int \exp(-a U^2) \phi^{(0)}(V') \mid V' \mid (\hat{V}' \cdot \hat{V}) g b db d\epsilon du .
\]

As mentioned when discussing type (III) integrals, this integral can be dealt with in the same way as for the previous one.
Thirdly, we have

\[ \int \exp(-\alpha U^2) \phi_c^{(0)}(U) \left| U \right| \left\langle \hat{U} . \hat{V} \right\rangle g \, d\theta \, d\phi \, d\xi \, d\nu . \]

This one can be written in the following form

\[ \int \exp(-\alpha U^2) \phi_c^{(0)}(U) \left| U \right| P_1(\hat{U} . \hat{V}) g \, db \, de \, du . \]

Now this integral is of type (II), and its final integrable form is given by (4.3.2).

Finally, we have, from the left-hand side of (4.5.6)

\[ \int \exp(-\alpha U^2) g \, db \, de \, du , \]

which is type (I), and has been discussed in conjunction with \( \lambda^{(0)} \).

So we now have integrable expressions for \( \phi_c^{(1)}(V) \), hence \( \lambda^{(1)} \) can be calculated. \( \lambda^{(1)} \) is given by

\[ - \lambda^{(1)} \nu T = - \int \frac{m}{2\alpha} \left( \frac{5}{2} - \alpha v^2 \right) n \left( \frac{\alpha}{\pi} \right)^{3/2} \exp(-\alpha v^2) \phi_c^{(1)}(V) V . \nu T \, dv \]

(4.5.7)

On substituting for \( \phi_c^{(1)}(V) \) from (4.5.6) and utilizing the above mentioned integral transformation, we obtain an expression for \( \lambda^{(1)} \) in terms of two different multi-integrals. Then, on changing to reduced variables and performing the angular integration of \( V \) analytically, the multi-integrals can be evaluated numerically on the computer using Simpson's rule again. The final result for \( \lambda^{(1)} \) is put in a form similar to that in Chapman and Cowling (8) and is as follows.
\[ \lambda^{(1)} = 0.2660 \left( \frac{k^3 \tau}{\mu} \right)^{\frac{3}{2}} \left( 1.0475 \pm 3 \times 10^{-4} \right) \] (4.5.8)

On comparing with equation (4.5.5), then \( \lambda^{(1)} \) is about 23% of the value of \( \lambda(\lambda_5) \).

Although two terms are not enough to predict that the \( \lambda^{(1)} \)'s form a series, we will assume, bearing in mind the case of the other two potential models considered, that they form a geometrical progression of the following form

\[
\lambda_{\theta}^{(0)} + \lambda_{\theta}^{(0)} \left( \frac{\lambda^{(1)}}{\lambda^{(0)}} \right) + \lambda_{\theta}^{(0)} \left( \frac{\lambda^{(1)}}{\lambda^{(0)}} \right)^2 + \ldots ,
\]

(4.5.9)

whose sum is given by

\[
\lambda_{\theta}^{(0)} = \frac{\lambda^{(0)}}{1 - \frac{\lambda^{(1)}}{\lambda^{(0)}}} .
\]

(4.5.10)

Substituting the values for \( \lambda^{(0)} \) and \( \lambda^{(1)} \) in (4.5.10), we obtain, for \( \lambda_{\theta}^{(0)} \), the following result

\[
\lambda_{\theta}^{(0)} = \frac{1}{\sigma^2} \left( \frac{k^3 \tau}{\mu} \right)^{\frac{3}{2}} \left[ 1.1385 \pm 5 \times 10^{-4} \right] .
\]

(4.5.11)

The value for \( \lambda_{\theta}^{(0)} \) obtained here is a good approximation and is about 95% of that for \( \lambda^{(1)} \), (4.5.5), obtained from the fifth approximation in the Chapman-Cowling method.

This good approximation to \( \lambda^{(0)} \) suggests that the \( \lambda^{(i)} \)'s may well approximate closely to a geometrical progression of the form given by (4.5.9). To try to substantiate this prediction, we
will now work out $\lambda^{(2)}$. The $\lambda^{(2)}$ term is calculated in a similar way to $\lambda^{(1)}$ and involves the numerical evaluation of multi-integrals of the same type as those for $\lambda^{(1)}$ but of higher orders.

The result, put in a similar form to that given by Chapman and Cowling, is as follows

$$
\lambda^{(2)} = \frac{0.2660}{\sigma^2} \left( \frac{k^3 T}{\pi m} \right)^{1/2} [0.634 \pm 0.009].
$$

Less accuracy is possible here than for the $\lambda^{(1)}$ case for the following reason. As mentioned a little earlier, the multi-integrals encountered for $\lambda^{(2)}$ are of higher orders than for $\lambda^{(1)}$ and, as they take longer to evaluate, the accuracy demanded has to be reduced in order to keep the computer run times reasonable.

On comparing the following ratios

$$
\frac{\lambda^{(1)}}{\lambda^{(0)}} = 0.5724 \pm 4 \times 10^{-4};
$$

$$
\frac{\lambda^{(2)}}{\lambda^{(1)}} = 0.605 \pm 9 \times 10^{-3};
$$

it can be seen that they do not differ much, about 3-7%, so this is further evidence for supposing the $\lambda^{(i)}$'s form an approximate geometrical progression.

Having calculated $\lambda^{(0)}$, $\lambda^{(1)}$ and $\lambda^{(2)}$ we can get a better approximation to $\lambda$, as mentioned in Chapter 2, by separating the approximate geometrical progression into the following terms

$$
\lambda_{\text{approx}} = \lambda^{(0)} + \frac{\lambda^{(1)}}{1 - \frac{\lambda^{(2)}}{\lambda^{(1)}}}.
$$
On substituting the values for the respective \( \lambda^{(i)} \)'s terms in (4.5.13), we get the following result

\[
\lambda_2 = \frac{1}{\sigma^2} \left( \frac{k^3 T}{\pi m} \right)^{\frac{1}{2}} [1.192 \pm .016]. \tag{4.5.14}
\]

This value for the thermal conductivity coefficient, \( \lambda \), is very close to that obtained by the Chapman and Cowling method, see equation (4.5.5), and is equivalent to 99.3 ± 1.3% of the latter's absolute result.

As can be seen from the preceding analysis, there is a fair amount of evidence to suggest that the \( \lambda^{(i)} \)'s, so generated by the iteration procedure, approximate closely to a geometrical progression. On assuming this we have obtained a result for the thermal conductivity which is close to that obtained by other methods. A further discussion of this geometrical progression concept is given in the final chapter.

4.6 Brief Outline of Calculation of the Coefficient of Viscosity for the Rigid Sphere Model

Although my primary interest has been in the calculation of the thermal conductivity coefficient, I think it worthwhile showing, in brief, that the procedure already used can be easily adapted to calculate the coefficient of viscosity.

Going back to the iterative relationships (Chapter 2, equations (2.1.16, 17)) then the two important relationships, for the viscosity case, are as follows
\[ \frac{4}{3} \alpha V^2 = \frac{2}{3} \varphi^{(1)}_n(V) V^2 \int n \left( \frac{\alpha}{\pi} \right)^{\frac{3}{2}} \exp(-\alpha U^2) \, g \, d\beta \, d\epsilon \, du \]  

(4.6.1)

and

\[ \frac{2}{3} \varphi^{(1)}_n(V) V^2 \int \exp(-\alpha U^2) \, g \, d\beta \, d\epsilon \, du \]

\[ = \int \exp(-\alpha U^2) \left\{ \varphi^{(o)}_n(V') \left( \hat{U}^{1o} \, \hat{V}^1 \right) \right\} V^2' \]

\[ + \varphi^{(o)}_n(U') \left( \hat{U}^{1o} \, \hat{V}^1 \right) \, U^2' - \varphi^{(o)}_n(U) \]

\[ \{ \hat{U}^{1o} \, \hat{V}^1 \} \, g \, d\beta \, d\epsilon \, du \]  

(4.6.2)

On comparing these relationships with the corresponding ones for the thermal conductivity case (see equations (4.2.4, 5)), the essential difference is as follows: for the thermal conductivity case we have terms which contain

\( (U^o \cdot \hat{V}) \) factors;

and for the viscosity case

\( (\hat{U}^{1o} \, \hat{V}^1) \) factors.

Now just as we wrote, for the thermal conductivity case

\( (U^o \cdot \hat{V}) = P_1(U^o \cdot \hat{V}) \);

then for the viscosity case we can write

\( (\hat{U}^{1o} \, \hat{V}^1) = P_2(\hat{U}^1 \cdot \hat{V}) \);

where \( P_n(X) \) is the Legendre polynomial of order \( n \).
This means that the only difference in the treatment is that for the viscosity case we replace \( P_1(X) \) by \( P_2(X) \). Having obtained integrable expressions for \( \phi_{\eta}^{(0)} \) and \( \phi_{\eta}^{(1)} \) we use the pressure tensor, instead of the heat flux vector, to determine the corresponding coefficients of viscosity \( \eta_s^{(0)} \) and \( \eta_s^{(1)} \). Once again we assume an approximate geometrical progression is exhibited in order to obtain a value for the coefficient of shear velocity, \( \eta_s \). This assumption is reasonable since, as for the thermal conductivity case, the \( \phi_{\eta}^{(i)} \)'s for the Maxwellian and Pseudo-Maxwellian models form an exact geometrical progression (see latter part of Chapter 3).
CHAPTER 5

Calculation of the Transport Coefficients for a
Binary Mixture Described by either
Maxwellian or Pseudo-Maxwellian Potential Models

Introduction

This Chapter is concerned with the calculation of the thermal conductivity and diffusion coefficients for a binary gas mixture whose molecules are described by either Maxwellian or Pseudo-Maxwellian potential models. As mentioned earlier, for these particular potential models the collision integrals are independent of the relative velocity, \( g \), and as a consequence the analysis is entirely analytical.

We will now consider the calculation of the respective transport coefficients.

5.1 Calculation of the Diffusion Coefficient, \( D_{12} \), for a Binary Mixture

The mathematical outline for the calculation of the diffusion coefficients for a binary mixture are given in Chapter 2, section 2, from which we can see that in order to obtain the transport coefficients we must perform the infinite sums indicated in equation (2.2.11). This is achieved in the single gas case (Chapter 3) by obtaining a relationship between the \( \phi^{(i)} \)'s by using the iterative relationships; so we will follow a similar line here.

From Chapter 2, equation (2.2.13), the zeroth iteration gives us an expression for \( \phi^{(o)}_{1d} \) and \( \phi^{(o)}_{2d} \) given by
\[ \phi_\text{id} V_i \cdot d_i = \frac{n_i}{n} \frac{V_i \cdot d_i}{\sum_j \int f_j^{(o)} [g_{ij}] \, du_j} , \]  

for \( i,j = 1,2 \), where we have defined the integral operator \([g_{ij}]\)

\[ [g_{ij}] = \int g_{ij} \, db \, de \, . \]

Since the denominator of (5.1.1) is not a function of \( V \) for these particular potential models, because the collision integrals are \( g \) independent, we can write equation (5.1.1) as follows

\[ \phi_\text{id} V_i \cdot d_i = \psi_\text{id} (o) V_i \cdot d_i , \]  

where \( \psi_\text{id} (o) \) are independent of the velocity variable, \( V \), for these models.

Then following as for the single gas case, we wish to show that any \( \psi_\text{id} \) can be written as

\[ \psi_\text{id} V_i \cdot d_i = \psi_\text{id} (h) V_i \cdot d_i , \]  

(\( \psi_\text{id} (h) \) are independent of \( V \)), with a view to summing the \( \psi_\text{id} \)'s .

To establish this, we will determine \( \psi_\text{id} (o) \) and \( \psi_\text{id} (1) \) and then generalise. From the first iteration equation (2.2.14), we obtain the following expression for \( \psi_\text{id} (1) \)

\[ \psi_\text{id} V_i \cdot d_i \{ \sum_j \int f_j^{(o)} [g_{ij}] \, du_j \} \]

\[ = \sum_j \int f_j^{(o)} [g_{ij}] \{ \phi_\text{id} V_i \cdot d_i + \phi_\text{id} V_i \cdot d_i \}

- \phi_\text{id} V_i \cdot d_i \} \, du_j \]  

(5.1.4)
Substituting for $\phi^{(1)}_i$ in the form given by equation (5.1.3) in equation (5.1.4) and separating out the self and cross collision integral terms we have

$$\phi^{(1)}_1 v_1 \cdot d_1 \{ \sum_j f^{(0)}_j [g_{ij}] \ du_j \}$$

$$= \int f^{(0)}_1 [g_{11}] \{ c^{(0)}_1 v_1 \cdot d_1 + c^{(0)}_1 u_1 \cdot d_1 - c^{(0)}_1 u_1 \cdot d_1 \} du_1$$

$$+ \int f^{(0)}_2 [g_{12}] \{ c^{(0)}_1 v_1 \cdot d_1 + c^{(0)}_2 u_2 \cdot d_2 - c^{(0)}_2 u_2 \cdot d_2 \} du_2;$$

(5.1.5)

and similarly for $\phi^{(1)}_2$ by interchanging suffices.

The integral containing just $c^{(0)}_1$ type terms can be treated in a similar way to the single component case, but the cross collision terms require a different treatment. We will consider the cross collision terms first, namely

$$c^{(0)}_1 v_1 \cdot d_1 + c^{(0)}_2 u_2 \cdot d_2 - c^{(0)}_2 u_2 \cdot d_2 .$$

For a binary mixture we can put $d_1 = -d_2$, and then on dotting each term with $v_1$ and using the conservation laws we rewrite the cross collision terms as follows

$$-c^{(0)}_2 \frac{m_1}{m_2} v_2 + \left( \frac{m_1}{m_2} c^{(0)}_2 + c^{(0)}_1 \right) v_1 \cdot v_1 ,$$

where we neglected linear terms in $u_2 \cdot v_1$ which do not contribute to the $u_2$ integration.

From the Appendix, (A.1), we have
\[
\mathbf{v}_1 \cdot \mathbf{v}_1 = \frac{1}{(m_1 + m_2)} \left\{ (m_1 + m_2 \cos \chi) \mathbf{v}_1^2 + m_2 (1 - \cos \chi) \mathbf{v}_1 \cdot \mathbf{u}_2 \right. \\
\left. - m_2 |\mathbf{v}_1 \cdot \mathbf{u}_2| \sin \chi \cos \epsilon \right\},
\]

which can be simplified. In this case we have only linear terms in \((\mathbf{v}_1 \cdot \mathbf{u}_2)\) and \(\cos \epsilon\) which do not contribute to the integration so we need only consider the

\[
\frac{(m_1 + m_2 \cos \chi)}{m_1 + m_2} \mathbf{v}_1^2
\]

term contained in the \(\mathbf{v}_1 \cdot \mathbf{v}_1\) expression.

The cross-collision integral becomes, on substituting for \(\mathbf{v}_1 \cdot \mathbf{v}_1\)

\[
\mathbf{v}_2^2 \int \frac{f_2^{(o)}}{2} [g_{12}] \left\{ c_1^{(o)} \frac{(m_1 + m_2 \cos \chi)}{m_1 + m_2} + c_2^{(o)} \frac{m_1 \cos \chi - m_2}{m_1 + m_2} \right\} \mathbf{d}_2.
\]

We now turn our attention to the self-collision integral. This is essentially the same as that given in Chapter 3 concerning the \(A^{(o)}\) terms in equation (3.1.4), the result of which is given by (3.1.10). On using this we obtain for the self-collision integral

\[
c_1^{(o)} \mathbf{v}_1^2 \int f_1^{(o)} [g_{11}] \mathbf{d}_1.
\]

Then, on performing the \(\mathbf{u}_1\) and \(\mathbf{u}_2\) integration, we finally obtain

for (5.1.5) the following

\[
\phi_1^{(1)} \mathbf{v}_1 \cdot \mathbf{d}_1 \left\{ [g_{11}] n_1 + [g_{12}] n_2 \right\} = \left\{ n_1 [g_{11}] c_1^{(o)} + n_2 [g_{12}] \right\} \frac{(m_1 + m_2 \cos \chi)}{m_1 + m_2} c_1^{(o)} + n_2 \frac{m_1 \cos \chi - m_2}{m_1 + m_2} c_2^{(o)} \mathbf{v}_1 \cdot \mathbf{d}_1
\]

\[
(5.1.6)
\]
and a similar expression for $\phi_{2d}^{(1)}$.

On examining equation (5.1.6) we find we can write $\phi_{id}^{(1)} v_i \cdot d_i$ in the following form

$$\phi_{id}^{(1)} v_i \cdot d_i = c_i^{(1)} v_i \cdot d_i,$$

where $c_i^{(1)}$ is independent of the velocity variable $v_i$. On looking at equations (5.1.2) and (5.1.7), since they are of similar form, and $\phi^{(i)}$ and $\phi^{(i+1)}$ are connected by an operator that does not change their functional form, then we can write any $\phi_{id}^{(h)} v_i \cdot d_i$ in the following form

$$\phi_{id}^{(h)} v_i \cdot d_i = c_i^{(h)} v_i \cdot d_i,$$

which is the desired form.

Before obtaining a relationship between $c_i^{(h)}$ and $c_i^{(h+1)}$ in order to perform the infinite sums we must, as described in Chapter 2, make sure that each of the $\phi_{id}^{(h)}$'s separately satisfy the auxiliary conditions.

Following Chapter 2, we can satisfy the auxiliary conditions by redefining the $\phi_{id}^{(h)}$'s as follows

$$\phi_{id}^{(h)} v_i \cdot d_i = \phi_{id}^{(h)} v_i \cdot d_i + a_{id}^{(h)} \cdot m_i v_i.$$

We can find the actual form of $\phi_{id}^{(h)}$ by using equation (5.1.8), and then satisfying the auxiliary conditions equations (2.2.19, 23). The resulting form of $\phi_{id}^{(h)}$ is as follows

$$\phi_{id}^{(h)} v_i \cdot d_i = \frac{(m_2 n_2 c_1^{(h)} + m_1 n_2 c_2^{(h)}) v_i \cdot d_i}{(m_1 n_1 + m_2 n_2)};$$

(5.1.10)
and similarly for $\phi_{2d}^{(h)}$ by interchanging the suffices.

The diffusion coefficient is essentially determined by performing the following infinite sums (see Chapter 2, equations (2.2.11))

$$\bar{\phi}_{id} = \sum_{h=0}^{\infty} \phi_{id}^{(h)}, \quad \text{for } i = 1, 2$$

(5.1.11)

Which, on using equation (5.1.10), becomes

$$\bar{\phi}_{id} = \sum_{h=0}^{\infty} \frac{m_2 n_2 c_{1}^{(h)} + m_1 n_2 c_{2}^{(h)}}{(m_1 n_1 + m_2 n_2)}$$

(5.1.12)

and similarly for $\bar{\phi}_{2d}$.

On examining equation (5.1.12), we see that we can perform the sum indicated if we can establish a relationship between $\phi_{id}^{(h)}$ and $\phi_{id}^{(h+1)}$ or the equivalent relationship involving the C's. Let us write this relationship as follows

$$m_2 n_2 c_{1}^{(h+1)} + m_1 n_2 c_{2}^{(h+1)} = \left\{ \frac{F(X)}{m_1 n_1 + m_2 n_2} \right\}$$

(5.1.13)

Now, from equations (5.1.2, 6, 7), we can establish a relationship for $h = 1, h = 0$ and then we can generalise. The actual relationship, arrived at after some lengthy algebra, is

$$m_2 n_2 c_{1}^{(1)} + m_1 n_2 c_{2}^{(1)} = \left\{ \frac{m_1 \cos X + m_2}{m_1 + m_2} + n_1 n_2 \left[ g_{22} \right] \left[ g_{12} \right] \cos X \right\}$$

(5.1.14)
Using equation (5.1.14) we can generalise to obtain relationships between the $h^{th}$ and $h+1^{th}$ terms. Since the relationship in (5.1.14) is of a geometrical progression type, then we can perform the sum indicated in (5.1.12). For a geometrical progression we have

$$
\phi_{1d} = \sum_{h} \phi_{1d}^{(h)} = \frac{\phi_{1d}^{(0)}}{1 - \frac{\phi_{1d}^{(1)}}{\phi_{1d}^{(0)}}}.
$$

On substituting for $h = 0$ and $h = 1$ in (5.1.10) and using equations (5.1.1, 2 and 14) then we obtain, after further lengthy algebra, the following expression for $\phi_{1d}$

$$
\phi_{1d} = \frac{n(m_1 + m_2)}{n_1(m_1 n_1 + m_2 n_2) \left[ g_{21} \right] (1 - \cos \theta)};
$$

and a similar expression for $\phi_{2d}$ by interchanging suffices in equation (5.1.16).

Having obtained $\phi_{1d}$ and $\phi_{2d}$ we are now in a position to calculate $D_{12}$.

If we substitute for $\phi_{1d}$ and $\phi_{2d}$ into equation (2.2.25), perform the velocity integration, and then compare the result with equation (2.2.26), we can extract the following expression for the diffusion coefficient, $D_{12}$

$$
D_{12} = \frac{(m_1 + m_2) kT}{m_1 m_2 n \left[ g_{21} \right] (1 - \cos \theta)}.
$$

Finally, we will obtain the actual form of $D_{12}$ for the respective potential models.
Maxwellian Molecules

If we remember that we defined \([g_{ij}]\) as follows (see after equation (5.1.1))

\[
[g_{ij}] = \int g_{ij} b \ dB \ d\epsilon .
\]

In the case of the Maxwellian potential model we can write

\[
g_{21} b \ dB \ d\epsilon = \left(\frac{(m_1 + m_2)^3 K_{12}}{m_1 m_2}\right)^{\frac{1}{2}} \nu_o \ dv_o \ d\epsilon .
\]

From C+C (Chapter 10, section 31), we can write

\[
s_{12} = \left[\frac{K_{12}}{2kT}\right]^\frac{1}{4} , \quad \int (1 - \cos \chi) \nu_o \ dv_o = A_1(5) .
\]

Then, on using these relationships we obtain the following form for \(D_{12}\)

\[
D_{12} = \left(\frac{kT(m_1 + m_2)}{2m_1 m_2}\right)^{\frac{1}{2}} \frac{1}{n} \frac{\nu_o}{\sigma_{12}^2} \frac{1}{2\pi} A_1(5) ,
\]

which agrees with the expected result (see C+C, equation 10.1.5 and 10.31.9).

Pseudo-Maxwellian Molecule

Here we can write

\[
g_{21} b \ dB \ d\epsilon = \frac{\sigma_{12}^2}{4} g_{21}^* \sin \chi \ dx \ d\epsilon ,
\]

where \(\sigma_{12}\) and \(g_{21}^*\) are characteristic parameters of the model.
On using this relationship in (5.1.17), and performing the $\chi$ integration, we obtain the following expression for $D_{12}$

$$D_{12} = \frac{\left(\frac{m_1 + m_2}{m_1 m_2}\right) kT}{\pi n} \frac{1}{\sigma^{12} g^{12}_{21}} ,$$

which agrees with the expected result (see C-C, Chapter 10, sections 10.1 and 10.31).

For convenience, I will leave the determination of the thermal diffusion coefficient, $D_T$, until after the coefficient of thermal conductivity, $\lambda$, has been determined.

5.2 Calculation of the Thermal Conductivity for a Binary Mixture

The relevant parts of the Boltzmann equations for a binary mixture from which the thermal conductivity can be determined are of the following form

$$-(S_2 - \alpha_1 V_1^2) \frac{V}{T} = \int f_1^{(o)}\{\phi_{1c}(V_1') V_1' \cdot \frac{V}{T} + \phi_{1c}(U_1') U_1' \cdot \frac{V}{T}$$

$$- \phi_{1c}(V_1) V_1 \cdot \frac{V}{T} - \phi_{1c}(U_1) U_1 \cdot \frac{V}{T}\} g_{11} b db du_1\; d\epsilon$$

$$+ \int f_2^{(o)}\{\phi_{1c}(V_1') V_1' \cdot \frac{V}{T} + \phi_{2c}(U_2') U_2' \cdot \frac{V}{T} - \phi_{1c}(V_1) V_1 \cdot \frac{V}{T}$$

$$- \phi_{2c}(U_2) U_2 \cdot \frac{V}{T}\} g_{12} b db du_2\; d\epsilon ,$$

and

$$\begin{align*}
\end{align*}$$
These two equations are re-arranged to aid iterative procedure and a short hand notation is introduced to reduce the cumbersomeness of the equation. We then have

\[ e_1 \phi_{1c} = X_{1c} + \frac{1}{e_1} S_1(e_1 \phi_{1c}) + \frac{1}{e_2} M_1(e_2 \phi_{2c}) \quad (5.2.3) \]

\[ e_2 \phi_{2c} = X_{2c} + \frac{1}{e_2} S_2(e_2 \phi_{2c}) + \frac{1}{e_1} M_2(e_1 \phi_{1c}) \quad (5.2.4) \]

where we define the following quantities

\[ X_{1c} = (\frac{5}{2} - a_i v_i^2) \quad (5.2.5) \]

\[ e_i = \sum_j \int f_j^{(o)} g_{ij} b \, db \, du_j \, dc \]

for \( i, j = 1, 2 \) \quad (5.2.6)

\[ S_1 \phi_{1c} = \frac{1}{v_1^2} \int f_1^{(o)} \left\{ \phi_{1c}(v_1') v_1' \cdot v_1 + \phi_{1c}(u_1') u_1' \cdot v_1 \\ - \phi_{1c}(u_1) u_1 \cdot v_1 \right\} g_{11} b \, db \, du_1 \\
+ \frac{1}{v_1^2} \int f_2^{(o)} \left\{ \phi_{1c}(v_1') v_1' \cdot v_1 \right\} g_{12} b \, db \, du_2 \, dc \quad , \]

(5.2.7)
\[ M_1 \phi_{2c} = \frac{1}{y_1^2} \int \cdots \int f_2^{(0)} \left\{ \phi_{2c}(U_2) \ U_2 \cdot V_1 - \phi_{2c}(U_2) \ U_2 \cdot V_1 \right\} \]

\[ g_{12} d\theta \ d\eta \ d\varepsilon , \quad (5.2.8) \]

with analogous expressions for \( S_2 \) and \( M_2 \). The expression \( \frac{1}{e_1} \frac{1}{e_1} S_1(e_1 \ \phi_{1c}) \) is merely \( S_1 \ \phi_{1c} \) since \( e_1 \) (for the Maxwellian model), is a constant w.r.t \( S_1 \) and is written in the former form for convenience.

Equations (5.2.3 and 4) can be written in matrix form and this will be exploited in the following development. In matrix form, equations (5.2.3 and 4) are as follows

\[
\begin{pmatrix}
  e_1 \ \phi_{1c} \\
  e_2 \ \phi_{2c}
\end{pmatrix} =
\begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} + \zeta \begin{pmatrix}
  S_1 \\
  M_1 \\
  M_2 \\
  S_2 \\
  e_1 \\
  e_1 \\
  e_2 \\
  e_2 \\
\end{pmatrix} \begin{pmatrix}
  e_1 \ \phi_{1c} \\
  e_2 \ \phi_{2c}
\end{pmatrix} , \quad (5.2.9)
\]

where \( \zeta \) is an order parameter eventually to be set equal to unity.

By iterating equation (5.2.9), we have the following relationships on equating powers of \( \zeta \)

\[
\begin{pmatrix}
  e_1 \ \phi^{(0)}_{1c} \\
  e_2 \ \phi^{(0)}_{2c}
\end{pmatrix} =
\begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} , \quad (5.2.10)
\]

\[
\begin{pmatrix}
  e_1 \ \phi^{(1)}_{1c} \\
  e_2 \ \phi^{(2)}_{2c}
\end{pmatrix} =
\begin{pmatrix}
  S_1 \\
  M_1 \\
  M_2 \\
  S_2 \\
  e_1 \\
  e_1 \\
  e_2 \\
  e_2 \\
\end{pmatrix} \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} =
W \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} . \quad (5.2.11)
\]
So that
\[
\begin{pmatrix}
  e_1 \phi_{1c}^{(n)} \\
  e_2 \phi_{2c}^{(n)}
\end{pmatrix}
= W^n \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix},
\]
(5.2.12)

where obviously \( W \) is the operator given by
\[
W = \begin{pmatrix}
  S_1 & M_1 \\
  e_1 & e_2 \\
  M_2 & S_2 \\
  e_1 & e_2
\end{pmatrix}.
\]
(5.2.13)

Here, as in earlier cases, we have expanded \( \phi_{1c}, \phi_{2c} \) in infinite series given by
\[
\phi_{1c} = \sum_{n=0}^{\infty} \zeta^n \phi_{1c}^{(n)}, \quad \phi_{2c} = \sum_{n=0}^{\infty} \zeta^n \phi_{2c}^{(n)}.
\]
(5.2.14)

On using equations (5.2.10-13), the sums indicated in (5.2.14) can be written as follows
\[
\begin{pmatrix}
  e_1 \phi_{1c} \\
  e_2 \phi_{2c}
\end{pmatrix}
= \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} + W \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} + \ldots W^n \begin{pmatrix}
  X_{1c} \\
  X_{2c}
\end{pmatrix} + \ldots
\]
(5.2.15)

In order to perform (5.2.15) formally, we must find the eigen-functions for \( W \) and express \( \begin{pmatrix} X_{1c} \\ X_{2c} \end{pmatrix} \) in terms of them.

Suppose that
\[
W \begin{pmatrix}
  \gamma X_{1c} \\
  \beta X_{2c}
\end{pmatrix} = \mu \begin{pmatrix}
  \gamma X_{1c} \\
  \beta X_{2c}
\end{pmatrix}
\]
(5.2.16)
where $\mu$ is an eigen value and \( \begin{pmatrix} \gamma X_{1c} \\ \beta X_{2c} \end{pmatrix} \) is an eigen function.

If we perform the vector integrations resulting from $W$ operating on \( \begin{pmatrix} X_{1c} \\ X_{2c} \end{pmatrix} \) we get

\[
W \begin{pmatrix} X_{1c} \\ 0 \end{pmatrix} = \begin{pmatrix} A \\ B \end{pmatrix}, \quad W \begin{pmatrix} 0 \\ X_{2c} \end{pmatrix} = \begin{pmatrix} C \\ D \end{pmatrix} ;
\]  \(5.2.17\)

the actual form of $A, B, C$ and $D$ will be presented later when the vector integrations are performed in detail, but we will find they are essentially of the form

\[
A = A X_{1c} ,
\]

where $A, B ...$ involves integrals containing the differential cross-section and complicated function of the scattering angle, $x$. On combining equations (5.2.16 and 17) we obtain the following equations

\[
\begin{align*}
\gamma A + \beta B &= \mu \gamma X_{1c} \\
\gamma D + \beta C &= \mu \beta X_{2c}
\end{align*}
\]  \(5.2.18\)

where we have assumed $\gamma$ and $\beta$ are constants wrt $W$ with a view to seeing whether it leads to a solution. On equating $\beta/\gamma$, after re-arranging (5.2.18), becomes

\[
\frac{\beta}{\gamma} = \frac{A - \mu X_{1c}}{B} = \frac{D}{C - \mu X_{2c}} . \tag{5.2.19}
\]

On solving for $\mu$ we get two solutions (since equation (5.2.19) is a quadratic), say $\mu_1$ and $\mu_2$, and hence we get two solutions
for \( Y \frac{Y_1}{\beta_1} \) and \( Y \frac{Y_2}{\beta_2} \). Thus we have two eigenfunctions

\[
\begin{pmatrix}
\gamma_1 X_1c \\
\beta_1 X_2c
\end{pmatrix}
\text{ and } \begin{pmatrix}
\gamma_2 X_1c \\
\beta_2 X_2c
\end{pmatrix},
\]

with eigen values \( \mu_1 \) and \( \mu_2 \) respectively for the operator \( W \).

We can now write \( \begin{pmatrix} X_1c \\ X_2c \end{pmatrix} \) in terms of the eigenfunctions in the following way

\[
\begin{pmatrix} X_1c \\ X_2c \end{pmatrix} = \frac{1}{a_1} \begin{pmatrix} \gamma_1 X_1c \\ \beta_1 X_2c \end{pmatrix} + \frac{1}{a_2} \begin{pmatrix} \gamma_2 X_1c \\ \beta_2 X_2c \end{pmatrix}, \quad (5.2.20)
\]

so that

\[
W \begin{pmatrix} X_1c \\ X_2c \end{pmatrix} = \frac{1}{a_1} \mu_1 \begin{pmatrix} \gamma_1 X_1c \\ \beta_1 X_2c \end{pmatrix} + \frac{1}{a_2} \mu_2 \begin{pmatrix} \gamma_2 X_1c \\ \beta_2 X_2c \end{pmatrix}; \quad (5.2.21)
\]

and that

\[
W^n \begin{pmatrix} X_1c \\ X_2c \end{pmatrix} = \frac{1}{a_1^n} \mu_1^n \begin{pmatrix} \gamma_1 X_1c \\ \beta_1 X_2c \end{pmatrix} + \frac{1}{a_2^n} \mu_2^n \begin{pmatrix} \gamma_2 X_1c \\ \beta_2 X_2c \end{pmatrix}. \quad (5.2.22)
\]

On using equations (5.2.20-22), equation (5.2.15) can be written in the following manner
Looking at (5.2.23) it is fairly evident that we have two sets of geometrical progressions which can be summed to produce the following results

\[
\begin{align*}
\begin{pmatrix}
e_1 \phi_{1c} \\
e_2 \phi_{2c}
\end{pmatrix}
&= \begin{pmatrix}
\gamma_1 X_{1c} \\
\gamma_1 X_{2c}
\end{pmatrix} + \frac{\bar{a}_1}{\beta_1} \begin{pmatrix}
\beta_1 X_{1c} \\
\beta_1 X_{2c}
\end{pmatrix} \cdots + \frac{\bar{a}_1}{\mu_1} \begin{pmatrix}
\gamma_1 X_{1c} \\
\gamma_1 X_{2c}
\end{pmatrix} + \cdots \\
+ \begin{pmatrix}
\gamma_2 X_{1c} \\
\gamma_2 X_{2c}
\end{pmatrix} + \frac{\bar{a}_2}{\mu_2} \begin{pmatrix}
\beta_2 X_{1c} \\
\beta_2 X_{2c}
\end{pmatrix} \cdots + \frac{\bar{a}_2}{\mu_2} \begin{pmatrix}
\gamma_2 X_{1c} \\
\gamma_2 X_{2c}
\end{pmatrix} + \cdots
\end{align*}
\]

(5.2.23)

Looking at (5.2.23) it is fairly evident that we have two sets of geometrical progressions which can be summed to produce the following results

\[
\begin{align*}
\begin{pmatrix}
e_1 \phi_{1c} \\
e_2 \phi_{2c}
\end{pmatrix}
&= \begin{pmatrix}
\frac{\bar{a}_1 \gamma_1 X_{1c}}{(1-\mu_1)} + \frac{\bar{a}_2 \gamma_2 X_{1c}}{(1-\mu_2)} \\
\frac{\bar{a}_1 \beta_1 X_{2c}}{(1-\mu_1)} + \frac{\bar{a}_2 \beta_2 X_{2c}}{(1-\mu_2)}
\end{pmatrix},
\end{align*}
\]

(5.2.24)

From which we can extract the corresponding expressions for \(e_1 \phi_{1c}\) and \(e_2 \phi_{2c}\) respectively.

Finally, we can obtain \(\bar{a}_1\) and \(\bar{a}_2\) in terms of \(\gamma_1\), \(\gamma_2\), \(\beta_1\) and \(\beta_2\), by using equation (5.2.20); this gives us two simultaneous equations to solve

\[
\begin{align*}
X_{1c} &= \frac{\bar{a}_1 \gamma_1 X_{1c} + \bar{a}_2 \gamma_2 X_{2c}}{}
\end{align*}
\]

(5.2.25)

which, on solving, gives us
\[
\bar{a}_1 = \frac{\beta_2 - \gamma_2}{\gamma_1 \beta_2 - \beta_1 \gamma_2}, \quad (5.2.26)
\]

and

\[
\bar{a}_2 = \frac{\beta_1 - \gamma_1}{\gamma_2 \beta_1 - \beta_1 \gamma_2}. \quad (5.2.27)
\]

To continue the development further, we require the actual form of \(\mu_1, \mu_2\) and hence all the other associated unknowns. This entails determining the form of \(\bar{A}, \bar{B}, \bar{C},\) and \(\bar{D}\) and involves operating with \(W\) on \(X_{1c}\) (see equation (5.2.17)). Now \(X_{1c}\) and \(X_{2c}\) are of the form \((5_2 - \alpha_1 y_1^2)\) and \((5_2 - \alpha_2 y_2^2)\) (see equation (5.2.5)), but for clarity we will consider the operation on more general functions of the form

\[
(A_1 + \alpha_1 B_1 V_1^2) \quad \text{and} \quad (A_2 + \alpha_2 B_2 V_2^2),
\]

where \(A_1, B_1, A_2\) and \(B_2\) are constants wrt to the operator \(W\). We will consider only the top column of the operator \(W\), i.e. \((S_1/e_1, M_1/e_2)\) since by interchanging the suffices we can obtain the other part.

We have the operation

\[
\begin{pmatrix}
S_1 & M_1 \\
e_1 & e_2 \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
A_1 + \alpha_1 B_1 V_1^2 \\
A_2 + \alpha_2 B_2 V_2^2
\end{pmatrix}, \quad (5.2.28)
\]

to consider.

Equations (5.2.6-8) define the quantities to be considered.

The single component term, that involving self-collisions, has already been considered and the result will be quoted. This involves the integrands with the factors \(s_{11}\) or \(s_{22}\) in it.
I shall use the short hand notation

\[ [g_{ij}] \equiv \int g_{ij} \, db \, dc \quad \text{for} \quad i,j = 1,2 \]

as defined after equation (5.1.1).

Having taken care of the self-collision part, the cross-collision part is of the following form

\[
\begin{align*}
&\frac{1}{v_1^2} \int f^{(o)}_2 [g_{12}] \left\{ \frac{(A_2 + a_2 B_2 u_2^2) u_2^1 \cdot v_1}{e_2} + \frac{(A_1 + a_1 B_1 v_1^2) v_1^1 \cdot v_1}{e_1} \right. \\
&\left. - \frac{(A_2 + a_2 B_2 u_2^2) u_2^1 \cdot v_1}{e_2} \right\} \, du_2 . \quad (5.2.29)
\end{align*}
\]

We will consider the \( A \) and the \( B \) terms separately in (5.2.29).

Firstly, the \( A \) terms

\[
\frac{1}{v_1^2} \int f^{(o)}_2 [g_{12}] \left\{ \frac{A_2}{e_2} u_2^1 \cdot v_1 + \frac{A_1}{e_1} v_1^1 \cdot v_1 - \frac{A_2}{e_2} u_2^1 \cdot v_1 \right\} \, du_2 . \quad (5.2.30)
\]

In (5.2.30), the \( (u_2 \cdot v_1) \) terms goes out on performing the angular part of the integration of the variable \( u_2 \); so we are left with

\[
\frac{1}{v_1^2} \int f^{(o)}_2 [g_{12}] \left\{ \frac{A_2}{e_2} u_2^1 \cdot v_1 + \frac{A_1}{e_1} v_1^1 \cdot v_1 \right\} \, du_2 . \quad (5.2.31)
\]

The difficult terms to be considered in the integrand of (5.2.31) are

\[ u_2^1 \cdot v_1 \quad \text{and} \quad v_1^1 \cdot v_1 . \]
On using conservation of momentum for unlike molecules, \( U_{12} \) can be expressed in terms of the other variables and the respective masses \( m_1 \) and \( m_2 \), so that the integrand in (5.2.31) becomes

\[
\frac{A_1}{e_2} \frac{m_1}{m_2} v_1^2 + v_1' \cdot v_1 \left( \frac{A_1}{e_1} - \frac{m_1 A_2}{m_2 e_2} \right).
\]

From the appendix we have

\[
v_1' \cdot v_1 = \frac{(m_1 + m_2 \cos \chi) v_1^2}{(m_1 + m_2)},
\]

where we have neglected the terms that do not contribute to the integration to be performed. Thus, on substituting the above and performing the \( u_2 \) integration, (5.2.31) becomes

\[
n_2 [g_{12}] \left( \frac{(m_1 + m_2 \cos \chi) A_1}{m_1 + m_2} + \frac{(m_1 - m_2 \cos \chi) A_2}{m_2 e_2} \right).
\]

Having considered the \( A \) terms, we now consider the \( B \) terms; the expression containing them is

\[
\frac{1}{V_1} \int [g_{12}] \left( \frac{B_1}{e_1} \frac{U_2}{v_1^2} (U_2' \cdot v_1) + \frac{B_1}{e_1} v_1^2 (v_1' \cdot v_1)
\]
\[
- \frac{B_2}{e_2} \frac{U_2}{v_1^2} (v_2 \cdot v_1) \right) \frac{du_2}{u_2}.
\]

On performing the angular part of the integration over the variable \( U_2 \), the term containing the \( (U_2 \cdot v_1) \) factor can be neglected since it does not contribute to the integrations. We can use the
conservation laws to reduce the remaining part of the integrand in (5.2.33) to the following expression

\[ \begin{align*}
\alpha_2 & \cdot \frac{B}{e_2} U_2^2 \left[ \frac{m_1}{m_2} v_1^2 + v_1 \cdot u_2 - \frac{m_1}{m_2} v_1' \cdot v_1 \right] \\
+ \alpha_1 & \cdot \frac{B}{e_1} (v_1' \cdot v_1) \left[ \frac{m_2}{m_1} u_2^2 + v_1^2 - \frac{m_2}{m_1} u_2^2 \right] 
\end{align*} \]  

(5.2.34)

As can be seen from the above expression, we have only two types of dashed velocity terms to consider

\( U_2^2 \) and \( v_1' \cdot v_1 \).

Note in the above curved bracket expression, the \( v_1' \cdot u_2 \) factor does not go out since \( U_2^2 \) will contain terms linear in \( u_2 \).

We must now try to write the dashed variables in terms of the undashed ones and the scattering angle, \( \chi \).

Taking \( U_2^2 \) first, from Appendix A1 we have

\[ U_2^2 = \frac{1}{(m_1 + m_2)^2} \left[ 2 m_1^2 v_1^2 (1 - \cos \chi) + U_2^2 \left( m_1^2 + m_2^2 + 2 m_1 m_2 \cos \chi \right) \right. \]

\[ + 2 v_1 \cdot u_2 \left( m_2 m_1 - m_1^2 \right) (1 - \cos \chi) \]

\[ + \frac{2 m_1}{m_1 + m_2} \left| v_1 \cdot u_2 \right| \sin \chi \cos \phi \]  

(Al.3)

Secondly, the \( v_1' \cdot v_1 \) term: from Appendix A1 we have

\[ v_1' \cdot v_1 = \frac{1}{(m_1 + m_2)^2} \left\{ (m_1 + m_2 \cos \chi) v_1^2 + m_2 (1 - \cos \chi) v_1 \cdot u_2 \right. \]

\[ - m_2 \left| v_1 \cdot u_2 \right| \sin \chi \cos \phi \} \]  

(Al.4)
Using equations (5.2.34) and (A1.3 and 4), we can now perform the $U_2$ integration in (5.2.33). We choose the angular part of $U_2$ to be defined as

$$\cos \theta = \frac{U_2 \cdot V_1}{|U_2| |V_1|} ,$$

so that

$$|V_1 \times U_2| = V_1 U_2 \sin \theta .$$

It must be noted that when the $\epsilon$ integration is performed, linear terms in $\cos \theta$ do not contribute.

After a good deal of algebraic manipulation, we arrive at the following result for the $B$ terms on performing the $U_2$ integration

$$\frac{B}{e^2} \frac{3}{4} \frac{n_2 [g_{12}^2]}{(m_1 + m_2)^3} \left( -\frac{20}{3} m_1^2 m_2 \cos^2 x + (-\frac{10}{3} m_1^3 + \frac{20}{3} m_1^2 m_2 \\
- \frac{10}{3} m_2^2 m_1 \cos x + \frac{10}{3} m_1^3 + \frac{10}{3} m_2^2 m_1) \right)$$

$$+ \frac{B}{e^2} \frac{2 m_1^2 m_2}{(m_1 + m_2)^3} [g_{12}^2] (1 - \cos x)^2 n_2 \alpha_1 V_1^2$$

$$+ \frac{B}{e^1} \frac{3}{4} \frac{n_2 [g_{12}^2]}{(m_1 + m_2)^3} \left( -\frac{20}{3} m_2^2 m_1 \cos x + (\frac{20}{3} m_2^2 m_1 - \frac{20}{3} m_1^2 m_2^2) \cos x \\
+ (\frac{20}{3} m_2^2 m_1) \right)$$

$$+ \frac{B}{e^1} \frac{m_1 + m_2 \cos x (m_1^2 + m_2^2 + 2 m_1 m_2 \cos x)}{(m_1 + m_2)^3} n_2 \alpha_1 V_1^2 .$$

(5.2.35)
We now add to this the single component terms obtained in Chapter 3, equation (3.1.19), for the single gas calculation

\[
\frac{5}{4} \left[ g_{11} \right] (1 - \cos^2 \chi) n_1 \frac{B_1}{e_1} + \frac{A_1}{e_1} \left[ g_{11} \right] n_1 \\
+ \frac{1}{e_1} \left[ g_{11} \right] \frac{1 + \cos^2 \chi}{2} n_1 a_1 v_1^2,
\]

(5.2.36)

where we have used the short hand notation which was defined after equation (5.3.1). If we now combine expressions numbered (5.2.32, 35 and 36), we have the total result for the operation indicated in (5.2.28). Since we are interested in the operation given in equation (5.2.17), we can adapt the above by putting

\[
A_1 = \frac{5}{2}, \quad A_2 = \frac{5}{2}, \quad B_1 = -1 \quad \text{and} \quad B_2 = -1,
\]

so that we have

\[
\begin{pmatrix}
\frac{S_1}{e_1} & \frac{M_1}{e_2} \\
0 & 0
\end{pmatrix}
\begin{pmatrix}
\frac{5}{2} - a_1 v_1^2 \\
\frac{5}{2} - a_2 v_2^2
\end{pmatrix}
= \begin{pmatrix}
\bar{A} + \bar{B} \\
0
\end{pmatrix}
\]

(5.2.37)

where \( \bar{A} \) and \( \bar{B} \) are as follows

\[
\bar{A} = \left( \frac{5}{2} - a_1 v_1^2 \right) \left[ g_{11} \right] n_1 \frac{(1 + \cos^2 \chi)}{2} + \frac{n_2 \left[ g_{12} \right]}{(m_1 + m_2)^3} \\
\left\{ (m_1^3 + m_1 m_2^2) + (m_2^3 + 3 m_1^2 m_2) \cos \chi + 2 m_1 m_2^2 \cos^2 \chi \right\} \frac{1}{e_1}
\]

(5.2.38)
\[ \bar{B} = (\tilde{S}_2 - \alpha_1 v_1^2) \left[ \frac{g_{12}}{n_2} \frac{2 m_1^2 m_2 \cos^2 \chi - 4 m_1^2 m_2 \cos \chi + 2 m_1^2 m_2}{(m_1 + m_2)^3} \right] \]
\[ \frac{1}{e_2} ; \quad (5.2.39) \]

and by interchanging the suffices we obtain expressions for \( \bar{C} \) and \( \bar{D} \) which are as follows

\[ \bar{C} = (\tilde{S}_2 - \alpha_2 v_2^2) \left[ \frac{g_{22}}{n_2} \frac{(1 + \cos^2 \chi)}{2} n_2 + \frac{n_1 [g_{21}]}{(m_1 + m_2)^3} \right] \]
\[ \frac{1}{e_2} \quad \frac{[(m_2^3 + m_2 m_1^2) + (m_1^3 + 3 m_2^2 m_1) \cos \chi + 2 m_2 m_1^2 \cos \chi]}{(m_2 + m_1)^3} \]
\[ (5.2.40) \]

and

\[ \bar{D} = (\tilde{S}_2 - \alpha_2 v_2^2) \left[ \frac{n_1 [g_{21}]}{(m_2 + m_1)^3} \frac{(2 m_1 m_2 \cos^2 \chi - 4 m_1^2 m_2 \cos \chi + 2 m_1^2 m_2)}{(m_2 + m_1)^3} \right] \]
\[ \frac{1}{e_1} \quad (5.2.41) \]

Now, for convenience, we write

\[ \bar{A} = A(\tilde{S}_2 - \alpha_1 v_1^2) \quad \bar{B} = B(\tilde{S}_2 - \alpha_1 v_1^2) \quad \bar{C} = C(\tilde{S}_2 - \alpha_2 v_2^2) \quad \bar{D} = D(\tilde{S}_2 - \alpha_2 v_2^2) \]
\[ (5.2.42) \]

the form of \( A, B, C, D \) being obvious on comparing (5.2.42) with equations (5.2.38:41). Then (5.2.37) becomes

\[ \begin{bmatrix} S_1 & M_1 \\ e_1 & e_2 \end{bmatrix} \begin{bmatrix} \tilde{S}_2 - \alpha_1 v_1^2 \\ \tilde{S}_2 - \alpha_2 v_2^2 \end{bmatrix} = \begin{bmatrix} A + B(\tilde{S}_2 - \alpha_1 v_1^2) \\ 0 \end{bmatrix} \quad (5.2.43) \]
Going back to equations (5.2.18 and 19), we can rewrite them in the following way, remembering the form of $X_{1c}$ and $X_{2c}$

\[ \gamma A + \beta B = \mu \gamma \]  

\[ \gamma D + \beta C = \mu \beta \]  

\[ \frac{B}{\gamma} = \frac{A - \mu}{B} = \frac{D}{C - \mu} . \]  

Having found the form of $A, B, C, D$ we can now solve (5.2.45) to obtain $\mu_1, \mu_2$ and, by using equation (5.2.24), $\phi_{1c}$ and $\phi_{2c}$.

On re-arranging (5.2.45) we have

\[ \mu^2 - (A + C)\mu + (AC - BD) = 0 , \]  

the solution of which is

\[ 2\mu = (A + C) \pm \sqrt{(A + C)^2 - 4(AC - BD)} \]

\[ = A + C \pm \sqrt{(A - C)^2 + 4BD} , \]

from which we have

\[ 2\mu_1 = (A + C) + \sqrt{(A - C)^2 + 4BD} \]

\[ 2\mu_2 = (A + C) - \sqrt{(A - C)^2 + 4BD} \]  

(5.2.47)
Then, putting $\mu_1$ and $\mu_2$ respectively in (5.2.45), we obtain expression for

\[
\frac{\gamma_1}{\beta_1} = -\frac{B}{(A - \mu_1)} = -\frac{(C - \mu_1)}{D}
\]

\[
= \frac{1}{2} \left( \frac{B}{(\mu_1 - A)} + \frac{\mu_1 - C}{D} \right)
\]

\[
= \frac{BD + (\mu_1 - C)(\mu_1 - A)}{2D(\mu_1 - A)}
\]

so that

\[
\gamma_1 = BD + (\mu_1 - C)(\mu_1 - A)
\]

and

\[
\beta_1 = 2D(\mu_1 - A)
\]

(5.2.48)

Similarly

\[
\frac{\gamma_2}{\beta_2} = -\frac{B}{A - \mu_2} = -\frac{(C - \mu_2)}{D}
\]

So that

\[
\gamma_2 = BD + (\mu_2 - C)(\mu_2 - A)
\]

and

\[
\beta_2 = 2D(\mu_2 - A)
\]

(5.2.49)

From equations (5.2.24, 26 and 27), we obtain the following expressions for $e_1 \phi_{1c}$ and $e_2 \phi_{2c}$ respectively
Using equations (5.2.47, 48 and 49), and after lengthy manipulations, we arrive at the following expressions for $\phi_{1c}$ and $\phi_{2c}$

$$e_1 \phi_{1c} = \frac{e_2 \phi_{2c}}{(5.2.50)}$$

and

$$e_2 \phi_{2c} = \frac{(\beta_1 - \gamma_1)\beta_2 (1 - \mu_1) - (\beta_2 - \gamma_2)\beta_1 (1 - \mu_2)}{\gamma_2 \beta_1 - \gamma_1 \beta_2 (1 - \mu_1)(1 - \mu_2)} \{5_2 - a_1v_1^2\}.$$  

Using equations (5.2.47, 48 and 49), and after lengthy manipulations, we arrive at the following expressions for $\phi_{1c}$ and $\phi_{2c}$

$$e_1 \phi_{1c} = \frac{\beta + \{1-c\}}{(1-A)(1-C) - BD} \{5_2 - a_1v_1^2\}.$$  

and

$$e_2 \phi_{2c} = \frac{D + \{1-A\}}{(1-A)(1-C) - BD} \{5_2 - a_2v_2^2\}.$$  

Before calculating the thermal conductivity coefficient, $\lambda$, we must make sure that $\phi_{1c}$ and $\phi_{2c}$ satisfy the auxiliary conditions. Substituting the expressions for $\phi_{1c}$ and $\phi_{2c}$ given by (5.2.52 and 53), into the auxiliary conditions, we find that they satisfy them.

We can now determine an expression for the thermal conductivity coefficient, $\lambda$. Following the procedure as used in Chapter 2, the thermal flux is given by

$$q = \int f_1 \frac{1}{2} m_1 v_1^2 v_1 dv_1 + \int f_2 \frac{1}{2} m_2 v_2^2 v_2 dv_2.$$  

(5.2.54)
functions, as defined in the Chapman-Enskog method, into equation (5.2.54) we have

\[
q = \int f_1^{(o)} \left\{ \phi_{1c} \frac{V_1}{T} + \phi_{1d} \frac{V_1}{T} \right\} \frac{1}{2} m_1 V_1^2 \, dv_1
\]

\[
+ \int f_2^{(o)} \left\{ \phi_{2c} \frac{V_2}{T} + \phi_{2d} \frac{V_2}{T} \right\} \frac{1}{2} m_2 V_2^2 \, dv_2 ;
\]

note that the viscosity term does not contribute. On making use of the definition of mean velocity, the above becomes

\[
\frac{q}{kT} - \frac{5}{2} \left( n_1 \overline{V_1} + n_2 \overline{V_2} \right) = \int f_1^{(o)} \left\{ \phi_{1c} \frac{V_1}{T} + \phi_{1d} \frac{V_1}{T} \right\}
\]

\[
\left( \alpha_1 V_1^2 - \frac{5}{2} \right) \overline{V_1} \, dv_1 + \int f_2^{(o)} \left\{ \phi_{2c} \frac{V_2}{T} + \phi_{2d} \frac{V_2}{T} \right\}
\]

\[
\left( \alpha_2 V_2^2 - \frac{5}{2} \right) \overline{V_2} \, dv_2 . \quad (5.2.55)
\]

On substituting the actual form of \( \phi_{1d} \) and \( \phi_{2d} \), equation (5.1.16), the parts of the integrals containing these factors yield zero on performing the integration, so we are left with

\[
q = \frac{5}{2} kT \left( n_1 \overline{V_1} + n_2 \overline{V_2} \right) - \lambda \overline{V} T , \quad (5.2.56)
\]

where \( \lambda \) is the thermal conductivity coefficient, given by

\[
\lambda = kT \left\{ \int f_1^{(o)} \phi_{1c} \frac{V_1}{T} \left( \frac{5}{2} - \alpha_1 V_1^2 \right) \overline{V_1} \, dv_1
\]

\[
+ \int f_2^{(o)} \phi_{2c} \frac{V_2}{T} \left( \frac{5}{2} - \alpha_2 V_2^2 \right) \overline{V_2} \, dv_2 \right\} . \quad (5.2.57)
\]

On substituting for \( \phi_{1c} \) and \( \phi_{2c} \) and performing the integration
indicated in equation (5.2.57), we obtain the expression for \( \lambda \) which is as follows

\[
\lambda = \frac{5}{2} k^2 T \left\{ \frac{n_1}{m_1} \frac{\{B + (1-C)\}}{\{(1-A)(1-C) - BD\}} \frac{1}{e_1} + \frac{n_2}{m_2} \frac{\{D + (1-A)\}}{\{(1-A)(1-C) - BD\}} \frac{1}{e_2} \right\}.
\]

(5.2.58)

**Maxwellian Molecules**

In comparing (5.2.58) with the result obtained in Chapman and Cowling for the Maxwellian molecules, we must try to obtain (5.2.58) in terms of factors of the type: \( A_1(5) \) and \( A_2(5) \); where

\[
A_1(5) = \int (1 - \cos \chi) v_o \, dv_o,
\]

and

\[
A_2(5) = \int (1 - \cos^2 \chi) v_o \, dv_o,
\]

for which \( \int v_o \, dv_o = gb \, db \); and \( \chi \) depends on the type of collision, i.e., like or unlike molecular collisions.

Now the \([g]\) type factors in \( A, B, C, \) and \( D \) contain the \( gb \, db \) term and so it is first a matter of manipulating the \( \chi \) functions in \( A, B, C, \) and \( D \) into the required two forms, namely \( A_1(5) \) or \( A_2(5) \).

From equations (5.2.39 and 40), after a little manipulation, we arrive at the following expression for \( B \) and \( D \)

\[
B = \frac{2}{(m_1 + m_2)^3} \frac{m_1^2 m_2 n_2 [5_{12}]}{e_2} \left\{ (\cos^2 \chi - 1) + 2(1 - \cos \chi) \right\},
\]

(5.2.59)
and

\[ D = \frac{2 m_2 c m_1}{(m_1 + m_2)^3} \left[ \frac{n_1 [g_{21}]}{e_1} \right] \{ \cos^2 \chi - 1 \} + 2 \{ 1 - \cos \chi \} \times \]  

(5.2.60)

The expressions of the type (1-A) and (1-C), on using equation (5.2.38), can also be manipulated into the required form as follows

\[
(1-A) = \left[ e_1 - \left[ \frac{[g_{11}]}{n_1} \frac{1 + \cos^2 \chi}{2} + \frac{n_2 [g_{12}]}{(m_1 + m_2)^3} \{ \frac{m_1^3 + m_1 m_2^2}{e_1} \} + \frac{m_1^3 + 2 m_2 m_1}{e_1} \} \right] \frac{1}{e_1} \right] \times
\]

(6.2.61)

Now

\[ e_1 = n_1 [g_{11}] + n_2 [g_{12}] \]

so that on substituting for \( e_1 \) into (1-A) expression, grouping like \([g]\) terms together and manipulating the \( \chi \) functions into the required forms we obtain for (1-A)

\[
(1-A) = \left[ \frac{[g_{11}]}{n_1} \frac{1 - \cos^2 \chi}{2} + \frac{n_2 [g_{12}]}{(m_1 + m_2)^3} \left\{ \frac{1 - \cos \chi}{e_1} \right\} \right] \times
\]

(6.2.61)

and similarly for (1-C) we have
\[ (1-C) = \left[ g_{22} \right] n_2 \frac{(1 - \cos^2 \chi)}{2} + \frac{n_1 \left[ g_{21} \right]}{(m_1 + m_2)^3} \left( 1 - \cos \chi \right) \hfill \]

\[ \left( m_1^3 + 2 m_2^2 m_1 \right) + (1 - \cos^2 \chi) \left( 2 m_2 m_1^2 \right) \hfill \]

\[ \frac{1}{e_2} \hfill \]

\[ (5.2.62) \]

Now the respective \( [g] \) terms for Maxwellian molecules are as follows

\[ [g_{12}] = \int 2\pi \left( \frac{(m_1 + m_2) \sqrt{k_{12}}}{m_1 m_2} \right)^{\frac{1}{2}} v_o \, dv_o \]

\[ [g_{11}] = \int 2\pi \left( \frac{2}{m_1} \sqrt{k_{11}} \right)^{\frac{3}{2}} v_o \, dv_o \]

\[ (5.2.63) \]

the form of \( [g_{21}] \) and \( [g_{22}] \) following from (5.2.63) by changing the indices.

Using equations (5.2.59-63) and identifying \( A_1(5) \) and \( A_2(5) \), equation (5.2.58), for \( \lambda \), takes on the final form

\[ \lambda = \frac{5}{2} \cdot \frac{k^2T}{2\pi} \cdot \frac{\left( n_2^2 \left[ E_{12} \right] + n_1^2 \left[ E_{21} \right] + n_1 n_2 \left[ F \right] \right)}{n_2^2 \left[ A_{12} \right] + n_1^2 \left[ A_{21} \right] + n_1 n_2 \left[ B \right]} \]

\[ (5.2.64) \]

where

\[ [A_{12}] = A_1(5) \left( \sqrt{k_{12}} \right)^{\frac{3}{2}} \left( \sqrt{k_{11}} \right)^{\frac{3}{2}} A_2(5) \cdot \frac{m_1(m_2)^{\frac{3}{2}} (3 m_2^2 + m_1)}{2^\frac{1}{2} (m_1 + m_2) \frac{5}{2}} \]

\[ + A_2(5) \left( \sqrt{k_{12}} \right)^{\frac{1}{2}} A_2(5) \left( \sqrt{k_{11}} \right)^{\frac{1}{2}} \frac{m_1(m_2)^{\frac{3}{2}} 2 m_1 m_2}{2^\frac{1}{2} (m_1 + m_2) \frac{5}{2}} \]
[A_{21}] is obtained by interchanging suffixes 1 and 2 in the above apart from $A_1(5)$ and $A_2(5)$ factors.

\[ [B] = A_2(5) \left( K_{11} \right)^{\frac{3}{2}} A_2(5) \left( K_{22} \right)^{\frac{1}{2}} \frac{m_1 m_2}{2} \left( \frac{m_1}{2} \right)^{\frac{1}{2}} + A_1(5) \left( K_{12} \right)^{\frac{1}{2}} A_1(5) \left( K_{12} \right)^{\frac{1}{2}} \frac{m_1 m_2}{2} \left( \frac{m_1}{2} \right)^{\frac{1}{2}} \]

\[ = \frac{m_1 m_2 3(m_1 - m_2)^2}{(m_1 + m_2)^3} + \frac{A_2(5) \left( K_{12} \right)^{\frac{1}{2}} A_1(5) \left( K_{12} \right)^{\frac{1}{2}} 8 m_1 m_2}{(m_1 + m_2)^3} , \]

\[ [E_{12}] = \frac{(m_1^2 + 3 m_2^2)(m_1 m_2)^{\frac{3}{2}} A_1(5) \left( K_{12} \right)^{\frac{1}{2}}}{(m_1 + m_2)^{5/2}} \]

\[ + \frac{2 (m_1 m_2)^{\frac{3}{2}} A_2(5) \left( K_{12} \right)^{\frac{1}{2}}}{(m_1 + m_2)^{5/2}} , \]

\[ [E_{21}] as for [A_{21}] , \]

\[ [F] = \left( \frac{m_1}{2} \right)^{\frac{1}{2}} A_2(5) \left( K_{11} \right)^{\frac{3}{2}} + \left( \frac{m_2}{2} \right)^{\frac{1}{2}} A_2(5) \left( K_{22} \right)^{\frac{3}{2}} \]

\[ + \frac{8 (m_1 m_2)^{\frac{3}{2}} A_1(5) \left( K_{12} \right)^{\frac{1}{2}}}{(m_1 + m_2)^{5/2}} - \frac{4 (m_1 m_2)^{\frac{3}{2}} A_2(5) \left( K_{12} \right)^{\frac{1}{2}}}{(m_1 + m_2)^{5/2}} . \]

With the thermal conductivity coefficient, $\lambda$, in this form, it can be shown to be equivalent to the form for $\lambda$ obtained by C -C, for Maxwellian molecules but, since this involves some tedious algebra, we prefer to leave $\lambda$ in the form given by equation (5.2.64).
Soft Sphere or Pseudo-Maxwellian Molecules

The result for \( \lambda \), equation (5.2.64), for the Maxwellian molecules can be quite easily converted to that for the soft sphere or Pseudo-Maxwellian molecules.

The conversion can be achieved by using the following transformation: write

\[
\left( \frac{2 \overline{k}_{11}}{m_1} \right)^{\frac{1}{2}} = \frac{\sigma_{11}^2}{4} g^8
\]

\[
\left( \frac{\left[ \frac{m_1 + m_2}{m_1 m_2} \right]}{k_{12}} \right)^{\frac{1}{2}} = \frac{\sigma_{12}^2}{4} g_{12}
\]

and similar expressions for \([22]\) and \([21]\) type collisions.

The above transformations come essentially from the fact that

\[
g b db = \left( \frac{m_1 + m_2}{m_1 m_2} k_{12} \right)^{\frac{1}{2}} v_o dv_o \quad \text{for Maxwellian molecules ,}
\]

\[
g b db = \frac{\sigma_{12}^2}{4} g_{12}^2 \sin x dx \quad \text{for Soft Sphere molecules .}
\]

Thus, we can also write

\[
\begin{align*}
A_1(5) & \rightarrow \int_0^\pi (1 - \cos x) \sin x dx + 2 \\
A_2(5) & \rightarrow \int_0^\pi (1 - \cos^2 x) \sin x dx + \frac{4}{3}
\end{align*}
\]

for the Soft sphere case.

Using these transformations, we obtain, for the soft sphere case, the following result for the thermal conductivity coefficient, \( \lambda \)
\[
\lambda = \frac{5 k^2 T}{2 \pi^2} \cdot \left( n_1^2 [E_{12}]_1 + n_2^2 [E_{21}]_1 + n_1 n_2 [F] \right) \quad (5.2.65)
\]

where

\[
[E_{12}]_1 = \frac{4}{9} \frac{\sigma^2_{11}}{4} \sigma^*_{11} + \frac{\sigma^2_{21}}{4} \sigma^*_{21} \frac{m_1 m_2}{(m_1 + m_2)^3} (9 m_2^2 + 3 m_1^2 + 8 m_1 m_2)
\]

\[
[A_{21}]_1 \text{ is obtained from } [A_{12}]_1 \text{ by interchanging indices}
\]

\[
[B] = \frac{4}{9} \frac{\sigma^2_{22}}{4} \sigma^*_{22} \cdot \frac{\sigma^2_{11}}{4} \sigma^*_{11} \frac{m_1 m_2}{(m_1 + m_2)^3}
\]

\[
+E \quad \frac{4}{3} \frac{\sigma^2_{12}}{4} \sigma^*_{12} \frac{\sigma^2_{21}}{4} \sigma^*_{21} \frac{m_1 m_2}{(m_1 + m_2)^3} \left( \frac{9 m_1^2 - 2 m_1 m_2 + 9 m_2^2}{(m_1 + m_2)^4} \right)
\]

\[
[E_{12}] = \frac{2}{3} \frac{\sigma^2_{12}}{4} \sigma^*_{12} \frac{m_1 m_2}{(m_1 + m_2)^3} \left( 3 m_1^2 + 9 m_2^2 + 3 m_1 m_2 \right)
\]

\[
[F] = 2 \frac{\sigma^2_{11}}{4} \sigma^*_{11} \frac{m_1}{(m_1 + m_2)^3} + 2 \frac{\sigma^2_{22}}{4} \sigma^*_{22} \frac{m_2}{(m_1 + m_2)^3} + \frac{8}{3} \frac{\sigma^2_{12}}{4} \sigma^*_{12} \frac{m_1 m_2}{(m_1 + m_2)^3}.
\]

As for the Maxwellian molecule case, the thermal conductivity coefficient, \( \lambda \), in this form can be shown to be equivalent to that obtained by the Chapman-Cowling method, but for the same reason as for the Maxwellian molecule case, a formal comparison will not be attempted here.
5.3 Calculation of the Thermal Diffusion Coefficient, $D_T$, for a Binary Mixture

Having obtained the form of $\phi_{1c}$ and $\phi_{2c}$, equations (5.2.52 and 53), we can now determine the thermal diffusion coefficient, $D_T$, for Maxwellian or Pseudo-Maxwellian potential models.

Going back to Chapter 2, we obtain the thermal diffusion coefficient from the equation resulting from considering the difference in the mean velocities, namely

$$\overline{V}_1 - \overline{V}_2 = \frac{1}{n_1} \int f_1 V_1 dV_1 - \frac{1}{n_2} \int f_2 V_2 dV_2.$$  \hspace{1cm} (5.3.1)

Then, on substituting the approximations to $f_1$ and $f_2$, as defined in the Chapman-Enskog method in (5.3.1), and neglecting non-contributory terms to the integration, to be performed later, we have

$$\overline{V}_1 - \overline{V}_2 = \frac{1}{n_1} \int f_1^{(o)} \left[ \phi_{1c} \overline{V}_1 \cdot \overline{d}_1 + \alpha_c \cdot m_1 \frac{V_1}{v_T} \right] V_1 dV_1$$

$$- \frac{1}{n_2} \int f_2^{(o)} \left[ \phi_{2c} \overline{V}_2 \cdot \overline{d}_2 + \alpha_c \cdot m_2 \frac{V_2}{v_T} \right] V_2 dV_2$$

$$+ \frac{1}{n_1} \int f_1^{(o)} \left[ \phi_{1c} \overline{V}_1 \cdot \nabla \ln T + \alpha_c \cdot m_1 \frac{V_1}{v_T} \right] V_1 dV_1$$

$$- \frac{1}{n_2} \int f_2^{(o)} \left[ \phi_{2c} \overline{V}_2 \cdot \nabla \ln T + \alpha_c \cdot m_2 \frac{V_2}{v_T} \right] V_2 dV_2.$$  \hspace{1cm} (5.3.2)

The diffusion coefficients are defined through the following equation (see equation (2.2.26))
\[ \vec{v}_1 - \vec{v}_2 = - \left( \frac{n_1^2}{n_1 n_2} D_1 \phi_1 c + \frac{n_1^2}{n_1 n_2} D_T \nabla n \right) . \] (5.3.3)

On comparing (5.3.2 and 3), we can see that the thermal diffusion coefficient, \( D_T \), is obtained by considering the integrals containing the \( \phi_1 c \), \( \phi_2 c \), and \( \phi_c \) terms in (5.3.2).

As mentioned in the previous section, the forms obtained for \( \phi_1 c \) and \( \phi_2 c \) for these particular models are such that they automatically satisfy the auxiliary conditions. This means we can substitute the expressions (5.2.52, 53) for \( \phi_1 c \) and put \( \phi_2 c = 0 \) in (5.3.2). On carrying out this substitution, and integrating, we find the integrals containing the \( \phi_1 c \) and \( \phi_2 c \) factors have a value of zero. Thus the value of the thermal diffusion coefficient, \( D_T \), for Maxwellian and Pseudo-Maxwellian molecules is zero. This agrees with the well-known result that the thermal diffusion coefficient for Maxwellian and Pseudo-Maxwellian molecules is zero (see C-C, p174).
CHAPTER 6

Analysis and Conclusions

Introduction

In this final Chapter, an analysis of the results for the transport coefficients, obtained in the preceding chapters, and a fairly detailed comparison of the iterative method with that of the standard Chapman-Cowling method, will be carried out. Finally, suggestions will be made for possible extensions of the work for future development.

6.1 Analysis of the Results Obtained for the Transport Coefficients

In the preceding chapters, we have calculated the transport coefficients for both binary and single component gases for the Maxwellian and Pseudo-Maxwellian potential models, and for the case of the rigid sphere potential model we have calculated the single component transport coefficients.

For the Maxwellian and Pseudo-Maxwellian potential models, we see that the \( \phi^{(i)} \)'s and hence the \( \lambda^{(i)} \)'s and \( \eta_s^{(i)} \)'s form exact geometrical progressions and that the analytical results for their sums are the same as those obtained by the Chapman-Cowling method.

For the rigid sphere model, however, the situation is not so clear cut, but we do find the numerical values for \( \lambda^{(0)} \), \( \lambda^{(1)} \) and \( \lambda^{(2)} \) closely follow a geometrical progression. On assuming an exact geometrical progression based on \( \lambda^{(0)} \) and \( \lambda^{(1)} \),
we obtain a value for the thermal conductivity coefficient which is about 95% of that obtained using the Chapman-Cowling method; and for one based on $\lambda^{(1)}$ and $\lambda^{(2)}$ we obtain a value as close as $99.3 \pm 1.3\%$ (this corresponds to using the padé approximant $[1,1]$ and on using the padé approximant $[0,2]$, we obtain an answer which is 99% of that of Chapman-Cowling). In all the cases here, the comparison is with the fourth approximation in the Chapman-Cowling method, namely $[\lambda^4]$, which is more than accurate enough for our purpose. The significance of these results is that we obtain good values for the transport coefficients by evaluating only the first two or three terms in the infinite series for the perturbation function, $\phi$, for which the calculations are relatively simple. This then makes the method quite a useful one, especially as it may well be feasible to extend it to more general repulsive potentials. (This point is discussed in more detail later on in this chapter.)

A comparison of the iterative method with the standard Chapman-Cowling method is discussed in some detail in the next section.

6.2 Comparison of Iterative Method with Standard Chapman-Cowling Method

Here we compare the two methods of solution of the second approximation to Boltzmann's equation within the Chapman-Enskog regime with an emphasis towards the determination of the actual form of the perturbation function. The Maxwellian and Pseudo-Maxwellian potential model case is considered first, followed by the rigid sphere case, with a brief mention of the general repulsive potential case.
The Maxwellian and Pseudo-Maxwellian cases afford a useful comparison of the two methods and will be used as a foundation for considering the rigid sphere model and more general potential cases.

From Chapter 2, for the iterative procedure, we rewrite the linear Boltzmann equation

\[ X_{c,n} = L \phi_{c,n} , \]  
(6.2.1)

in the following form

\[ X_{c,n} = L_0 \phi_{c,n} + \xi L_1 \phi_{c,n} , \]  
(6.2.2)

where \( c,n \) refer to functions associated with gradients in temperature, \( \nabla T \), and mass average velocity, \( \nabla u_o \), and hereafter the subscript(s) will be understood.

On iterating (6.2.2) we have

\[ \phi^{(o)}(V) = \frac{X}{L_0}(V) , \quad \phi^{(n)}(V) = \left( \frac{L_1}{L_0} \right)^n \frac{X}{L_0} . \]  
(6.2.3)

Now for Maxwellian and Pseudo-Maxwellian potential models, \( L_0 \) is independent of the velocity variable, \( V \), so we can write (6.2.3) as

\[ \phi^{(o)}(V) = \frac{X}{L_0}(V) , \quad \phi^{(n)}(V) = \frac{1}{L_0^{n+1}} L_1^n X . \]  
(6.2.4)

From Chapter 3 we have

\[ L_1 X = \left[ \int F(\chi) \, d\chi \right] X . \]  
(6.2.5)
so that we can see that the $\phi^{(n)}$'s form geometrical progressions based on $X$, or in other words that

$$\phi = a X,$$  

(6.2.6)

where $a$ is the constant of proportionality.

Finally, when we insert the perturbation function, (6.2.6), into the appropriate flux equations, to obtain the transport coefficients, we have

$$\lambda = \frac{-5n \frac{k^2T}{m} a_c}{},$$

(6.2.7)

$$\eta_s = \frac{-n \frac{k^2T}{m} a_\eta}{}.$$

For the Chapman-Cowling method one writes

$$\phi_c = \frac{A}{\varphi} = \sum_{p=1}^{\infty} a_p S_{\frac{3}{2}}^{(p)}(a\nu^2) V$$

$$\phi_\eta = \frac{B}{\varphi} = \sum_{p=1}^{\infty} b_p S_{\frac{3}{2}}^{(p-1)}(a\nu^2) \nu^\nu V.$$

(6.2.8)

Then, following the method shown in Chapter 1, we have

$$\lambda = \frac{2 \frac{k^2T}{3m}}{[A, A]}$$

$$= \frac{2 \frac{k^2T}{3m}}{\sum_{p=1}^{\infty} a_p \frac{[a^{(p)}, A]}{}}$$

$$= \frac{5 \frac{k^2T}{2m}}{a_1},$$

(6.2.9)
where \( \tilde{a}^{(p)} \) is defined by
\[
\tilde{a}^{(p)} = S_{\frac{3}{2}^2}^{(p)}(\nu v^2) \nu .
\]

In practice, as shown in Chapter 1, we can only find approximations to \( a_1 \) (except for Maxwell type potentials); namely, \( a^{(m)}_1 \), for which only
\[
a_1^{(1)} = \frac{15}{4} \frac{1}{a_{11}} , \quad a_1^{(2)} = \frac{15}{4} \frac{a_{22}}{(a_{11} a_{22} - a_{12}^2)} ,
\]
(6.2.10)

where
\[
a_{pq} = [\tilde{a}^{(p)}, \tilde{a}^{(q)}] = [S_{\frac{3}{2}^2}^{(p)}(\nu v), S_{\frac{3}{2}^2}^{(q)}(\nu v)] ,
\]
are appreciably different in value from \( a_1 \).

For the Maxwellian and Pseudo-Maxwellian potential models, we have

\[
a_1^{(1)} = a_1^{(2)} = a^{(m)}_1 = \frac{15}{4} \frac{1}{a_{11}}
\]

and hence we have

\[
a_1 = \frac{15}{4} \frac{1}{a_{11}} .
\]

On substituting this value of \( a_1 \) into (6.2.9), we obtain a result for the thermal conductivity coefficient which is the same as that obtained by the iterative method, equation (6.2.7).

In the case of the Maxwellian and Pseudo-Maxwellian potential models, only \( p=1 \) contributes in the Sonine polynomial expansion.
for $\phi_c$, namely

$$
\phi_c = a_1^{(1)} S_2^{(1)} (\alpha V^2) V = a_1^{(1)} X_c
$$

$$
= a_1 X_c .
$$

(6.2.11)

This result is not so surprising, since $X_c$ is an eigenfunction of the operator $L$ and thus is also the solution of the eigen equation

$$
X_c = L \phi_c ,
$$

which we are trying to solve.

Thus we can appreciate why exact results for the transport coefficients, using the Chapman-Cowling method, are obtained for the Maxwellian and Pseudo-Maxwellian potential models.

Since the functional form of $\phi$ obtained by both the iterative method, (6.2.6), and the Chapman-Cowling method, (6.2.11), are identical, we can thus appreciate why the values for transport coefficients are the same for both methods.

Having carried out a fairly detailed comparison of the two methods for the Maxwellian and Pseudo-Maxwellian potential models, we find that a similar treatment for the rigid sphere model and for more general repulsive potential models is much more difficult, but some qualitative comparisons will be made.

In the case of the Chapman-Cowling method, we have seen from above that

$$
\lambda = \frac{5 k^2 T}{2m} a_1 .
$$

(6.2.9)
We obtain approximations to \( a_1 \), namely

\[
a_1^{(1)} = \frac{15}{4} \frac{1}{a_{11}}, \quad a_1^{(2)} = \frac{15}{4} \frac{a_{22}}{(a_{11} a_{22} - a_{21}^2)},
\]

where for the rigid sphere model

\[
a_1^{(2)} = \frac{45}{44} a_1^{(1)},
\]

and hence we can obtain approximations to \( \lambda \) by substituting into (6.2.9).

Finally, for the Chapman-Cowling method, if we consider the expansion

\[
A = \sum_{n=1}^{\infty} a_n S_{\frac{3}{2}}^{(n)}(aV^2) V
\]

then for the rigid sphere model we find \( a_2 = \frac{1}{11} a_1 \) so that the main contribution to \( A \) comes from

\[
a_1 S_{\frac{3}{2}}^{(1)}(aV^2) V = a_1 X_c
\]

[see also Figure (9)] for the velocity range for which we are interested, since \( A \) is usually weighted with \( \exp(-aV^2) \).

For the iterative procedure we have

\[
\phi^{(0)}(V) = \frac{X}{L_0}, \quad \phi^{(1)}(V) = \frac{1}{L_0} L_1 \frac{X}{L_c}, \quad (6.2.12)
\]

but \( L_0 \) for the rigid sphere model is now a function of \( V \), as can be seen from examining its form.
\[ L_0 = (\text{constant}) \int e^{-\alpha u^2} (v^2 + u^2 - 2u \cdot v)^{\frac{1}{2}} \frac{\sigma^2}{\pi} \sin \chi \, dv \, ds \, du \]

(6.2.13)

where we have put

\[ |g| = (v^2 + u^2 - 2u \cdot v)^{\frac{1}{2}} ; \]

and hence the geometrical progression development does not follow.

However, we do find \( \lambda^{(0)}, \lambda^{(1)}, \lambda^{(2)} \) follow an approximate geometrical progression, and that good results for the thermal conductivity coefficient, \( \lambda \), have been obtained by assuming exact geometrical progressions based on \( \lambda^{(0)} \) and \( \lambda^{(1)} \); and \( \lambda^{(1)} \) and \( \lambda^{(2)} \) respectively, for the rigid sphere model.

Further, since any \( \lambda^{(n)} \) is obtained from

\[ \lambda^{(n)} = \int (s^2 - \alpha v^2) \, f^{(n)}(v) \, \phi_c^{(n)}(v) \, dv \]

(see Chapter 2, equation (2.1.28)), where the \( \phi_c^{(n)} \)'s are obtained by a repeated process. Then, one is tempted to suggest that the functional forms of the \( \phi_c^{(n)} \)'s may be similar. The drawback with using the \( \lambda^{(n)} \)'s to establish a possible representation of the \( \phi_c^{(n)} \)'s and hence \( \phi_c \) is as follows. The form of the integral for \( \lambda^{(n)} \), namely

\[ \int e^{-\alpha v^2} (s^2 - \alpha v^2) \, \phi_c^{(n)}(v) \, dv \]

can be written as

\[ \int e^{-\alpha v^2} S_3^{(1)}(\alpha v^2) \, \phi_c^{(n)}(v) \, dv \].
If we take account of the orthogonal properties of $S^{(1)}_{\frac{3}{2}}(aV^2)$, then only the $S^{(1)}_{\frac{3}{2}}(aV^2)V$ factors contained in $\phi^{(n)}_c(V)$ contribute to the integral for $\lambda^{(n)}$. This means that using the $\lambda^{(n)}$'s does not give us a true picture of the possible forms of the $\phi^{(n)}_c(V)$'s.

Thus, in order to try to explain this geometrical progression effect, the possible functional forms of the $\phi^{(n)}_c(V)$'s need to be ascertained.

If we examine $L_0$ more closely, we find that it is only weakly dependent on $V$, see Figure (4), for the range of $V$ we need consider, since the functions with which we are likely to be concerned are weighted with $\exp(-aV^2)$. Thus, on looking at the iterative relationships equation (6.2.12), the $\phi^{(i)}_c$'s may well have similar functional forms. We can ascertain the actual forms of $\phi^{(o)}_c$ and $\phi^{(1)}_c$ by examining plots of the functions. We will now do so.

Brooker and Green\(^{(11)}\) have solved the second approximation to Boltzmann's equation for the rigid sphere model by converting the equation into a differential one, and have obtained the perturbation function, which we shall call $\phi_{BG}$, numerically. A graph of this perturbation function, $\phi_{BG}$, is available and will serve as a comparison for our approximations to $\phi_c$.

If we plot $\phi^{(o)}_c$ on the same graph as $\phi_{BG}$, see Figure (5), we can see that they have a similar functional form except that their minima are slightly displaced. Further, if we plot $\phi^{(1)}_c$ on the same graph as $\phi_{BG}$, see Figure (6), then as for $\phi^{(o)}_c$, a similar phenomenon occurs. Indeed, if we examine $\phi^{(o)}_c$ and
Fig. 4: $V$ dependence of $L_0$ for the Rigid Sphere model.
Fig. 5: Approximations to the velocity distribution function for Thermal Conduction.
Approximations to the velocity distribution function for Thermal Conduction.

\[ \phi_{BG}(V) \times e^{-V^2} \]

\[ \phi_{C}(V) \times e^{-V^2} \times \text{scaling factor} \]

Scaling factor = \[ \left[ \frac{0.42}{0.73} \right] \cdot 4\pi \cdot \frac{1}{2} \]
Approximations to the velocity distribution function for Thermal Conduction.

Scaling factor: \(-\frac{0.42}{1.48} \cdot 4 \pi \cdot \frac{1}{2}\)
Fig. 8: Approximation to the velocity distribution function for Thermal Conduction.
Fig. 9: Approximations to the velocity distribution function for Thermal Conduction.
\( \hat{\phi}_c^{(1)} \), see Figures (7) and (8), they also are similar, but to a slightly higher degree since there is a closer fitting of the functions around the second root, which might have been expected since these particular functions are forced to obey the auxiliary conditions as is \( \phi_{BG} \).

Now \( \phi_c^{(1)} \) and the higher \( \phi_c^{(i)} \)s are obtained by operating with the integral operator \( L_1/L_0 \) on \( \phi^{(o)}_c \), and so it is worth looking at the qualitative effect produced by the integral operator, \( L_1/L_0 \), more closely.

As we have seen from the graphs of \( \phi^{(o)}_c \) and \( \phi^{(1)}_c \), they have similar functional forms, but the minimum of \( \phi_c^{(1)} \) has shifted to the right wrt that of \( \phi_c^{(o)} \); so the effect of operating with \( L_1/L_0 \) appears to be that of changing the functional form slightly by shifting the minimum. I have computed the effect of operating on the following functions -

\( \phi^{(o)}_c \), \((\sqrt{2} - V^2) V\), \( \phi^{(o)}_c L_o \) and \((\sqrt{2} - V^2) V^{3/2} \) - which for \( V \) in the range we are interested, are of similar functional form with their minima lying progressively further to the right wrt \( \phi_c^{(o)} \) in the order given. The effect of operating with \( L_1/L_0 \) on the above functions is that their functional forms are changed to the extent that their minima are shifted to the right for the case of the first two functions, and to the left for the other two. I have chosen the above functions to try to simulate the form of \( \phi^{(o)} \), \( \phi^{(1)} \), \( \phi^{(2)} \) ..., obtained by repeated operation of \( L_1/L_0 \) on \( \phi^{(o)} \). We can see, from the above information, that the position of the minima appears to oscillate about a mean point for this particular range of functions when operated on by \( L_1/L_0 \).
This evidence may well be a pointer to the possible functional forms of the $\phi_c^{(i)}$'s. The apparent similarity of $\phi_c^{(0)}$ and $\phi_c^{(1)}$ and, from the above evidence, possibly the higher $\phi_c^{(i)}$'s with each other as well as with the total perturbation function, $\phi_c(\phi_{BG})$, may well shed some light on why the $\lambda^{(i)}$'s follow an approximate geometrical progression for the rigid sphere model; but clearly a more detailed investigation is necessary before any firm conclusions may be drawn.

Now we will examine the possible extension to other repulsive potentials. The rigid sphere model and the Maxwellian potential model represent the two extremes of the repulsive potential models for dilute gases. For the Maxwellian model, the $\phi_c^{(i)}$'s, for the iterative method, are related to an eigenfunction of the operator $L_1/L_0$ and follow an exact geometrical progression, as do the $\lambda^{(i)}$'s. For the rigid sphere model we have seen, earlier in this section, that the functional forms of the $\phi_c^{(i)}$'s are slightly different from each other because $L_1/L_0$ is now weakly dependent on $V$; but the $\lambda^{(i)}$'s follow an approximate geometrical progression. Now for a more general repulsive potential model $L_1/L_0$ is also weakly dependent on $V$, (the dependence is, in fact, weaker than for the rigid sphere model [see Appendix A2]), so one might expect the $\lambda^{(i)}$'s, obtained from the $\phi_c^{(i)}$'s, in this case, also to follow a sequence which is close to a geometrical progression.

6.3 Possible Future Developments

(i) Extension to more general repulsive potentials

As already stated in the previous section, it seems a reason-
able guess that the \( \lambda^{(i)} \)'s may follow an approximate geometrical progression for a general repulsive potential. If this is found to be the case, then the calculation of the transport coefficients for these potentials should be feasible. On considering other repulsive potential models, we will have to apply a cut off in the scattering angle, \( \chi \), but this is dealt with in many books and papers. In particular, Grad\(^{(12)}\) and Cercignani\(^{(13)}\) have dealt with the manipulation of the collision integral terms involving \( L_0 \) and \( L_1 \) into very convenient forms for integrating, and so it seems likely that this will not present too much of a problem.

(ii) Higher order mixtures

We consider the extension of the iterative method to deal with higher order mixtures for the case of the Maxwellian and Pseudo-Maxwellian potential models and the extension of the method to deal with binary and higher order mixtures for the case of the rigid sphere and more general repulsive potential models.

For the Maxwellian and Pseudo-Maxwellian potential cases, we have seen in Chapter 5 that we can write the Boltzmann equation in a matrix form, equation (5.2.9), which we can iterate to obtain the \( \phi_{ic}^{(n)} \)'s and hence \( \lambda \) for a binary mixture. For the case of higher order mixtures with \( N \) components, say, the \( W \) operator of equation (5.2.13) becomes a \( N \) by \( N \) matrix which operates on a \( N \)-dimensional column vector. On continuing in a way similar to that described in Chapter 5, section 2, we can obtain the thermal conductivity coefficient, \( \lambda \), for a mixture of \( N \)-components.
The calculation of the coefficients of diffusion and thermal diffusion for higher order mixtures, for the case of Maxwellian and Pseudo-Maxwellian potential models, is somewhat more complicated but the iterative method could be extended to these cases with the aid of Chapter 18 in C-C.

With regard to the rigid sphere model, then just as we obtained good approximations for the transport coefficients for the single component case, for which approximate geometrical progressions were exhibited, we might expect, using similar procedures, to obtain reasonable approximations to the transport coefficients for binary and higher order mixtures for the rigid sphere model. We cannot, however, follow the method used for Maxwell-type potentials because of the $V$-dependence of $g$ in the collision integrals.

Finally, just as we envisage considering the extension of the iterative method to deal with more general repulsive potentials for the single component case, it seems natural to consider the extension of the method to deal with binary and higher order mixtures for these more general repulsive potentials.
Transformation of Dashed to Undashed Velocity Variables

By using the conservation laws, the only dashed velocity variable expressions which need be treated are the following two

\[ U'_{2} \quad \text{and} \quad V' \cdot V' \]

where

- \( U'_{2} \) is the peculiar velocity of particle two after collision
- \( V' \) is the peculiar velocity of particle one after collision
- \( V'_{1} \) is the peculiar velocity of particle one before collision

and

- \( U'_{2} \) is the peculiar velocity of particle two before collision.

The respective masses of particles one and two are \( m_{1} \) and \( m_{2} \).

To perform the transformation it is necessary to use a centre of mass co-ordinate system.

The following velocity variables are defined:

\[ G = \frac{m_{1} V'_{1} + m_{2} U'_{2}}{m_{1} + m_{2}} = G' \]

being the centre of mass velocity before and after a collision (relative to axes moving with the mass average velocity of the gas).
being the relative velocity before a collision.

\[ g'_{21} = u'_2 - v'_1 \]
being the relative velocity after a collision.

The scattering angle \( \chi \) is defined in Figure (10), which relates the relative orientations of the velocity variable defined above.

First we will consider \( U_{2}^{12} \).

Using the defined velocity variables then we can express \( U_{2}^{12} \) in the following way

\[
U_{2}^{12} = \left( \frac{m_1}{m_1 + m_2} g'_{21} \right) \cdot \left( \frac{m_1}{m_1 + m_2} g'_{21} \right) = G^2 + \left( \frac{m_1}{m_1 + m_2} \right)^2 g^2_{21} + \frac{2 m_1}{m_1 + m_2} G \cdot g'_{21} \quad \text{(A1.1)}
\]

Now from Figure (10)

\[
G \cdot g^2_{21} = G \cdot (g_{21} \cos \chi + |g_{21}| \sin \chi \cos \phi + |g_{21}| \sin \chi \sin \phi),
\]

which on using the fact that \( G \perp j \), we have

\[
G \cdot g^2_{21} = G \cdot g_{21} \cos \chi + |G| |g_{21}| \sin \chi \sin \phi,
\]

so that substituting for \( G \cdot g^2_{21} \) into (A1.1), we obtain

\[
U_{2}^{12} = G^2 + \left( \frac{m_1}{m_1 + m_2} \right)^2 g^2_{21} + \frac{2 m_1}{m_1 + m_2} G \cdot g'_{21} \cos \chi
\]

\[
+ \frac{2 m_1}{m_1 + m_2} |G| |g_{21}| \sin \chi \sin \phi \cos \phi \quad \text{(A1.2)}
\]
fig [10]
We can now convert (A1.2) back into the original velocity variables $V_1$ and $U_2$ using the following relationships

\[
G^2 = \frac{(m_1 V_1 + m_2 U_2) \cdot (m_1 V_1 + m_2 U_2)}{(m_1 + m_2)^2},
\]

\[
e_{21}^2 = (U_2 - V_1) \cdot (U_2 - V_1),
\]

\[
(G \cdot e_{21}) = \frac{(m_1 V_1 + m_2 U_2) \cdot (U_2 - V_1)}{(m_1 + m_2)}.
\]

and that

\[
|G| |e_{21}| \sin \alpha = |G \cdot e_{21}| = \frac{(|m_1 V_1 + m_2 U_2| \cdot (U_2 - V_1|}{(m_1 + m_2)}
\]

\[
= |V_1 \cdot U_2|.
\]

On converting we obtain

\[
U_2^2 = \frac{1}{(m_1 + m_2)^2} \left\{ \frac{2}{m_1} V_1^2 (1 - \cos \chi) + \frac{U_2^2 (m_1^2 + m_2^2 + 2 m_1 m_2 \cos \chi)}{m_1 + m_2} \right\}
\]

\[
+ 2 V_1 \cdot U_2 (m_2 m_1 - m_1^2) (1 - \cos \chi) + \frac{2 m_1}{m_1 + m_2} |V_1 \cdot U_2| \sin \chi \cos \chi.
\]

(A1.3)

Secondly, we will consider $V_1' \cdot V_1$.

Following a similar procedure to that for $U_2^2$ we have

\[
V_1' \cdot V_1 = \left(G - \frac{m_2}{m_1 + m_2} e_{21}'\right) \cdot \left(G - \frac{m_2}{m_1 + m_2} e_{21}\right)
\]

\[
= g^2 + \left(\frac{m_2}{m_1 + m_2}\right)^2 e_{21}' \cos \chi - \frac{m_2}{m_1 + m_2} G \cdot e_{21}' - \frac{m_2}{m_1 + m_2} G e_{21}.
\]
Now $G_2 g_2^g$ has been obtained for the previous expression and on converting back to the original velocity variable, we obtain

\[
\begin{align*}
V_1 \cdot V_1 &= \frac{1}{m_1 + m_2} \left\{ (m_1 + m_2 \cos \chi) V_1^2 + (m_2 - m_2 \cos \chi) V_1 \cdot U_2 \right\} \\
&- \frac{m_2}{m_1 + m_2} |V_1 \cdot U_2| \sin \chi \cos \chi .
\end{align*}
\]  

(A1.4)

Finally, we have to obtain the equivalent expressions for the single gas case. This can easily be done by merely putting $m_1 = m_2 = m$, $V_1 = V$ and $U_2 = U$ in (A1.3) and (A1.4). On doing this we have

\[
U'^2 = \frac{1}{2} \left\{ V^2 (1 - \cos \chi) + U^2 (1 + \cos \chi) \right\} + |V \cdot U| \sin \chi \cos \epsilon ,
\]  

(A1.5)

and

\[
V' \cdot V = \frac{1}{2} \left\{ (1 + \cos \chi) V^2 + (1 - \cos \chi) V \cdot U \right\} \\
- \frac{1}{2} |V \cdot U| \sin \chi \cos \epsilon .
\]  

(A1.6)
APPENDIX A2

Collision Dynamics and the
Calculation of Differential Cross-Sections

The equation of motion of two molecules, exerting forces
of $P_1$, $-P_1$ on each other, are

$$m_1 \ddot{r}_1 = -P_1,$$  \hspace{1cm} (A2.1)

$$m_2 \ddot{r}_2 = P_2,$$  \hspace{1cm} (A2.2)

where $r_1$ and $r_2$ are position vectors.

On combining equations (A2.1 and A2.2) we have

$$\mu \ddot{r}_{21} = P,$$  \hspace{1cm} (A2.3)

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad \text{and} \quad \ddot{r}_{21} = \ddot{r}_2 - \ddot{r}_1.$$

Equation (A2.3) represents the motion of a particle, of
reduced mass $\mu$, about a fixed centre of force $P$. On using
polar co-ordinates $(r, \theta)$, as shown in Figure (11), the
equations of angular momentum and of energy are

$$\mu r^2 \dot{\theta} = \text{const} = \mu gb,$$  \hspace{1cm} (A2.4)

$$\frac{1}{2} \mu (r^2 + r^2 \dot{\theta}^2) + V_{12}(r) = \text{const} = \frac{1}{2} \mu g^2,$$  \hspace{1cm} (A2.5)

where $g$ is the relative velocity, $b$ is the impact parameter.
By eliminating the time between (A2.4) and (A2.5) and integrating we obtain

\[ \theta = \int_{r}^{\infty} \left[ \frac{r^4}{b^2} \left( 1 - \frac{2V_{12}(r)}{\mu g^2} \right) - r^2 \right]^{-\frac{1}{2}} \, dr \]  

(A2.6)

where \( \theta \) is measured from an axis parallel to the initial asymptote of the orbit [see Figure (11)]. The apse OA, where \( r = r_o \), of the orbit corresponds to \( \frac{dr}{d\theta} = 0 \), i.e.

\[ \frac{2V_{12}(r_o)}{\mu g^2} = 1 - \frac{b^2}{r_o^2} \]  

(A2.7)

On using the relationships between \( \theta_o \), \( r_o \) and \( \chi \) from Figure (11), we have for (A2.6)

\[ \chi = \pi - 2 \int_{r_o}^{\infty} \left[ \frac{r^4}{b^2} \left( 1 - \frac{2V_{12}(r)}{\mu g^2} \right) - r^2 \right]^{-\frac{1}{2}} \, dr \]  

(A2.8)

We will now consider the form of (A2.8) for inverse power-law forces.

**Inverse power-law forces**

Suppose \( P \) is a repulsive force given by

\[ P = \frac{K_{12}}{r^s}, \quad V_{12}(r) = \frac{K_{12}}{(s-1) r^{s-1}} \]  

(A2.9)
If we defined the following reduced quantities

\[ v = \frac{b}{r}, \quad v_0 = b \left( \frac{\mu g^2}{K} \right)^{(s-1)}, \quad v_\infty = \frac{b}{\infty} \]  

(A2.10)

then, on substituting (A2.9) and (A2.10) into (A2.8), we have

\[ \chi = \pi - 2 \int_0^{v_\infty} \left( 1 - v^2 - \frac{2}{s-1} \left( \frac{v}{v_0} \right)^{s-1} \right)^{\frac{3}{2}} dv. \]  

(A2.11)

Note the quantity \( v_\infty \) is the only positive root of the equation

\[ 1 - v^2 - \frac{2}{s-1} \left( \frac{v}{v_0} \right)^{s-1} = 0, \]  

(A2.12)

which corresponds to equation (A2.7) with the above quantities substituted.

On examining equations (A2.11 and 12), we can see that \( \chi \) depends only on \( s \) and \( v_0 \).

We will now consider the form of (A2.11) and the corresponding differential cross-sections for the three particular potential models used throughout this thesis.

Rigid elastic sphere (hard sphere)

The potential for this model, \( V(r) \), is given by

\[ V(r) = \frac{K}{r^{s-1}}. \]  

(A2.13)
If we write \( K = K' \sigma^{s-1} \), then on substituting (A2.13) into (A2.11) and integrating we obtain

\[
\chi = 2 \arccos \left( \frac{b}{\sigma} \right), \quad \text{for} \quad b < \sigma
\]

\[
\chi = 0 \quad \text{for} \quad b > \sigma \quad (A2.14)
\]

from which we have

\[
\sigma \cos \frac{\chi}{2} = b \quad (A2.15)
\]

where \( \sigma \) is the diameter of the rigid sphere.

The differential cross-section, on using (A2.15), becomes

\[
b \, db = \frac{\sigma^2}{4} \sin \chi \, d\chi \quad \text{.} \quad (A2.16)
\]

Pseudo-Maxwellian (or soft sphere) potential model

The potential in this case is given by

\[
V(r) = \frac{K}{r^{s-1}} \quad \text{.} \quad (A2.17)
\]

If we write

\[
K = K' \sigma^{s-1} \left( \frac{g^*}{\sigma} \right)^{\frac{s-1}{2}} \quad ,
\]

where \( g^* \) is invariant, then on substituting (A2.17) into (A2.11) and integrating we obtain

\[
\chi = 2 \arccos \left( \frac{b \left( \frac{g^*}{\sigma} \right)^{\frac{1}{2}}}{} \right), \quad \text{for} \quad b g^{\frac{1}{2}} \leq \sigma g^*\frac{1}{2}
\]

\[
\chi = 0 \quad \text{for} \quad b g^{\frac{1}{2}} > \sigma g^*\frac{1}{2} \quad . \quad (A2.18)
\]
From (A2.18), we obtain

\[ \sigma g^{\frac{1}{2}} \cos \frac{\chi}{2} = g^\frac{1}{2} b \] \hspace{1cm} (A2.19)

and hence

\[ g \cdot b \, db = \frac{g^2}{4} g^\frac{3}{2} \sin \chi \, d\chi \] \hspace{1cm} (A2.20)

Here, as for the Maxwellian model which follows, \( g \)
vanishes in the collision integrand, and as a consequence the
treatment is very much simplified. For this model each
collision appears like a collision between two solid spherical
bodies, although the diameters (cross-sections) vary inversely
with \( g \).

**Maxwellian potential model**

For this model, the potential is as follows

\[ V_{12}(r) = \frac{\bar{K}_{12}}{4 r^4} \] \hspace{1cm} (A2.21)

and by (A2.10), we have the following relationship

\[ g \cdot b \, db = \left( \frac{\bar{K}_{12}}{\mu} \right)^{\frac{1}{2}} v_o \, dv_o \] \hspace{1cm} (A2.22)

for which the element \( g \cdot b \, db \) does not depend on \( g \), but only
on \( v_o \).

An important result required for the transport coefficients
for the Maxwellian model is the evaluation of the following
\[ A_\lambda(s) \equiv \int_0^\infty (1 - \cos \lambda \chi) v_0 \, dv_0 , \quad (A2.23) \]

for \( s = 5 \) and \( \lambda = 1, 2 \)

where the required relationships are given in equations (A2.11) and (A2.12).

The values for \( A_\lambda(s) \) are given in C-C, so in this thesis (A2.23) will be used and not the actual value for the respective \( A_\lambda(s) \) terms.
REFERENCES


