The Theory of Dissipative Processes in Gases

by

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Yours sincerely,

Ian L. McLaughlin

ILM:lp

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<u>NOTE</u>:- The author of the thesis has published one article during the course of the work. This article was submitted for publication on 28th October, 1963, and appeared in the Journal of Chemical Physics <u>40</u>, 3166 (1964). A further note on this work by the author has been accepted for publication by the Journal and will appear under "Comments on".

PREFACE

The thesis contains the results of research which was carried out during the years 1961-1964 in the Department of Mathematical Physics of the University of Adelaide. The work was supervised by Professor H.S. Green.

I would like to express my gratitude to Professor H.S. Green for his stimulating discussions, advice and unfailing encouragement during the course of this work. I am also very grateful to Professor C.A. Hurst, Dr. I.E. McCarthy and Dr. P.W. Seymour for their lively discussions and encouragement throughout my years in the Department.

I wish also to thank the Commonwealth Government for the financial assistance provided through a Commonwealth Post Graduate Award.

ABSTRACT.

A special ensemble, called a fluctuation ensemble, is discussed and the corresponding phase space distribution function is rigorously defined. The special subensemble is obtained by choosing, from the grand ensenble, at a specified time, t=o say, those configurations in which a molecule is at a given point $\underline{x}_1$ moving with a specified velocity $\underline{v}_1$. In a dilute gas, it is shown that the fluctuation ensemble contains configurations which are realized when a molecule is injected or allowed to diffuse into a gas originally, i.e. at time t=o , in equilibrium. The one particle velocity distribution function corresponding to the special subensemble is rigorously defined, and is divided into two separate contributions - one associated with the motion of the distinguished molecule, and the other with the rest. A general subensemble in which the distinguished molecule has a specified distribution at time t=o is also discussed, and the one particle velocity distribution functions rigorously defined. These functions are then connected with those of the special sub-ensemble.

The distribution functions are obtained for a general subensemble in which the velocity of the distinguished molecule is specified at time t=o . The velocity distribution functions associated with the motion of this distinguished molecule are obtained for a general molecular model from forward and backward Boltzmann equations, and, in

particular, for Maxwellian molecules. The distribution function associated with the motion of the other molecules for the Maxwellian molecular model is also calculated.

The Kubo-type transport coefficients of thermal conduction and viscosity are evaluated, from the above distribution functions, for Maxwellian molecules forming a dilute gas, using a method developed by Green, and, as expected, the values obtained are those given by the Chapman-Enskog method. The exact mean-free-path coefficients are obtained by using the distribution function associated with the motion of the distinguished molecule, and are compared with the exact transport coefficients as given by the Kubo method.

The corresponding general and special subensembles of the grand ensemble of non-equilibrium are discussed, and the corresponding distribution functions rigorously defined. It is shown, as in the equilibrium case, that in dilute gases this special subensemble is equivalent to considering a system in which a molecule is distinguished at time $t=o$ by its position and velocity, and is surrounded by a gas in a "steady" state of non-equilibrium at time $t=o$. The distribution functions, corresponding to those of the equilibrium case, are found using forward and backward Boltzmann equations for a general molecular model, and, in particular, discussed for Maxwellian molecules. An experimental procedure which involves the injection or

diffusion of radioactive particles into a gas, is suggested as a method of confirming the results.

The distribution functions are used to define various mean accelerations in a gas, in both equilibrium and non-equilibrium, as suggested by the statistical theory of fluids developed by Kirkwood. These mean accelerations are evaluated for Maxwellian molecules. In the equilibrium case, a "forward" mean acceleration is shown to be equivalent to that defined by O'Toole and Dahler. The equivalence of all the definitions of mean accelerations involved in kinetic theory is precisely discussed, and it is shown rigorously that the definition used in the thesis, and so by O'Toole and Dahler, is not equivalent to that defined by Kirkwood.

I, Ian Leonard McLaughlin, certify that this thesis contains no material which has been accepted for the award of any other degrees or diploma in any University, and that, to the best of my knowledge and belief, the thesis contains no material previously published or written by any other person, except where reference is made in the text of the thesis.

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GENERAL INTRODUCTION

The earliest attempt to describe transport phenomena in dilute gases was by the mean free path theory which was developed by Maxwell, Stefan, Boltzmann and Meyer. This theory gave a good physical picture of the processes occurring but did not yield exact results for the transport coefficients. This defect was partly overcome by the modification of the theory to account, to some extent, for the persistence of velocities in the collisions[*]. However, the obtained results for the transport coefficients were still not as exact as those obtained by the exact mathematical theory of Hilbert, Chapman and Enskog developed some years later. In this exact theory, described fully by Chapman and Cowling (C.C.), the one particle velocity distribution function $f(t, \underline{v}, \underline{x})$, for a system of molecules forming a dilute gas in non-equilibrium, were calculated for a number of different molecular models[†] (specified by their two body force laws) from the now well-known Boltzmann transport equation. This transport equation has the following form,

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{x}} = [f, f], \tag{1}$$

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[*] The mean free path theory together with these modifications are fully discussed by Jeans, ref. (1) Chapters 11, 12 and 13.

[†] Maxwell had solved the equation for a special model called the Maxwellian molecules.

where the rate of change in the distribution function f, due to collisions is given by,

$$[f,\ f] = \iint \{f(\underline{v}_0)f(\underline{v}_0{}') - f(\underline{v})\ f(\underline{v}')\}\ \sigma\ \underline{db}\ \underline{d}v', \qquad (2)$$

in which $\sigma = |\underline{v}-\underline{v}'|$, and $\underline{db}$ is an element of cross-section for the collision $(\underline{v}_0,\ \underline{v}_0{}') \rightarrow (\underline{v},\ \underline{v}')$. From these distribution functions the coefficients of thermal conduction and viscosity were calculated for the models. The coefficient of thermal conduction, K, is defined by

$$\underline{q} = -K\ \frac{1}{T}\ \frac{\partial T}{\partial \underline{x}}\ , \qquad (3)$$

where $\underline{q}$ is the local thermal flux. The coefficients of viscosity, η and Υ are defined by,

$$\underline{\underline{P}} = p\ \underline{\underline{U}} - 2\eta\overline{\frac{\partial s\underline{u}}{\partial \underline{x}}} - \Upsilon\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\ \underline{\underline{U}} \qquad (4)$$

where $\underline{\underline{P}}$ is the local pressure tensor; $\left(\overline{\frac{\partial s\underline{u}}{\partial \underline{x}}}\right)_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right) - \frac{1}{3}\left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right)\delta_{ij}$; η is the coefficient of shearing viscosity, and Υ the coefficient of volume viscosity. In a dilute gas the coefficient of volume viscosity is negligible compared with that of shearing viscosity. The diffusion coefficients were, of course, obtained from the distribution functions for a mixture.

Monchick(2) has attempted to reconcile the mean free path theory with the Chapman-Enskog theory but in doing so has introduced "an effective transition probability". In Chapter IV, the mean free path coefficients of thermal conduction and viscosity are calculated for Maxwellian molecules* taking account of the persistence of velocities exactly, and these are then compared with the exact coefficients. All these coefficients are calculated using another approach which was first introduced about ten years ago by M.S. Green(3) who obtained expressions for the transport coefficients using the theory of Markoff processes. In 1957, Kubo(4) derived his quantum mechanical formula for the electrical conductivity, and, since then, many authors, e.g. refs. (5) to (10), applied similar methods to derive and evaluate expressions for the other transport coefficients. These formulae were introduced primarily for the calculation of the transport coefficients in dense gases or liquids, as the Chapman-Enskog method is mainly restricted to dilute gases although Born and Green(11) have generalized to some extent this theory to dense

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* Maxwellian molecules are defined by the two body force law

$$\underset{\sim}{F} = - \frac{\kappa \, \hat{r}}{r^5} ,$$

where κ = constant and $\underset{\sim}{r}$ is the distance apart of the two interacting molecules.

fluids. However, the calculation of these Kubo-type coefficients - as they are now called - for dilute gases is of interest as one would expect them to be equivalent with those obtained from the Chapman-Enskog theory. Mori(6), Montroll(7), Green(10), and others have established the equivalence of the methods for low densities, and Green(10) has also discussed a general proof of the equivalence of the methods for dense fluids. In Chapter IV the Kubo-type coefficients of viscosity and thermal conduction are evaluated for Maxwellian molecules forming a dilute gas and, as expected, have the same values as those given by the Chapman-Enskog method. Mori(6) has also evaluated these Kubo-type coefficients for Maxwellian molecules and shown their equivalence with the Chapman-Enskog method. Mori uses the master and binary collision operators, and obtains the approximate eigenvalues of the master collision operator corresponding to the fluxes of viscosity and thermal conduction. For Maxwellian molecules, in the classical limit, these eigenvalues are exact, and, using these, Mori calculates the corresponding coefficients for the Maxwellian molecules. The eigen values are the inverse relaxation times corresponding to the different modes of relaxation, and the values obtained by Mori are the same as those found in Chapter IV.

The Kubo-type integrals of Green$^{(10)}$ have the form,

$$I = a\langle \tau(\underline{W}_i)\int_0^\infty \Sigma_j \tau(\underline{W}_j{}')dt'\rangle_i^0 ,$$

where the values of "a" and "τ" depend on the particular coefficient being considered*, and $\underline{W}_j{}'$ is the peculiar velocity of the jth molecule at time t' - the summation of j being over all the molecules in the system. The average $\langle\ldots\rangle_i^0$ is formed with an equilibrium distribution function. In Chapter IV, a method introduced by Green$^{(10)}$ is employed in the evaluation of these integrals. In this method, Green introduced a subensemble of the grand ensemble of statistical equilibrium. This subensemble is obtained by separating, at time t=o, from the configurations forming the grand ensemble, those configurations in which a molecule is at a specified point, $\underline{x}_1$ say, and moving with a specified velocity, $\underline{v}_1$ say. Helfand$^{(12)}$ has also applied similar subensembles to the Kubo-type coefficients. In dilute gases, the introduction of such an above subensemble is equivalent to considering a gas in equilibrium, into which a molecule of the same type is injected with velocity $\underline{v}_1$ at the point $\underline{x}_1$. This subensemble is discussed more fully in Chapter I, and the corresponding subensemble of the grand ensemble of non-equilibrium is also constructed. It is shown

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* The precise form for the coefficients of thermal conduction and viscosity are given in Chapter IV.

that, in dilute gases, the latter subensemble is equivalent to considering a molecule entering a system of molecules of the same type forming a gas in a state of non-equilibrium. The correlation functions corresponding to the above processes are defined in Chapter I, i.e. the time dependent velocity distribution functions associated with the "incoming" molecule and those associated with the system as a whole. In the latter part of the chapter, the concept of "backward" distribution functions is introduced in order to describe the fluctuation ensembles prior to the time t=o at which the distinguished molecule has velocity $\underline{v}_1$ at the point $\underline{x}_1$.

In Chapters II and III the distribution functions are found from "forward" and "backward" Boltzmann equations for the general molecular model and for the particular case of the Maxwellian molecules. In Chapter II it is shown that the velocity distribution function $g(t, \underline{v}, \underline{v}_1)$ associated with a molecule entering a system in absolute equilibrium with peculiar velocity $\underline{v} = \underline{v}_1 - \underline{u}$ satisfies the Boltzmann equation,

$$\frac{\partial g}{\partial t} = [\, g, f^{(o)}] \, .$$

Kac(13) has also considered the same problem for a one-dimensional model and Prigogine(14) for weakly coupled gases.

The basic equation of non-equilibrium processes in fluids is the Liouville equation,

$$\frac{\partial F_N}{\partial t} + \sum_{i=1}^{N} \left\{ \underline{v}^{(i)} \cdot \frac{\partial F_N}{\partial \underline{x}^{(i)}} - \frac{1}{m} \frac{\partial \Phi_N}{\partial \underline{x}^{(i)}} \cdot \frac{\partial F_N}{\partial \underline{v}^{(i)}} \right\} = 0 \qquad (5)$$

in which $F_N(t, \underline{x}^{(1)}, \ldots; \underline{x}^{(N)}, \underline{v}^{(1)}, \ldots \underline{v}^{(N)})$ is the probability distribution function for finding only N molecules, considered to be all of the same type, occupying the ranges in positions and velocities $(\underline{x}^{(1)}, \underline{x}^{(1)} + d\underline{x}^{(1)})$, ... $(\underline{v}^{(N)}, \underline{v}^{(N)} + d\underline{v}^{(N)})$. The total potential energy of the system of N-molecules is denoted by Φ_N. This equation is essentially a continuity equation in 6N dimensional phase space.

By using a simple averaging process in (5), the equation for the one particle distribution function, $f(t, \underline{v}, \underline{x})$, defined by

$$f(t, \underline{v}, \underline{x}) = \Sigma_N \int F_N \, \Sigma_i \delta(\underline{x} - \underline{x}^{(i)}) \delta(\underline{v} - \underline{v}^{(i)}) \, d\underline{x}^{(1)} \ldots d\underline{x}^{(N)} d\underline{v}^{(1)} \ldots d\underline{v}^{(N)} / N!$$

is derived. This equation, sometimes called the Liouville equation also, has the following form,

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{x}} + \frac{\partial}{\partial \underline{v}} \cdot f \underline{a}_L = 0 \qquad (6)$$

where the mean acceleration, $\underline{a}_L$, at time t of a molecule moving with velocity $\underline{v}$ at the point $\underline{x}$ is given by the rigorous expression (external force zero),

$$\underline{\Omega}_L = -\frac{1}{m}\iint \frac{f_2(t, \underline{v}^{(1)}, \underline{x}^{(1)}, \underline{v}^{(2)}, \underline{x}^{(2)})}{f(t, \underline{v}^{(1)}, \underline{x}^{(1)})} \frac{\partial\phi^{(12)}}{\partial\underline{x}^{(1)}}\, d\underline{x}^{(2)} d\underline{v}^{(2)}, \tag{7}$$

where f_2 is the two particle distribution function defined by

$$f_2(t, \underline{v}, \underline{x}, \underline{v}', \underline{x}') = \Sigma_N \int F_N \Sigma_i \delta(\underline{x}-\underline{x}^{(i)})\delta(\underline{v}-\underline{v}^{(i)}) \sum_{j=1} \delta(\underline{x}'-\underline{x}^{(j)})\delta(\underline{v}'-\underline{v}^{(j)})\, d\underline{x}^{(1)} d\underline{v}^{(1)} \ldots d\underline{x}^{(N)} d\underline{v}^{(N)}/N!$$

and $\phi^{(12)}$ is the 2 particle potential energy. It should be noted that Equation (6) may be regarded as an exact form of Boltzmann's equation valid for both gases and liquids. In fact, Green$^{(15)}$ has rigorously derived the Boltzmann equation for dilute gases (i.e. Equation (1)) from Equation (6), together with an appropriate statistical hypothesis.

As mentioned above, the theory of dissipative processes in gases was extended by Born and Green to dense fluids (especially liquids). At about the same time Kirkwood$^{(16)}$ introduced another approach in which the theory of Brownian motion was used as a guide. In this theory, approximations were used which were suggested by the theory of Brownian motion, and so the theory is not exact. However, the calculations of the transport coefficients which have been performed using this theory appear to agree moderately well with experiment.

In Chapter V, using the distribution functions associated with the distinguished molecule, which are defined in Chapter I, we define various mean accelerations for a molecule moving in a dilute gas corresponding to those defined by Kirkwood. We then calculate these mean accelerations for Maxwellian molecules and obtain the corresponding friction coefficient which has also been calculated by O'Toole and Dahler(17) using a different approach.

We now describe the theories of Kirkwood and O'Toole and Dahler with special attention to the mean accelerations. In Chapter V a detailed comparison is made between these accelerations and also those introduced in the thesis.

In the theory* of Kirkwood, the mean acceleration, $\underline{a}_K$, of a molecule at the point $\underline{x}^{(1)}$ in the fluid moving with velocity $\underline{v}^{(1)}$ at time t is defined by,

$$\underline{a}_K\,(t,\,\underline{x}^{(1)},\,\underline{v}^{(1)}) = \frac{1}{2\tau}<\rho_0{}^{(1)}+\rho^{(1)}>, \tag{7a}$$

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*The form of expressions used here are following H.S. Green(18) pp.113-114.

where

$$\langle \ldots \rangle = \Sigma_N \int \frac{F_{N+1}}{f(t, \underline{v}^{(1)}, \underline{x}^{(1)})} \ldots \underline{dx}^{(2)} \underline{dv}^{(2)} \ldots$$

$$\ldots \underline{dx}^{(N+1)} \underline{dv}^{(N+1)} / N! \qquad (8)$$

$\rho_o^{(1)}$ is the change of velocity of molecule 1 during the interval from $t-\tau$ to τ, i.e.,

$$\rho_o^{(1)} = -\int_{t-\tau}^{t} \frac{1}{m} \frac{\partial \Phi_{N+1}}{\partial \underline{x}^{(1)}} \, dt' = \frac{1}{m} \int_{t-\tau}^{t} \underline{F}_1(t') \, dt' \qquad (9)$$

[$\underline{F}_1$ = force on molecule 1 due to its interaction with the other molecules in the system.]

$\rho^{(1)}$ is the change of velocity of molecule 1 during the interval from t to $t+\tau$, i.e.,

$$\rho^{(1)} = -\int_{t}^{t+\tau} \frac{1}{m} \frac{\partial \Phi_{N+1}}{\partial \underline{x}^{(1)}} \, dt' \;. \qquad (10)$$

Note that in the average (8), the position and velocity of the particle 1 are kept fixed at time t. From (9) and (10), η_K may also be written as

$$\eta_K = \frac{1}{2\tau} \left\langle -\int_{t-\tau}^{t+\tau} \frac{1}{m} \frac{\partial \Phi_{N+1}}{\partial \underline{x}^{(1)}} \, dt' \right\rangle \;. \qquad (11)$$

The method expresses η_K in terms of a friction tensor $\underline{\underline{\zeta}}$ given by

$$\underline{\underline{\zeta}} = \frac{m}{kT} \frac{1}{2\tau} \langle \rho_o^{(1)} \rho_o^{(1)} \rangle \;, \qquad (12)$$

and in doing so, another mean acceleration $\underline{n}_+$, defined by

$$\underline{n}_+ = \frac{1}{\tau} \langle \rho^{(1)} \rangle \ , \tag{13}$$

is introduced. The expression obtained is as follows,

$$\underline{n}_K = \underline{n}_+ - \frac{kT}{mf} \frac{\partial}{\partial \underline{v}^{(1)}} \cdot f \, \underline{\underline{\zeta}} . \tag{14}$$

In equilibrium the mean force acting on a molecule is zero. So, using the Maxwell distribution, Equation (14) becomes

$$\underline{n}_+^{(0)} = \left\{ -(\underline{v}^{(1)} - \underline{u}) + \frac{kT}{m} \frac{\partial}{\partial \underline{v}^{(1)}} \right\} \cdot \underline{\underline{\zeta}}^{(0)} \ , \tag{15}$$

i.e.,

$$\underline{n}_+^{(0)} = -\zeta \, \underline{V}^{(1)} \ , \tag{16}$$

where $\underline{V}^{(1)} = \underline{v}^{(1)} - \underline{u}$, and ζ has been termed the friction coefficient. It should be noted that Equation (16) is the analogue of the Langevin equation of the Brownian motion theory. However, unlike (16), Langevin's equation has not been averaged over an ensemble, but is the equation of motion of a single molecule considered from a microscopic point of view.

If the deviation of the friction tensor from its equilibrium value is neglected, then from (14) and (15), $\underline{n}_K$ may be expressed in the following manner,

$$\underline{n}_K = \underline{n}_+' - \left\{ \frac{kT}{mf} \frac{\partial f}{\partial \underline{v}^{(1)}} + \underline{V}^{(1)} \right\} \cdot \underline{\underline{\zeta}}^{(0)} \tag{17}$$

where $\underline{n}_+' = \underline{n}_+ - \underline{n}_+^{(0)}$. Actually, Kirkwood assumes the following value for $\underline{n}_+'$,

$$\underline{n}_+' = \frac{1}{mn}\frac{\partial}{\partial \underline{x}}(nkT-p) \tag{18}$$

(p = hydrostatic pressure).

The formula (17) for the mean acceleration of a molecule whose position and velocity at time t are $\underline{x}=\underline{x}^{(1)}$ and $\underline{v}=\underline{v}^{(1)}$ respectively is taken as the mean acceleration, $\underline{n}_L$, defined by the Liouville equation and substituted in this equation; the result being essentially that of Kirkwood. However, Kirkwood assumed that the friction tensor $\underline{\underline{\zeta}}^{(0)}$ reduced to a multiple of the unit tensor, i.e.,

$$\underline{\underline{\zeta}}^{(0)} = \zeta^{(0)}\underline{\underline{\delta}} \tag{19}$$

Kirkwood also supposed that there was a range of τ - called the "plateau time" - where $\zeta^{(0)}$ is constant* in value, and published a plateau value without derivation$^{(19)}$. However, Rice and Kirkwood$^{(20)}$ and Collins and Raffel$^{(21)}$ have derived this same value approximately by different methods for dense fluids. The latter derivation is of interest as the subensemble used by Green$^{(10)}$ and referred to above is introduced to define

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* If this plateau value is assumed, then $\zeta^{(0)}$ and ζ in Equation (16) are, of course, identical.

the friction coefficient. However, certain assumptions are introduced which do not appear to be necessarily accurate, although the "correct" expression for the plateau value, i.e., agreeing with Rice and Kirkwood, is obtained.

The plateau time is important as we see from the formulae (11), (13) and (10) that in the limit $\tau \rightarrow 0$, $\underline{\eta}_K$ and $\underline{\eta}_+$ are identical, and also the friction tensor approaches zero with τ.

Helfand$^{(22)}$, Collins and Raffel$^{(23)}$, and others have discussed the friction terms for dense fluids. However, in this thesis we consider dilute gases in which only binary collisions are accounted for.

The friction coefficient for dilute gases has been calculated by O'Toole and Dahler$^{(17)}$ for a number of molecular models. Their method makes use of the formula (16). The mean change in momentum during a collision of a specified molecule with one of its neighbours is considered. In particular, their expression for $\underline{\eta}_+^{(0)}$ is,

$$\underline{\eta}_+^{(0)}(t,\underline{v}_1) = \left\langle \frac{1}{\tau} \int_t^{t+\tau} \underset{\sim}{F}_1(t')dt' \right\rangle^0 =$$

$$= \iint f^{(0)}(v')\,(\underline{v}_f - \underline{v}_1)\,\sigma\,\underline{db}\,\underline{dv}' \qquad (20)$$

when a collision process $(\underline{v}_1, \underline{v}') \rightarrow (\underline{v}_f, \underline{v}_f')$ is considered. To obtain (20), in going from Kirkwood's definition to theirs, O'Toole and Dahler suppose that the plateau time τ is considerably larger than the time taken for a binary collision but less than the recurrence time for multiple collisions. They finally take τ to be of the order of the mean transit time for a free path length. This choice is, as pointed out by the authors, impossible for a dense fluid as the two limits are of the same order.

The calculation of formula (20) for Maxwellian molecules is comparatively simple, and the result obtained is

$$\underline{n}_+^{(0)} = - n\kappa A_1(5) \left(\frac{2\kappa}{m}\right) \underline{V}_1 \, . \tag{21}$$

In Chapter V, it is shown that $\underline{n}_+^{(0)}$ of O'Toole and Dahler is equivalent to that introduced in this thesis but is different from that defined by Kirkwood. It is interesting to note that, in the definition of the mean acceleration $\underline{n}_+^{(0)}$ in this thesis, it does not appear necessary to introduce a plateau time like that of O'Toole and Dahler.

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CHAPTER I ENSEMBLES AND SUBENSEMBLES

1-1 INTRODUCTION

Any system of molecules forming a gas is so complex that it is impossible to specify the configuration of the system at any instant of time by the positions and velocities of every molecule in the system. For this reason an ensemble is introduced to represent the state of the gas. This ensemble consists of an uncountable set of configurations constructed so that the configuration of an actual gas may be imagined to be taken at random from the ensemble. When probabilities and averages are calculated they are always defined relative to the constructed ensemble. In order to evaluate the unconditional average of any function of the positions and velocities of the molecules, a phase space distribution function, $F_N(t,\underline{x}^{(1)},\ldots,\underline{x}^{(N)},\underline{v}^{(1)},\ldots,\underline{v}^{(N)})$, is introduced. This function is usually defined as follows: if a gas consists of N molecules (all of the same type), and $d\Omega_N$ is an element of configuration space, i.e.,

$$d\Omega_N = \underline{dx}^{(1)}\ldots\underline{dx}^{(N)}\underline{dv}^{(1)}\ldots\underline{dv}^{(N)}/N! \,, \qquad (1\text{-}1)$$

the probability that the configuration of the gas under consideration is in this element is $F_N \, d\Omega_N$. The normalization is

$$\Sigma_{N=0}^{\infty} \int F_N \, d\Omega_N = 1 \; ,$$

and so the unconditional mean of any function G of positions and velocities is

$$\langle G \rangle = \Sigma_{N=0}^{\infty} \int F_N G \, d\Omega_N \; . \qquad (1\text{-}2)$$

From this phase space distribution function it is possible to define the one-particle distribution function $f(t,\underline{x},\underline{v})$ by the following,

$$f(t,\underline{x},\underline{v}) = \langle \Sigma_{i=1}^{N} \delta(\underline{x}-\underline{x}^{(i)}) \delta(\underline{v}-\underline{v}^{(i)}) \rangle \; . \qquad (1\text{-}3)$$

This velocity distribution function has the property that $f(t,\underline{x},\underline{v})\underline{dx}\;\underline{dv}$ is the probability of finding, at time t, a molecule of the gas in the volume element $(\underline{x},\underline{x}+\underline{dx})$ with velocity in the range $(\underline{v},\underline{v}+\underline{dv})$.

In this chapter subensembles of the grand ensembles of statistical equilibrium and non-equilibrium are discussed. Firstly, we will discuss the special subensemble which was introduced by Green$^{(1)}$ (note also Helfand$^{(2)}$ and Collins and Raffel$^{(3)}$ - see General Introduction). This subensemble is constructed by separating from the complete (i.e., grand) ensemble of equilibrium, those configurations in which a molecule is at a specified point in a gas and moving with a specified velocity at a specified time. The corresponding subensemble for the grand ensemble of non-equilibrium is also constructed. A more general subensemble of which the special subensemble is a special case is introduced. It is found possible to obtain the one particle distribution functions corresponding to the more general subensemble from those corresponding to the special subensemble.

1-2 EQUILIBRIUM

For a gas to be in a state of statistical equilibrium, the following necessary and sufficient conditions hold in the whole region occupied by the gas,

$$\frac{\partial T}{\partial \underline{x}} = 0 ,$$

$$\frac{\partial \underline{u}}{\partial \underline{x}} + \overline{\frac{\partial \underline{u}}{\partial \underline{x}}} = 0 ,$$

and $$\frac{\partial}{\partial \underline{x}} (\mu + \phi - \tfrac{1}{2} u^2) = 0 ,$$

where T is the absolute temperature, $\underline{u}$ the mass velocity,

$$\left(\frac{\partial \underline{u}}{\partial \underline{x}} + \overline{\frac{\partial \underline{u}}{\partial \underline{x}}} \right)_{ij} = \frac{\partial u_j}{\partial x_i} + \frac{\partial u_i}{\partial x_j} ,$$

$\mu \equiv$ thermodynamic potential,

and ϕ = potential per unit mass due to external forces. The solution to the second condition above is

$$\underline{u} = \underline{u}_0 + \underline{\omega} \times \underline{x}$$

where $\underline{u}_0$ and $\underline{\omega}$ are arbitrary constants, and so the gas moves as a rigid body with constant translational velocity and constant angular velocity.

The one particle distribution function corresponding to a state of equilibrium is the Maxwellian velocity distribution

$$f^{(0)} = n\left(\frac{\beta m}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta m w^2} ,$$

where the peculiar velocity $\underline{w}=\underline{v}-\underline{u}$,
and $\beta = \frac{1}{kT}$.

In general, the one particle distribution function for equilibrium will depend implicitly on the spatial variable $\underline{x}$ in the number density n and mass velocity $\underline{u}$ in a special way. However, in uniform equilibrium (C.C. p.69) - sometimes called "absolute equilibrium" - the distribution function is independent of the spatial variable. In this case, the gas moves with a constant translational velocity and there is no rigid body rotation.

The phase space distribution function corresponding to the state of absolute equilibrium will be denoted by F_N° and so the unconditional mean, with respect to this ensemble, of any function G of positions and velocities is denoted by,

$$\langle G\rangle^{\circ} = \Sigma_{N=0}^{\infty} \int F_N^{\circ} G d\Omega_N . \qquad (1-4)$$

1-2-1 SPECIAL SUBENSEMBLE

From the grand ensemble of equilibrium, the special subensemble is defined by separating at a specified time, t=o say, those configurations in which a molecule is at the point $\mathbf{x}_1$ and moving with velocity $\mathbf{v}_1$. We denote the phase space distribution function corresponding to this ensemble by x_N° $(t,\mathbf{x}^{(1)},\ldots\mathbf{x}^{(N)},\mathbf{v}^{(1)}\ldots\mathbf{v}^{(N)})$. The state represented by this subensemble is not one of equilibrium but a non-steady state.

So, at time t=o, x_N° has the value

$$x_N^\circ(o) = F_N^\circ \, \Sigma_{i=1}^{N} \, \delta(\mathbf{x}_1-\mathbf{x}_o^{(i)})\delta(\mathbf{v}_1-v_o^{(i)})/ f^{(o)}(\mathbf{x}_1,\mathbf{v}_1) \, , \qquad (1\text{-}5)$$

where $\mathbf{x}_o^{(i)}$, $\mathbf{v}_o^{(i)}$ are the position and velocity of the ith molecule at time t=o. This distribution function is correctly normalized as

$$\Sigma_N\int x_N^\circ(o)\, d\Omega_{oN}$$

$$= \Sigma_N \int F_N^\circ \, \Sigma_i \, \delta(\mathbf{x}_1-\mathbf{x}_o^{(i)})\delta(\mathbf{v}_1-\mathbf{v}_o^{(i)}) \, d\Omega_{oN}/f^{(o)}(\mathbf{x}_1,\mathbf{v}_1)$$

$$= f^{(o)}(\mathbf{x}_1,\mathbf{v}_1)/f^{(o)}(\mathbf{x}_1,v_1)$$

$$= 1.$$

In principle, the distribution function $x_N^\circ(t)$ could be found from the integration of Liouville's equation with the application of the boundary condition (1-5). However, in practice, this task is far too complex and the one particle distribution function is used. The one particle distribution function for the special subensemble, denoted by $f_X^{(e)}(t,\mathbf{X},\mathbf{Y})$, is defined by the following,

$$f_X^{(e)}(t,\mathbf{X},\mathbf{Y};\mathbf{X}_1,\mathbf{Y}_1) = \langle \Sigma_j \delta(\mathbf{X}-\mathbf{X}^{(j)})\delta(\mathbf{Y}-\mathbf{Y}^{(j)})\rangle^X$$

$$= \Sigma_N \int \chi_N^*(t)\, \Sigma_j \delta(\mathbf{X}-\mathbf{X}^{(j)})\delta(\mathbf{Y}-\mathbf{Y}^{(j)})d\Omega_N \qquad (1\text{-}6)$$

Now, by Liouville's theorem,

$$\chi_N^*(o)\, d\Omega_{o_N} = \chi_N^*(t)\, d\Omega_N$$

where $d\Omega_N$ is the element of phase space at time t derived by natural motion from the element $d\Omega_{o_N}$ at time t=o. (Also, it is a well-known result that this element remains constant in time.) So,

$$f_X^{(e)} = \Sigma_N \int \chi_N^*(o)\Sigma_j \delta(\mathbf{X}-\mathbf{X}^{(j)})\delta(\mathbf{Y}-\mathbf{Y}^{(j)})d\Omega_{o_N}/f^{(e)}(\mathbf{X}_1,\mathbf{Y}_1)$$

$$= \Sigma_N \int \frac{F_N^*}{f^{(e)}(\mathbf{X}_1,\mathbf{Y}_1)} \Sigma_i \delta(\mathbf{X}_1-\mathbf{X}_o^{(i)})\delta(\mathbf{Y}_1-\mathbf{Y}_o^{(i)})\delta(\mathbf{X}-\mathbf{X}^{(i)})\delta(\mathbf{Y}-\mathbf{Y}^{(i)})d\Omega_N$$

$$+ \Sigma_N \int \frac{F_N^*}{f^{(e)}(\mathbf{X}_1,\mathbf{Y}_1)} \Sigma_i \delta(\mathbf{X}_1-\mathbf{X}_o^{(i)})\delta(\mathbf{Y}_1-\mathbf{Y}_o^{(i)}) \sum_{j\neq i} \delta(\mathbf{X}-\mathbf{X}^{(j)})\delta(\mathbf{Y}-\mathbf{Y}^{(j)})d\Omega_N$$

where each term in the first integral may be interpreted as following the motion of the ith molecule which has a position

$\underline{X}_1$ at time t=o and velocity $\underline{Y}_1$. The second integral may be interpreted as following the motion of the molecules other than the distinguished ith molecule. Hence we define the one particle distribution functions $g_\chi^{(o)}(t, \underline{X}, \underline{Y}; \underline{X}_1, \underline{Y}_1)$ - the distribution function associated with the distinguished molecule - and $\Gamma_\chi^{(o)}(t, \underline{X}, \underline{Y}; \underline{X}_1, \underline{Y}_1)$ - the distribution function associated with all molecules except the distinguished one. These functions are therefore given by,

$$g_\chi^{(o)} = \Sigma_N \int \frac{F_N^{\circ}}{f^{(o)}(\underline{X}_1, \underline{Y}_1)} \Sigma_i \delta(\underline{X}_1 - \underline{X}_0^{(i)}) \delta(\underline{Y}_1 - \underline{Y}_0^{(i)}) \delta(\underline{X} - \underline{X}^{(i)}) \delta(\underline{Y} - \underline{Y}^{(i)}) d\Omega$$

and

$$\Gamma_\chi^{(o)} = \Sigma_N \int \frac{F_N^{\circ}}{f^{(o)}(\underline{X}_1, \underline{Y}_1)} \Sigma_i \delta(\underline{X}_1 - \underline{X}_0^{(i)}) \delta(\underline{Y}_1 - \underline{Y}_0^{(i)})$$
$$\sum_{j \neq i} \delta(\underline{X} - \underline{X}^{(j)}) \delta(\underline{Y} - \underline{Y}^{(j)}) \, d\Omega_N .$$

So, at time t=o,

$$g_\chi^{(o)}(o) = \Sigma_N \int \frac{F_N^{\circ}}{f^{(o)}(\underline{X}_1, \underline{Y}_1)} \Sigma_i \delta(\underline{X}_1 - \underline{X}_0^{(i)}) \delta(\underline{Y}_1 - \underline{Y}_0^{(i)})$$
$$\delta(\underline{X} - \underline{X}_0^{(i)}) \delta(\underline{Y} - \underline{Y}_0^{(i)}) \, d\Omega_{o_N}$$
$$= \delta(\underline{X} - \underline{X}_1) \delta(\underline{Y} - \underline{Y}_1) , \qquad (1\text{-}7)$$

and

$$\Gamma_{\chi}^{(0)}(0) = \Sigma_N \int \frac{F_N^{0}}{f^{(0)}(\underline{X}_1,\underline{Y}_1)} \Sigma_i \, \delta(\underline{X}_1-\underline{X}_0^{(i)})\delta(\underline{Y}_1-\underline{Y}_0^{(i)})$$

$$\sum_{j\neq i} \delta(\underline{X}-\underline{X}_0^{(j)})\delta(\underline{Y}-\underline{Y}_0^{(j)}) \, d\Omega_{0_N}$$

$$= f^{(0)}(\underline{X},\underline{Y}) \, , \qquad (1\text{-}8)$$

for dilute gases, to the order we consider in the Boltzmann equation, viz., $O(n)$. For gases dilute enough to apply the "binary encounter" approximation, $f_{\chi}^{(0)}(t,\underline{X},\underline{Y})$ will satisfy the Boltzmann equation which may be linearized. The functions $g_{\chi}^{(0)}$ and $\Gamma_{\chi}^{(0)}$ will also satisfy Boltzmann equations.

From the results (1-7) and (1-8), we see that the system represented by the special subensemble is one in which at a specified time, $t=0$, a molecule is moving with velocity $\underline{Y}_1$ at the point $\underline{X}_1$ in the system, and all the other molecules in the system are in statistical equilibrium. This distinguished molecule is not in equilibrium with the other molecules. This is equivalent, for time $t \geq 0$, to considering a molecule entering, at time $t=0$, a system of similar molecules, forming a gas in equilibrium, with velocity $\underline{Y}_1$ at the point $\underline{X}_1$ in the system. As time progresses this distinguished molecule will exchange momentum and energy with the molecules of the system by collision, thus forming an unsteady state. After a short time, however, this originally distinguished molecule will be in equilibrium with its neighbours as the steady equilibrium state is reached.

1-2-2 GENERAL SUBENSEMBLES

In the above section we have considered a subensemble which is obtained by choosing at a specified time certain configurations from the grand equilibrium ensemble. These configurations were such that a molecule is at a particular point moving with a specified velocity, as is expressed by the condition (1-7). The phase space distribution function χ_N^{*} corresponding to this subensemble was constructed and a one particle distribution function constructed from it.

In this section we wish to discuss a more general subensemble. The general subensemble is obtained from the grand ensemble of equilibrium by separating, at time t=o and with statistical frequency $\phi(\underline{x},\underline{v})$, those configurations in which a molecule has position $\underline{x}$ and velocity $\underline{v}$. This means that the distinguished molecule in the system we are considering has a specified distribution $\phi(\underline{x},\underline{v})$ at time t=o. If we denote the one particle distribution function corresponding to the general subensemble by $f_{\phi}^{(*)}(t,\underline{x},\underline{v})$, then it is divided as above, viz.,

$$f_\phi^{(o)}(t,\underline{X},\underline{V}) = g_\phi^{(o)}(t,\underline{X},\underline{V}) + \Gamma_\phi^{(o)}(t,\underline{X},\underline{V}) \, , \qquad (1\text{-}10)$$

where $g_\phi^{(o)}$ is associated with the distinguished molecule and $\Gamma_\phi^{(o)}$ with the rest. Hence, for t=o,

$$g_\phi^{(o)}(o,\underline{X},\underline{V}) = \phi(\underline{X},\underline{V}) \qquad (1\text{-}11)$$

(note: $\phi(\underline{X},\underline{V})$ is normalized so that $\int\phi(\underline{X},\underline{V})\underline{dX}\ \underline{dV} = 1$),

and

$$\Gamma_\phi^{(o)}(o,\underline{X},\underline{V}) = f^{(o)} \, . \qquad (1\text{-}12)$$

We are able to obtain the functions $g_\phi^{(o)}$ and $\Gamma_\phi^{(o)}$ from the functions $g_\chi^{(o)}$ and $\Gamma_\chi^{(o)}$ (i.e., the "fundamental solutions" ref. (4), p. 76) in the following manner. Since $g_\chi^{(o)}$ satisfies a Boltzmann equation then the function

$$\iint g_\chi^{(o)}(t,\underline{X},\underline{V};\underline{X}_o,\underline{V}_o)\phi(\underline{X}_o,\underline{V}_o)\ \underline{dX_o}\ \underline{dV_o}$$

will also satisfy the same equation. Also, at t=o,

$$\iint g_\chi^{(o)}(o,\underline{X},\underline{V};\underline{X}_o,\underline{V}_o)\phi(\underline{X}_o,\underline{V}_o)\ \underline{dX_o}\ \underline{dV_o}$$

$$= \iint \delta(\underline{X}-\underline{X}_o)\delta(\underline{V}-\underline{V}_o)\phi(\underline{X}_o,\underline{V}_o)\ \underline{dX_o}\ \underline{dV_o}$$

$$= \phi(\underline{X},\underline{V}) \, ,$$

and so the distribution function in the general subensemble corresponding to the function g_χ in the special subensemble can be expressed by the following,

$$g_\phi^{(o)}(t,\underline{X},\underline{Y}) = \iint g_\chi^{(o)}(t,\underline{X},\underline{Y};\underline{X}_o,\underline{Y}_o)\phi(\underline{X}_o,\underline{Y}_o)\, \underline{dX_o}\, \underline{dY_o}. \qquad (1\text{-}13)$$

Similarly, the function $\Gamma_\phi^{(o)}(t,\underline{X},\underline{Y})$ may be obtained from the corresponding function $\Gamma_\chi^{(o)}$ for the special subensemble, by using the following relation,

$$\Gamma_\phi^{(o)}(t,\underline{X},\underline{Y}) = \iint \Gamma_\chi^{(o)}(t,\underline{X},\underline{Y};\underline{X}_o,\underline{Y}_o)\phi(\underline{X}_o,\underline{Y}_o)\, \underline{dX_o}\, \underline{dY_o} . \qquad (1\text{-}14)$$

1-3 NON-EQUILIBRIUM

In the above sections we have discussed the grand ensemble of equilibrium and obtained subensembles from it by separating certain configurations at a specified time. In this section we apply the above to the grand ensemble of non-equilibrium, and so obtain similar distribution functions corresponding to subensembles of this grand ensemble.

In a uniform equilibrium state, the macroscopic parameters, absolute temperature T, mass velocity $\underline{u}$ and number density n, are all constant in space and time. In non-equilibrium, of course, these parameters are no longer constant, and so gradients of all the above may exist. The phase space distribution function corresponding to the grand ensemble of non-equilibrium is denoted by F_N and is usually expanded as follows;

$$F_N = F_N^o + F_N^{(1)} + \ldots$$

where F_N^0 has the generalized equilibrium form and so is independent of the gradients of the macroscopic parameters $\underline{u}(\underline{x},t)$, $T(\underline{x},t)$ and $n(\underline{x},t)$, and $F_N^{(1)}$ is linear in the gradients, and so on to higher orders.

The one particle distribution function for a dilute gas is also expressible in the above form, i.e.,

$$\begin{aligned} f(t,\underline{x},\underline{v}) &= \Sigma_N \int (F_N^0 + F_N^{(1)} + \ldots)\, \Sigma_i\, \delta(\underline{x}-\underline{x}^{(i)})\delta(\underline{v}-\underline{v}^{(i)})\, d\Omega_N \\ &= f^{(0)} + f' + \ldots \end{aligned}$$

and may be found from the Boltzmann equation via the Chapman-Enskog method (see C.C.). The terms linear in the gradients, i.e., those represented by the first order f', are usually sufficient for most work in kinetic theory. This is due, of course, to the fact that the coefficients involved in the theory of the irreversible processes, e.g., thermal conduction and viscosity, are expressed in empirical equations linear in the macroscopic gradients. These equations defining the coefficients of thermal conduction, K, and shear viscosity, η, are given by Equations (3) and (4) in the General Introduction. In this thesis, we neglect terms of second and higher orders in the gradients.

1-3-1 SPECIAL SUBENSEMBLE

As in the equilibrium case, we select a special subensemble by separating from the grand ensemble of non-equilibrium those configurations in which a molecule is at the point $\underline{x}_1$ moving with velocity $\underline{v}_1$ at time t=o.

If the phase space distribution function corresponding to this subensemble is denoted by $\chi_N(t,\underline{x}^{(1)},..\underline{x}^{(N)};\underline{v}^{(1)},..\underline{v}^{(N)})$, then at the specified time t=o,

$$\chi_N(o) = F_N(o) \sum_{i=1}^{N} (\underline{x}_1-\underline{x}_o^{(i)})\delta(\underline{v}_1-\underline{v}_o^{(i)})/f(o,\underline{x}_1,\underline{v}_1) \ , \qquad (1\text{-}15$$

and so it is correctly normalized, i.e.,

$$\int \chi_N(o)\, d\Omega o_N = \frac{1}{f(o,\underline{x}_1,\underline{v}_1)} \int F_N(o) \Sigma_i\, \delta(\underline{x}_1-\underline{x}_o^{(i)})\delta(\underline{v}_1-\underline{v}_o^{(i)})\, d\Omega o_N$$

$$= 1 \ .$$

The one-particle distribution function, $f_\chi(t,\underline{x},\underline{v};\underline{x}_1,\underline{v}_1)$, corresponding to this special subensemble can be divided into two distribution functions in the same manner as $f_\chi^{(e)}$ in section 1-2-1 above. One velocity distribution function is associated with the distinguished molecule, the other function with the remaining molecules. Hence, as in (1-7) and (1-8),

$$f_\chi = \Sigma_N \int \chi_N(t)\ \Sigma_j\ \delta(\underline{X}-\underline{X}^{(j)})\delta(\underline{Y}-\underline{Y}^{(j)})\ d\Omega_N$$

$$= \Sigma_N \int \chi_N(o)\ \Sigma_j\ \delta(\underline{X}-\underline{X}^{(j)})\delta(\underline{Y}-\underline{Y}^{(j)})\ d\Omega o_N$$

$$= \Sigma_N \int \frac{F_N(o)}{f(o,\underline{X}',\underline{Y}')}\ \Sigma_i\ \delta(\underline{X}'-\underline{X}o^{(i)})\delta(\underline{Y}'-\underline{Y}o^{(i)})$$

$$\delta(\underline{X}-\underline{X}^{(i)})\delta(\underline{Y}-\underline{Y}^{(i)})\ d\Omega o_N$$

$$+ \Sigma_N \int \frac{F_N(o)}{f(o,\underline{X}',\underline{Y}')}\ \Sigma_i\ \delta(\underline{X}'-\underline{X}o^{(i)})\delta(\underline{Y}'-\underline{Y}o^{(i)})$$

$$\sum_{j\neq i} \delta(\underline{X}-\underline{X}^{(j)})\delta(\underline{Y}-\underline{Y}^{(j)})\ d\Omega o_N$$

$$= \Sigma_N \int \frac{F_N(t)}{f(o,\underline{X}',\underline{Y}')}\ \Sigma_i\ \delta(\underline{X}'-\underline{X}o^{(i)})\delta(\underline{Y}'-\underline{Y}o^{(i)})$$

$$\delta(\underline{X}-\underline{X}^{(i)})\delta(\underline{Y}-\underline{Y}^{(i)})\ d\Omega_N$$

$$+ \Sigma_N \int \frac{F_N(t)}{f(o,\underline{X}',\underline{Y}')}\ \Sigma_i\ \delta(\underline{X}'-\underline{X}o^{(i)})\delta(\underline{Y}'-\underline{Y}o^{(i)})$$

$$\sum_{j\neq i} \delta(\underline{X}-\underline{X}^{(j)})\delta(\underline{Y}-\underline{Y}^{(j)})\ d\Omega_N$$

$$= g_\chi\ (t,\underline{X},\underline{Y};\underline{X}',\underline{Y}') + \Gamma_\chi\ (t,\underline{X},\underline{Y};\underline{X}',\underline{Y}')\ .$$

So g_χ is associated with the distinguished molecule and Γ_χ with the rest. For t=o,

$$g_\chi(o) = \Sigma_N \int \frac{F_N(o)}{f(o,\underline{X}_1,\underline{V}_1)} \Sigma_i \, \delta(\underline{X}_1-\underline{X}_o^{(i)})\delta(\underline{V}_1-\underline{V}_o^{(i)})$$

$$\delta(\underline{X}-\underline{X}_o^{(i)})\delta(\underline{V}-\underline{V}_o^{(i)}) \, d\Omega_{o_N}$$

$$= \delta(\underline{X}-\underline{X}_1)\,\delta(\underline{V}-\underline{V}_1) \,, \tag{1-16}$$

and $\Gamma_\chi(o)$ is given by*,

$$\Gamma_\chi(o) = \Sigma_N \int \frac{F_N(o)}{f(o,\underline{X}_1,\underline{V}_1)} \Sigma_i \, \delta(\underline{X}_1-\underline{X}_o^{(i)})\delta(\underline{V}_1-\underline{V}_o^{(i)})$$

$$\sum_{j\neq i} \delta(\underline{X}-\underline{X}_o^{(j)})\delta(\underline{V}-\underline{V}_o^{(j)}) \, d\Omega_{o_N}$$

$$= f^{(o)} + f' \,. \tag{1-17}$$

Hence, to calculate the distribution function g_χ associated with the distinguished molecule, we can consider the equivalent problem of a molecule entering a system of molecules of the same type in a "steady" non-equilibrium state whose distribution function is denoted by (1-17) at time t=o. This molecule is injected at time t=o with velocity $\underline{V}_1$ at the point $\underline{X}_1$. The presence of this extra molecule causes a "non-

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*The actual expression is given by $f_2(o, \underline{X}, \underline{V}, \underline{X}_1, \underline{V}_1)/f(o, \underline{X}_1, \underline{V}_1)$. However, in a gas the probability that the distinguished molecule is undergoing a collision or has just completed a collision with another molecule may be neglected. This is not, of course, true for a liquid.

steady" non-equilibrium state to arise which, after a short time, settles to the "steady" non-equilibrium state.

1-3-2 GENERAL SUBENSEMBLE

As in sections 1-2, we introduce a general subensemble of which the subensemble in 1-3-1 is a special case. This general subensemble is obtained by separating, at time t=o, with frequency $\phi(\underline{X},\underline{Y})$, those configurations in which a molecule has position $\underline{X}$ and velocity $\underline{Y}$. So if f_ϕ is the one particle distribution function corresponding to this subensemble, then we take

$$f_\phi(t,\underline{X},\underline{Y}) = g_\phi(t,\underline{X},\underline{Y}) + \Gamma_\phi(t,\underline{X},\underline{Y})$$

where g_ϕ is the distribution function associated with the distinguished molecule and Γ_ϕ with the rest. For t=o,

$$g_\phi(o,\underline{X},\underline{Y}) = \phi(\underline{X},\underline{Y}) \; ,$$

and
$$\Gamma_\phi(o,\underline{X},\underline{Y}) = f^{(o)} + f' .$$

The functions g_ϕ and Γ_ϕ may be calculated from the corresponding functions for the special subensemble in the same manner as the subensembles of the equilibrium state, i.e.,

$$g_\phi(t,\underline{X},\underline{Y}) = \int g_\chi(t,\underline{X},\underline{Y}|\underline{X}_0,\underline{Y}_0)\phi(\underline{X}_0,\underline{Y}_0)\, \underline{dX_0}\, \underline{dY_0} \; ,$$

and
$$\Gamma_\phi(t,\underline{X},\underline{Y}) = \int \Gamma_\chi(t,\underline{X},\underline{Y}|\underline{X}_0,\underline{Y}_0)\phi(\underline{X}_0,\underline{Y}_0)\, \underline{dX_0}\, \underline{dY_0} \; .$$

1-4 BACKWARD DISTRIBUTIONS

In the preceding sections, we have implied that the distribution functions are "forward" in time, i.e., they predict future distributions with the initial conditions specified. For instance, in the special subensemble the velocity and position of the distinguished molecule is specified at time $t=0$ and the distribution function g_χ is such that $g_\chi(t, \underline{x}, \underline{v}; \underline{x}_1, \underline{v}_1)\, \underline{dx}\, \underline{dv}$ is the probability that the position and velocity of the distinguished molecule lie respectively in the ranges $(\underline{x}, \underline{x} + \underline{dx})$ and $(\underline{v}, \underline{v} + \underline{dv})$ at some <u>subsequent time</u> t. For dilute gases, we have shown that this is equivalent to considering a molecule entering, at time $t=0$, a system in equilibrium, or non-equilibrium, with the specified velocity at the specified point in the system. Hence, we have implied that the distribution functions are only valid for $t \geq 0$ and do not "predict" events in the "past", i.e., for $t<0$. Distribution functions of this type are termed "forward distribution functions" and the equations satisfied by these functions are termed "forward equations" - this terminology being used in the theory of Markov processes(5).

We may also ask what is the probability that the position and velocity of the distinguished molecule were in the range $(\underline{x}, \underline{x} + \underline{dx})$ and $(\underline{y}, \underline{y} + \underline{dy})$ respectively at a time earlier than t=o. In this case the final conditions are specified and the probability of events, which occur before the time t=o, are calculated. Hence, distribution functions of this type are termed "backward distribution functions", and the equations satisfied by them termed "backward equations" - this terminology also being used in the theory of Markov processes(5).

The backward distributions can be included in the distribution functions defined in sections 1-2-1, 1-2-2, 1-3-1 and 1-3-2 above, if we allow the possibility of negative t. However, the "forward" Boltzmann equations are time irreversible, and so the "backward" Boltzmann equations are used to find the backward distribution functions. These backward equations are discussed in Chapters II and III.

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CHAPTER II EQUILIBRIUM SOLUTION

2-1 INTRODUCTION

Suppose we have a system of molecules forming a dilute gas in equilibrium. A molecule of the same type is injected at the point $\underline{x}$, with velocity $\underline{v}$, into this system. The injected molecule will collide with those of the system, so causing an unsteady state to arise. However, as time progresses and the molecule imparts more and more of its energy and momentum to the system by collisions with members of this system, a steady state of equilibrium will again be reached. In this chapter, the motion of this incoming molecule, and its effect on the motion of the molecules of the system, in equilibrium, is studied statistically by considering the equations for the velocity distribution functions involved in the theory.

In a system in equilibrium[†] the macroscopic parameters are constant in space, and so the actual point of entry into the system has no effect on the calculation of the distribution function which gives the probability that the injected molecule has velocity in the range $\underline{v}, \underline{v}+d\underline{v}$ at time t later, irrespective of

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[†] i.e. absolute equilibrium.

its position. In chapter I, it was pointed out that the above is equivalent to considering certain distribution functions, corresponding to subensembles in which certain configurations are selected from the complete equilibrium ensemble. For these reasons, at time $t=0$, we separate from the grand ensemble of equilibrium, the subensemble with those configurations in which a molecule is moving with velocity $\underline{v}_1$ irrespective of its position. This is equivalent to the subensemble obtained by choosing, at time $t=0$, with frequency $\phi(\underline{x},\underline{v})$, where

$$\phi(\underline{x},\underline{v}) = \frac{1}{V}\,\delta(\underline{v}-\underline{v}_1),$$

those configurations, from the complete equilibrium ensemble, in which a molecule has position $\underline{x}$ and velocity $\underline{v}$. In doing this, we are replacing the boundary condition, (1-7), on the distribution function $g_{\chi}^{(0)}(t,\underline{x},\underline{v};\underline{x}_1,\underline{v}_1)$ i.e.

$$g_{\chi}^{(0)}(0,\underline{x},\underline{v};\underline{x}_1,\underline{v}_1) = \delta(\underline{x}-\underline{x}_1)\,\delta(\underline{v}-\underline{v}_1)$$

by $$g_{\phi}^{(0)}(0,\underline{v};\underline{v}_1) = \frac{1}{V}\,\delta(\underline{v}-\underline{v}_1).$$

So, we are replacing the spatial delta function by the probability, $\frac{1}{V}$, of finding the molecule per unit volume in the equilibrium system.

In chapter I, it was pointed out that the distribution function, $g_{\chi}^{(0)}(t)$, is only defined for $t \geq 0$ i.e. this distribution is a forward distribution and the equation it satisfies is a forward Boltzmann equation. The backward distribution function, $g_{b}^{(0)}(t)$, which gives the probability that the distinguished molecule had velocity in the range $\underline{v},\underline{v}+\underline{dv}$ at time t earlier than t=0, is also found for the equilibrium situation. This velocity distribution function satisfies a backward Boltzmann equation.

We will consider the velocities measured with respect to the mass velocity, and so will regard the distribution functions as functions of these velocities $\underline{w} = \underline{v}-\underline{u}$, where $\underline{u}$ = mass velocity = mean value of the actual velocity $\underline{v}$, i.e. we will take

$$g_{\phi}^{(0)}(0,\underline{v},\underline{v}_1) = \bar{g}_{\phi}(0,\underline{w},\underline{w}_1) = \frac{1}{V}\ \delta(\underline{w}-\underline{w}_1)$$

$$= \frac{1}{V}\ g(0,\underline{w},\underline{w}_1).$$

2-2 DERIVATION OF THE FORWARD EQUATION

The velocity distribution function of a system of gas molecules in equilibrium is $f^{(0)}(w)$, where

$$f^{(0)} = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\beta m w^2) \qquad (2\text{-}1)$$

and n = number density, $\beta = \frac{1}{kT}$. Suppose that a molecule enters the system with velocity $\underline{w}_1=\underline{v}_1-\underline{u}$ at time t=0. We wish to follow statistically the motion of this molecule as it enters this system and collides with members of this system, and so calculate the probability, $g(t,\underline{w},\underline{w}_1)\underline{dw}$, that the velocity of this distinguished molecule will lie in the range $(\underline{w},\underline{w}+\underline{dw})$ at some subsequent time t. The assumption is made that the gas is so dilute that only binary collisions need be considered - the probability of many body collision processes being regarded as negligible. This assumption enables the Boltzmann equation to be used.

In following the motion of this distinguished molecule, we are, in fact, distinguishing it from the others in the system for all time. Therefore the velocity distribution function, g, satisfies the Boltzmann equation

$$\frac{\partial g}{\partial t} = [g,f^{(0)}] \quad , \qquad (2\text{-}2)$$

in which the rate of change of the distribution g is due to the rate of change, $[g,f^{(0)}]$, due to collisions of the incoming molecule with those of the equilibrium system (see C.C.p.65). This equation may be regarded as the Boltzmann equation for a mixture in which we do not need to consider collisions (among themselves) of the "molecules" specified by g, as there is only one molecule present in the system; therefore we do not have a term $[g,g]$ in equation (2-2). In equation (2-2) the collision term is defined by

$$[g,f^{(0)}] = \iint \left\{ g(\underline{w}_0)f^{(0)}(\underline{w}_0') - g(\underline{w})f^{(0)}(\underline{w}') \right\} \sigma \underline{db} \; \underline{dw}' \qquad (2\text{-}3)$$

in which we consider a collision between the distinguished molecule and one of the molecules in equilibrium - the actual velocities when the molecules enter the "sphere of influence" at time t_0 being $\underline{v}_0$ and $\underline{v}_0'$ respectively and the velocities when leaving at time t being $\underline{v}$ and $\underline{v}'$. The term involving $g(\underline{v}_0)\ f^{(0)}(\underline{v}_0')$ gives the change in g due to the two molecules entering the sphere of influence and the term involving $g(\underline{v})\ f^{(0)}(\underline{v}')$ the change due to the molecules leaving the sphere of influence. Also, $\sigma = |\underline{v}-\underline{v}'|$, and $\underline{db}$ is an element of cross-section for such a collision. It should be noted that in equation (2-2) we are considering only terms to order $\frac{1}{V}$, and so in (2-2), to this order, the distribution of the molecules, into which the molecule enters, can be regarded as that of equilibrium for all time (see section 2-3 below).

From equation (2-3) we define the linear integral operator "L" which operates on the function g giving the rate of change of g due to collisions with the molecules of the system in equilibrium, and so,

$$Lg = [g, f^{(0)}] \ . \tag{2-4}$$

The equation (2-2) is linear, whereas the Boltzmann equation usually used in kinetic theory is non-linear, and is given by

$$\frac{\partial f}{\partial t} = [f,f] \, , \qquad (2\text{-}5)$$

where f is the single particle velocity distribution for a dilute gas. However, this equation is linearized to give (C.C. Chapter 7),

$$\frac{\partial f}{\partial t} = [f,f^{(0)}] + [f^{(0)},f] \, . \qquad (2\text{-}6)$$

From (2-6), we may define a linear operator $L_{;}$ such that $L_{;}f$ is the rate of change of the distribution function, f, due to collisions among the molecules, i.e.

$$L_{;}f = [f,f^{(0)}] + [f^{(0)},f] \, . \qquad (2\text{-}7)$$

Comparing (2-2) with (2-6), equation (2-2) will be termed the "half Boltzmann equation", whilst equation (2-6), the "full Boltzmann equation". The operator L will be termed the "half Boltzmann collision operator" and $L_{;}$ the "full Boltzmann collision operator".

The velocity dependent eigenfunctions, g_{rl} and f_{rl}, and velocity independent eigenvalues, λ_{rl} and μ_{rl}, of the two operators are defined by the following,

$$L \, g_{rl}(\mathbf{W}) = -\lambda_{rl} g_{rl}(\mathbf{W}) \qquad (2\text{-}8)$$

and $$L_{;} \, f_{rl}(\mathbf{W}) = -\mu_{rl} f_{rl}(\mathbf{W}) \, . \qquad (2\text{-}9)$$

The eigentheory of the full Boltzmann collision operator has been developed by Wang Chang and Uhlenbeck(1) for the Maxwellian molecules.

2-2-1 THE SOLUTION OF THE FORWARD EQUATION FOR THE GENERAL MOLECULAR MODEL.

At time $t=0$ the molecule has velocity $\underline{w}'$, so that the boundary condition to be imposed on g is

$$g(0,\underline{w},\underline{w}') = \delta(\underline{w}-\underline{w}') \ . \qquad (2\text{-}10)$$

Using this condition, we expand the solution of (2-2) in the eigenfunctions of the collision operator L, taking the eigenvalues as the inverse relaxation times. This expansion is possible if the eigenfunctions form a complete orthogonal set.

The orthogonality is proved as follows:
If $e^{-\frac{1}{2}\beta m w^2} g_{rl}$ is an eigenfunction of the collision operator L, then, from (2-8),

$$-\lambda_{rl}\, e^{-\frac{1}{2}\beta m w^2} g_{rl} = [e^{-\frac{1}{2}\beta m w^2} g_{rl}, f^{(0)}]$$

and so

$$-\int \lambda_{rl}\, e^{-\frac{1}{2}\beta m w^2} g_{rl} g_{kl} \, d\underline{w}$$

$$= \int g_{kl} [e^{-\frac{1}{2}\beta m w^2} g_{rl}, f^{(0)}] \, d\underline{w}$$

$$= \int g_{kl}(\underline{w}) \iint e^{-\frac{1}{2}\beta m(w^2+w'^2)}(g_{rl}(\underline{w}_o)-g_{rl}(\underline{w}))\sigma \underline{gb}\, \underline{dw}'\underline{dw} \quad (2\text{-}11)$$

Now, we use the property of an integral of this type given on page 66 of C.C. This property is due to the fact that $\underline{dw}\,\underline{dw}' = \underline{dw}_o\,\underline{dw}_o'$ (Jacobian of the transformation unity), and $\underline{w}_o$ and $\underline{w}$ can be interchanged because of the microscopic reversibility of a collision. Then equation (2-11) becomes,

$$\int g_{rl}(\underline{w}) \iint e^{-\frac{1}{2}\beta m(w^2+w'^2)}(g_{kl}(\underline{w}_o) - g_{kl}(\underline{w}))\sigma \underline{gb}\, \underline{dw}'\, \underline{dw}$$

$$= \int g_{rl}[e^{-\frac{1}{2}\beta mw^2} g_{kl}, f^{(o)}]\underline{dw}$$

$$= - \int \lambda_{kl}\, e^{-\frac{1}{2}\beta mw^2} g_{rl} g_{kl} \underline{dw}\ .$$

Hence

$$(\lambda_{kl}-\lambda_{rl}) \int e^{-\frac{1}{2}\beta mw^2} g_{rl} g_{kl}\, \underline{dw} = 0,$$

and so, if $r \neq k$, $\lambda_{kl} \neq \lambda_{rl}$ then,

$$\int e^{-\frac{1}{2}\beta mw^2} g_{rl}\, g_{kl} \underline{dw} = 0 \quad (2\text{-}12)$$

Take $g_{rl} = L_{rl}(\frac{1}{2}\beta mw^2)P_l(\cos\theta)w^l$ for the general molecular model. Then for different values of "l" the Legendre polynomials are orthogonal, and relation (2-12) ensures the orthogonality for different values of "r". We assume that the polynomials form a complete set. However, in the case of the Sonine polynomials (see section 2-5 below), the completeness is known.

Therefore, the solution of equation (2-2) for the general molecular model, applying the boundary condition (2-10) is

$$g(t,\underline{W},\underline{W}_1) = e^{-\frac{1}{2}\beta m w^2} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} c_{rl} L_{rl}(\tfrac{1}{2}\beta m w_1^{2}) L_{rl}(\tfrac{1}{2}\beta m w^2)$$

$$P_l(\cos\theta)(ww_1)^l \, e^{-\lambda_{rl} t} \qquad (2\text{-}13)$$

where c_{rl} are constants determined by (2-10); $ww_1\cos\theta = \underline{W}\cdot\underline{W}_1$, and, in applying the condition (2-10), an expansion of the delta function in the orthogonal polynomials has been used.

2-3 THE FULL BOLTZMANN EQUATION APPLYING TO THE WHOLE SYSTEM.

The equation (2-2), which gives the distribution function associated with the incoming molecule, may be connected with the full Boltzmann equation (2-7) which gives the distribution function for the whole system i.e. the incoming molecule and the gas in equilibrium. This full Boltzmann equation has been used by authors in the evaluation of the Kubo-type transport coefficients (see Introduction and Chapter IV).

If F is the velocity distribution function for the whole system then,(2)

$$F = f^{(0)} + \frac{\Gamma(t,\underline{W},\underline{W}_1)}{V} ,$$

where V = volume occupied. From (2-5), neglecting terms of order $\frac{1}{V^2}$, Γ must satisfy the linear equation,

$$\frac{\partial \Gamma}{\partial t} = [f^{(0)},\Gamma]+[\Gamma,f^{(0)}] \quad . \tag{2-14}$$

We may now divide the distribution function, F, into two separate distribution functions as was done in Chapter I. The first part, g, is associated with the motion of the incoming molecule and so is defined as above. The second part, γ, is such that $f^{(0)} + \frac{\gamma}{V}$ is the distribution function associated with the molecules other than the incoming molecule. At time t=0 the distinguished molecule is moving in an equilibrium environment so that the boundary condition on γ is

$$\gamma(0,\underline{W},\underline{W}_1) = 0 \ . \tag{2-15}$$

The linear equation (2-14) then may be divided into (2-2), and

$$\frac{\partial \gamma}{\partial t} = [f^{(0)},\gamma]+[\gamma,f^{(0)}] + [f^{(0)},g] \quad . \tag{2-16}$$

As the molecule enters the system with which it is not in equilibrium, collisions with the molecules will cause an unsteady state to arise. Some time later, the originally distinguished molecule will be indistinguishable from the rest as the steady state is reached. However, owing to the introduction of this one extra molecule to the system, the temperature, mass velocity, and number density will be slightly altered. Suppose, at time $t=0$, these parameters are $T(0)$, $\underline{u}(0)$ and $n(0)$. Then, at time $t=\infty$, they become $T(0)+\Delta T$, $\underline{u}(0)+\Delta\underline{u}$, and $n(0)+\Delta n$ where the increments ΔT, $\Delta\underline{u}$ and Δn are given by the conservation laws.

(a) The increment in the number density:

The equation corresponding to the conservation of mass in a system in equilibrium (or non-equilibrium) is

$$\frac{\partial}{\partial t} \int n \, d\underline{x} = 0 \; .$$

Using the definition of the number density from the velocity distribution function, F, for the system, this equation becomes

$$\frac{\partial}{\partial t} \iint F \, d\underline{x} \, d\underline{v} = 0 \; .$$

Now at time $t=0$ $F(0) = \frac{1}{V} \; \delta(\underline{v}-\underline{u}(0) - \underline{v}_1+\underline{u}(0)) + f^{(0)}(0)$ (2-17a)

and at time $t=\infty$ $F(\infty) = f^{(0)}(\infty)$, (2-17b)

$$f^{(0)}(0) = n(0) \left(\frac{\beta(0)m}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\beta(0)m(\underline{v}-\underline{u}(0))^2) \; ,$$

and similarly with $f^{(0)}(\infty)$.

Hence

$$\iint F(0) \, d\underline{x} \;\; d\underline{v} = \iint F(\infty) \, d\underline{x} \;\; d\underline{v}$$

i.e.

$$1 + \int n(0)\underline{dx} = \int n(\infty)\underline{dx}$$

but

$$\int \Delta n \, \underline{dx} = \int (n(\infty) - n(0))\underline{dx} = 1,$$

and as the number density is uniform in space in a system in equilibrium,

$$\Delta n = \frac{1}{V} \quad . \tag{2-18}$$

(b) Increment in the mass velocity:

The equation for the conservation of momentum in an equilibrium system is

$$\frac{\partial}{\partial t} \int n \, \underline{u} \, \underline{dx} = 0$$

$$\text{i.e.} \quad \frac{\partial}{\partial t} \iint n \, F \, \underline{v} \, \underline{dx} \; \underline{dv} = 0 \quad .$$

Substituting from (2-17a) and (2-17b) we obtain,

$$\underline{X}_1 + \int n(0) \, \underline{u}(0) \, \underline{dx} = \int n(\infty) \, \underline{u}(\infty) \, \underline{dx}$$

$$\text{i.e.} \quad \frac{\underline{X}_1}{V} = n(\infty) \, (\underline{u}(\infty) - \underline{u}(0))$$

and so the increment in the mass velocity is given by

$$\frac{\underline{M}'}{V} = n\Delta\underline{u} \quad . \qquad (2-19)$$

Since we are considering changes to order $\frac{1}{V}$, the number density in (2-19) may be $n(0)$ or $n(\infty)$.

(c) Increment in the temperature:

The equation expressing the conservation of energy in a system in equilibrium is given by

$$\frac{\partial}{\partial t} \int n\, W\, \underline{dx} = 0$$

where W is defined by $\rho W = \frac{m}{2}\int F\, w^2 \underline{dw}$, and the temperature T by $\rho W = \frac{3}{2} nkT$.

Hence by substituting the values of F given by (2-17a) and (2-17b) we obtain,

$$\frac{1}{V}\frac{m}{2} w_1^{2} = \frac{3}{2} k\, n(\infty)\, (T(\infty)-T(0)) + \frac{3}{2} kT(0)\, [n(\infty)-n(0)]$$

i.e.

$$\frac{3}{2} n\, Vk\, \Delta T = \tfrac{1}{2}mw_1^{2} - \frac{3}{2} kT \quad . \qquad (2-20)$$

If the values $n+\Delta n$, $T+\Delta T$ and $\underline{u}+\Delta\underline{u}$ are substituted in the equilibrium distribution function, and the expansion made to terms of the first order in the increments, then at time $t=\infty$,

$$g = \left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\beta m w^2) \qquad (2\text{-}21a)$$

$$\gamma = \left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\beta m w^2)[\beta m \underline{w}\cdot\underline{w}_1 + \frac{1}{6}(\beta m w_1^2-3)(\beta m w^2-3)] \qquad (2\text{-}21b)$$

2-4 DERIVATION AND SOLUTION OF THE BACKWARD EQUATION.

In this section, we are to derive the equation that is satisfied by the backward distribution function $g_b(t,\underline{w},\underline{w}_1)$ defined such that $g_b(t,\underline{w},\underline{w}_1)d\underline{w}$ is the probability that the molecule, which was distinguished at time $t=0$, had velocity in the range $(\underline{w},\underline{w}+d\underline{w})$ at time t earlier.

Consider a collision between two molecules, the distinguished molecule and one of the molecules in the equilibrium surroundings. The respective velocities before and after the collision being $\underline{w}_0$, $\underline{w}_0'$ and $\underline{w}_r$, $\underline{w}_r'$, where all velocities are measured with respect to the mass velocity. Define the quantities $q(\underline{w},\underline{w}_r)$ and $p(\underline{w}_r)$ in the following manner;

$q(\underline{w},\underline{w}_r)d\underline{w}\,\tau$ is the probability that there has been a collision in the interval of time τ and that the velocity was in the range $(\underline{w},\underline{w}+d\underline{w})$ at time t if the velocity at time $t+\tau$ is $\underline{w}_r$.

$p(\underline{w}_f)\tau$ is the probability that a collision has occurred in the interval τ earlier, if the velocity of the molecule is $\underline{w}_f$ at time $t+\tau$.

In the above definitions τ is, of course, supposed so small that only one collision can occur in the interval t to $t+\tau$ and that the distribution of the molecules other than the distinguished molecule is the distribution $f^{(0)}(\underline{w}_f')$ of equilibrium at time $t+\tau$.

Therefore,

$$q(\underline{w},\underline{w}_f) = \iint f^{(0)}(\underline{w}_f')\, \delta(\underline{w}-\underline{w}_0)\, \sigma\, \underline{db}\, \underline{dw}_f' \qquad (2\text{-}22)$$

and

$$p(\underline{w}_f) = \iint f^{(0)}(\underline{w}_f')\, \sigma\, \underline{db}\, \underline{dw}_f' \quad .$$

Using these functions, we wish to calculate the change in the backward distribution function during the interval $t, t+\tau$. If the probability that the molecule had velocity in the range $(\underline{w},\underline{w}+\underline{dw})$ at time t is $g_b(t,\underline{w},\underline{w}_1)\underline{dw}$ when its velocity is $\underline{w}_1$ at time $t=0$ then,

$$g_b(t,\underline{w},\underline{w}_1)\underline{dw} = \int q(\underline{w},\underline{w}_f)\underline{dw}\, \tau\, g_b(t+\tau,\underline{w}_f,\underline{w}_1)\underline{dw}_f$$

$$+\; g_b(t+\tau,\underline{w},\underline{w}_1)\underline{dw}\, (1-p(\underline{w})\tau)$$

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where the first term takes account of all the possible collisions during the interval τ and the second is the contribution to the range $(\underline{W},\underline{W}+\underline{dW})$ if no collisions occurred during the interval. Using the values of (2-22) and taking the limit t->0, then

$$- \frac{\partial g_b(t,\underline{W},\underline{W}_1)}{\partial t} = \iiint f^{(0)}(\underline{W}_f') \delta(\underline{W}-\underline{W}_o) g_b(t,\underline{W}_f,\underline{W}_1)(\sigma \underline{db}) \underline{dW}_f' \, \underline{dW}_f$$

$$- \iint f^{(0)}(\underline{W}') g_b(t,\underline{W},\underline{W}_1) \sigma \, \underline{db} \, \underline{dW} \qquad (2\text{-}23)$$

In the first integral the collision process $(\underline{W}_o,\underline{W}_o') \rightarrow (\underline{W}_f,\underline{W}_f')$ is being considered. Hence, by using the property of such an integral given in section (2-2-1) in equation (2-11), this integral

$$= \iiint f^{(0)}(\underline{W}_o') \; \delta(\underline{W}-\underline{W}_f) \; g_b(t,\underline{W}_o,\underline{W}_1) \sigma \, \underline{db} \, \underline{dW}_f' \, \underline{dW}_f \; .$$

On removal of the delta function, the equation becomes,

$$\frac{\partial g_b(t,\underline{W},\underline{W}_1)}{\partial t} = - \iint \left\{ g_b(\underline{W}_o) f^{(0)}(\underline{W}_o') - g_b(\underline{W}) f^{(0)}(\underline{W}') \right\} \sigma \underline{db} \, \underline{dW}' \, ,$$

which, on comparison with the forward equation (2-2) may be written as

$$\frac{\partial g_b}{\partial t} = -\left[g_b, f^{(0)}\right] \qquad (2\text{-}24)$$

Hence, in going from the forward equation to the backward equation, we have reversed the sign of the collision integral, which is the microscopic rate of change of the distribution function. Moyal$^{(3)}$ has obtained a similar result assuming that the collision processes are Markovian.

The equation (2-24) is a backward Boltzmann equation and its solution, together with the boundary condition,

$$g_b(0, \mathbf{W}, \mathbf{W}_1) = \delta(\mathbf{W} - \mathbf{W}_1), \qquad (2\text{-}25)$$

will give the required backward velocity distribution function. At time $t = -\infty$, the distinguished molecule will have the velocity distribution of equilibrium i.e.,

$$g_b(-\infty, \mathbf{W}, \mathbf{W}_1) = \left(\frac{\beta m}{2\pi}\right)^{3/2} \exp(-\tfrac{1}{2}\beta m w^2). \qquad (2\text{-}26)$$

Using the result (2-13), derived from the forward equation, the solution to the backward equation is

$$g_b(t, \mathbf{W}, \mathbf{W}_1) = e^{-\frac{1}{2}\beta m w^2} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} c_{rl} L_{rl}(\tfrac{1}{2}\beta m w_1^{\,2}) L_{rl}(\tfrac{1}{2}\beta m w^2)$$

$$P_l(\cos\theta)(w w_1)^l e^{+\lambda_{rl} t} \, . \qquad (2\text{-}27)$$

The forward and backward Boltzmann equations are both irreversible in time as the replacement of "t" by "-t" alters the form of these equations. However, the solutions obtained are symmetric in time about the specified time at which we imposed the fluctuation on the system i.e. t=0. In the forward case, we are considering the molecule "entering" the system in equilibrium and at some time later gaining a velocity distribution of equilibrium. However, in the backward case, we are considering the time reversed situation of a molecule, which was originally in equilibrium with its neighbours, "leaving" the system in such a way that this molecule is not in equilibrium with the system.

2-5 MAXWELLIAN MOLECULES.

In the above sections, the solutions were expressed in terms of the eigenfunctions of the collision operator for the general molecular model. However, the eigenfunctions of the collision operators, defined by equations (2-4), (2-7), (2-8) and (2-9), are not known for all molecular models. In fact, the exact eigenfunctions are only[†] known for the so-called "Maxwellian Molecules" which are defined by the two body repulsive force-law, $F = \frac{\kappa}{r^s}$, where r is the distance

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[†] However, the method of Cotter(4) should allow the eigenfunctions for the Rigid Sphere Model to be calculated.

apart of the two molecules. Use is made of these eigenfunctions, the Sonine polynomials, in the Chapman-Enskog method in which the transport coefficients for dilute gases are calculated. In this method, the "steady-state" velocity distribution function is calculated for a number of molecular models (see C.C. Chapter 10) in non-equilibrium. The evaluation of the distribution function to the first order in the temperature and velocity gradients requires the solution of the equations

$$L_1 f^{(0)} A_1(\tfrac{1}{2}\beta m w^2)\, \underline{W} = f^{(0)}(\tfrac{1}{2}\beta m w^2 - {}^5\!/2)\underline{W} \qquad (2\text{-}28)$$

and

$$L_1 f^{(0)} A_2(\tfrac{1}{2}\beta m w^2)\, (\underline{W}\,\underline{W} - \tfrac{1}{3} w^2\, \underline{\delta}) = f^{(0)}(\underline{W}\,\underline{W} - \tfrac{1}{3} w^2 \underline{\delta}) \qquad (2\text{-}29)$$

In the case of Maxwellian molecules, the solution of (2-28) and (2-29) presents no difficulty as the eigenfunctions are known. For the other molecular models, because the eigenfunctions are not known, the following expansions in terms of the Sonine polynomials*, $S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta m w^2)$,

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* In this thesis the polynomial $S^{(n)}_m(x)$ is the coefficient of s^n in the expansion of $(1-s)^{-m-1}\exp\{-xs/1-s|\}, |s|<1$. The usual Sonine polynomials are numerical multiples of $S^{(n)}_m(x)$. The $S^{(n)}_m(x)$ are equivalent to the Laguerre polynomials defined in "Higher Transcedental Functions" Bateman Manuscript Project Vol.2, p188. However, for historical reasons, the author will call $S^{(n)}_m(x)$, the Sonine Polynomial.

$$A_1(\tfrac{1}{2}\beta mw^2) = \sum_{r=0}^{\infty} a_r \, S^{(r)}_{3/2}$$

and $$A_2(\tfrac{1}{2}\beta mw^2) = \sum_{r=0}^{\infty} b_r \, S^{(r)}_{5/2} \quad ,$$

are used in the integral equations. The values of the coefficients a_r and b_r are dependent upon the particular model being used, and determine the values of the transport coefficients. As one would expect from the expansions, the values of the transport coefficients for the Maxwellian molecules turn out to be the first approximations in the transport coefficients for the other models. Consequently, the Maxwellian molecules are of interest in any theory of dilute gases.

In Appendix A, it is shown that the Sonine polynomials are also the eigenfunctions of the half Boltzmann collision operator. So the solutions of the forward and backward equations (2-2) and (2-24) are,

$$g = e^{-\frac{1}{2}\beta mw^2} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} c_{rl} S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta mw_1^2) S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta mw^2) P_l(\cos\theta)(ww_1)^l e^{-\lambda_{rl} t} \tag{2-30}$$

and $$g_b = e^{-\frac{1}{2}\beta mw^2} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} c_{rl} S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta mw_1^2) S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta mw^2) P_l(\cos\theta) (ww_1)^l e^{+\lambda_{rl} t} \tag{2-31}$$

where,

$$c_{rl} = \frac{1}{\pi} (l+\tfrac{1}{2}) (\tfrac{1}{2}\beta m)^{l+3/2} \frac{r!}{(l+r+\frac{1}{2})!} \quad ,$$

and the eigenvalues, λ_{rl}, may be obtained by direct calculation (see Appendix A); some are given below;

$$\lambda_{00} = 0 \quad \lambda_{10} = n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} \quad \lambda_{20} = n\pi(A_1(5)+A_2(5))\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}$$

$$\lambda_{01} = n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} \quad \lambda_{11} = n\pi(A_1(5) + \tfrac{1}{2}A_2(5))\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}$$

$$\lambda_{02} = n\pi(A_1(5) + {}^3/_4\, A_2(5))\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}$$

where $A_l(5)$ are well known constants (see C.C. p.172 table 3). Using these values and taking the limit as $t \to \infty$, the conditions (2-21a) and (2-26) are satisfied.

If we use the eigenfunctions for the full Boltzmann collision operator, equation (2-16) is solved to give,

$$\gamma = e^{-\frac{1}{2}\beta m w^2} \sum_{l=0}^{\infty} \sum_{r=0}^{\infty} c_{rl}\, S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta m w_1^{\,2}) P_l(\cos\theta)\, S^{(r)}_{l+\frac{1}{2}}(\tfrac{1}{2}\beta m w^2)$$
$$(w w_1)^l [e^{-\mu_{rl} t} - e^{-\lambda_{rl} t}] \qquad (2\text{-}32)$$

where c_{rl} are as above, and μ_{rl} are the eigenvalues of the full Boltzmann collision operator (see C.C. and ref (1));

$$\mu_{00} = \mu_{10} = \mu_{01} = 0, \quad \mu_{11} = n\pi A_2(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}$$
$$\mu_{02} = {}^3/_2\, n\pi A_2(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} .$$

Using the eigenvalues given above, the solution (2-32) satisfies the conditions (2-15) at $t=0$ and (2-21b) as $t \to \infty$.

In the above chapter we have considered a molecule moving with a specified velocity in a system of molecules in equilibrium. In the following chapter, we will consider a molecule moving in a system of molecules in a "steady state" of non-equilibrium.

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CHAPTER III NON-EQUILIBRIUM SOLUTIONS.

3-1 INTRODUCTION

In the previous chapter we discussed the case of a molecule entering a system in equilibrium in which there were no external forces, including centrifugal forces (i.e. no rotation). In this chapter, we discuss the case of a molecule entering a system in a "steady" state non-equilibrium in which there are no external forces.

We first consider the general case in which a molecule enters at the point $\underline{x}_1$ at time t=o with velocity $\underline{v}_1$ i.e. we consider the distribution function associated with the special subensemble discussed in Chapter I. This special subensemble was obtained by separating, at time t=o, from the grand ensemble of non-equilibrium, those configurations in which a molecule is moving with velocity $\underline{v}_1$, at the point $\underline{x}_1$.

In the previous chapter the spatial dependence of the distribution function was not considered and the spatial delta function was replaced by a factor $\frac{1}{V}$ where V is the volume occupied by the gas. This amounted to the consideration of another sub-ensemble of the general type discussed in Chapter I. In this chapter, a similar simplification is introduced by replacing the spatial delta function by the factor $\frac{n(\underline{x},o)}{\int n d\underline{x}}$, where $n(\underline{x},t)$ is the number density at the point $\underline{x}$ at time t. This factor, $\frac{n(\underline{x},o)d\underline{x}}{\int n d\underline{x}}$, is the probability of finding a specified molecule in the volume element $(\underline{x},\underline{x}+d\underline{x})$ at time $t=o$. In equilibrium, this reduces to the factor used in the previous chapter. The velocity distribution function is first calculated for a molecule entering a system in which there are only temperature and number density gradients and the mass velocity gradient is zero. The distribution function is then calculated for a molecule entering a system with a mass velocity gradient. As the equations for the distribution functions are all linear we may add the solutions to obtain the distribution function when considering a molecule moving in a general system in "steady" state non-equilibrium.

3-2 GENERAL PROBLEM

If at time $t=o$ a molecule enters with velocity $\underline{v}_1$ at the point $\underline{x}_1$ a system of similar molecules in "steady" state non-equilibrium, we wish to calculate the velocity distribution function $g_\chi(t,\underline{x},\underline{v};\underline{x}_1,\underline{v}_1)$ associated with this molecule. This function will give the probability, $g_\chi \, d\underline{x} \, d\underline{v}$, that the incoming molecule will be in the volume element $(\underline{X},\underline{X}+d\underline{X})$ and have velocity in the range $(\underline{V},\underline{V}+d\underline{V})$ at a time t later. As shown in Chapter I, in dilute gases this is equivalent to considering a special sub-ensemble in which we separate, from the grand ensemble of non-equilibrium, those configurations in which a molecule is at the point $\underline{X}_1$ and moving with velocity $\underline{V}_1$ at time $t=0$. If Γ_χ is the velocity distribution function for the molecules other than the incoming molecule then the equation satisfied by g_χ is the forward half-Boltzmann equation,

$$\frac{Dg_\chi}{Dt} \equiv \frac{\partial g_\chi}{\partial t} + \underline{V}\cdot\frac{\partial g_\chi}{\partial \underline{X}} = [g_\chi,\Gamma_\chi] \qquad (3\text{-}1)$$

where $[g_\chi,\Gamma_\chi]$ is the collision integral given by (2-3) i.e.

$$[g_\chi,\Gamma_\chi] = \iint \left\{ g_\chi(t,\underline{X},\underline{V}_0)\Gamma_\chi(t,\underline{X},\underline{V}_0') - g_\chi(t,\underline{X},\underline{V})\Gamma_\chi(t,\underline{X},\underline{V}') \right\} \sigma \underline{db}\, d\underline{V}'.$$

The boundary conditions for $t=0$ are,

$$g_\chi(0,\underline{X},\underline{V};\underline{X}_1,\underline{V}_1) = \delta(\underline{V}-\underline{V}_1)\delta(\underline{X}-\underline{X}_1) \qquad (3\text{-}2)$$

$$\Gamma_\chi(0,\underline{X},\underline{V};\underline{X}_1,\underline{V}_1) = f^{(0)}+f' , \qquad (3\text{-}3)$$

where f' involves the terms in the velocity distribution function which are linear in the temperature and mass velocity gradients.

The equation (3-1) has the same form as equation (2-2) except that the distribution function is now spatially dependent as well as velocity dependent.

The introduced molecule will alter the distribution function for the 'steady"state non-equilibrium, but, one would expect, to a good approximation, that in equation (3-1), Γ_χ may be replaced by $f^{(0)}+f'$ for all t. So equation (3-1) will then become

$$\frac{Dg_\chi}{Dt} = [g_\chi, f^{(0)}+f'] \, . \qquad (3\text{-}4)$$

However, in equilibrium, the spatial detla function was replaced by the factor $\frac{1}{V}$, and it was found that by neglecting terms of order higher than $\frac{1}{V}$ the equation

$$\frac{\partial g_\chi}{\partial t} = [g_\chi, f^{(0)}] \qquad (3\text{-}5)$$

was obtained. In non-equilibrium we will introduce a factor $\frac{n}{\int n d\underline{x}}$ to replace the spatial detla function, and then the distribution function satisfies equation (3-4) to this order.

As well as an explicit dependence on time and position in the distribution function g_χ, for non equilibrium there is also an implicit dependence through the spatial and time dependence of the number density $n(\underline{x},t)$, temperature

$T(\underline{x},t)$ and mass velocity $\underline{u}(\underline{x},t)$ (see reference (1) page 124 and C.C.). We may therefore write,

$$\frac{D}{Dt} = \left(\frac{D}{Dt}\right)_{\text{explicit}} + \left(\frac{D}{Dt}\right)_{\text{implicit}} .$$

The operator $\left(\frac{D}{Dt}\right)_{\text{implicit}}$ operates on the implicit variables contained in the macroscopic parameters, and so is associated with the macroscopic motion. However, the operator $\left(\frac{D}{Dt}\right)_{\text{explicit}}$ operates on the explicit variables and so may be associated with the microscopic motion. Hence equation (3-4) could be written as

$$\frac{\partial g_\chi}{\partial t}_{\text{imp.}} + \frac{\partial g_\chi}{\partial t}_{\text{exp}} + \underline{v}\cdot\frac{\partial g_\chi}{\partial \underline{x}}_{\text{imp.}} + \underline{v}\cdot\frac{\partial g_\chi}{\partial \underline{x}}_{\text{exp}} = [g_\chi, f^{(0)}+f'] .$$

However, for brevity, we will not differentiate between the explicit and implicit variables except in ambiguous cases.

The solution of equation (3-4) together with the boundary condition (3-2) for $t=0$ would give the required result. However, as already indicated, we shall simplify the problem to some extent by considering, not the special subensemble, but another subensemble in which, at $t=0$, from the grand ensemble of non-equilibrium, we choose with frequency $\phi(\underline{x},\underline{v})$, where

$$\phi(\underline{x},\underline{v}) = \frac{n(\underline{x},o)}{\int n d\underline{x}} \; \delta(\underline{v}-\underline{v}_1), \qquad (3-6)$$

those configurations in which a molecule is at the point $\underline{x}$ moving with velocity $\underline{v}$. In equilibrium (3-6) reduces to

$$\phi(\underline{x},\underline{v}) = \frac{1}{V}\,\delta(\underline{v}-\underline{v}_1)$$

which was used in the previous chapter.

Since the velocity distribution function associated with the distinguished molecule will have the distribution given by equation (3-6) for t=o, we have replaced the spatial delta function by $\frac{n(\underline{x},o)d\underline{x}}{\int n d\underline{x}}$ which is the probability of finding the molecule in the volume element $(\underline{x},\underline{x}+d\underline{x})$ in the system in steady state non-equilibrium at time t=o. We are, in effect, supposing that the incoming molecule assumes the number density distribution of the molecules of the system into which it enters.

Now let F be the velocity distribution function for the complete system i.e. the incoming molecule and the system into which it enters. Suppose that the function Γ is defined by the following,

$$F = f^{(o)} + f' + \frac{n}{\int n d\underline{x}}\,\Gamma. \qquad (3\text{-}7)$$

The Boltzmann equation is satisfied by F, i.e.

$$\frac{DF}{Dt} = [F,F]\,,$$

and so, substituting from (3-7) and considering terms linear in the gradients and neglecting terms of order $\frac{1}{(\int n d\underline{x})^2}$,

$$\frac{Df^{(0)}}{Dt} + \frac{1}{\int n d\underline{x}} \frac{Dn\Gamma}{Dt} = [f', f^{(0)}] + [f^{(0)}, f']$$

$$+ \left[\frac{n}{\int n d\underline{x}} \Gamma, f^{(0)}\right] + \left[\frac{n}{\int n d\underline{x}} \Gamma, f'\right]$$

$$+ \left[f^{(0)}, \frac{n}{\int n d\underline{x}} \Gamma\right] + \left[f', \frac{n}{\int n d\underline{x}} \Gamma\right].$$

$$(3\text{-}8)$$

Now from the Chapman-Enskog theory

$$\frac{Df^{(0)}}{Dt} = [f', f^{(0)}] + [f^{(0)}, f'] ,$$

and so equation (3-8) becomes

$$\frac{Dn\Gamma}{Dt} = [n\Gamma, f^{(0)} + f'] + [f^{(0)} + f', n\Gamma] . \qquad (3\text{-}9)$$

From (3-7) and (3-6) the boundary condition for two is

$$\Gamma = \delta(\underline{v} - \underline{u}(\underline{x}, o) - \underline{v}_1 + \underline{u}(\underline{x}, o))$$

$$= \delta(\underline{v} - \underline{v}_1).$$

As in Chapter I, the function Γ may be divided into two separate parts, i.e.

$$\Gamma = g + \gamma$$

such that g is associated with the incoming molecule and $f^{(0)}+f'+\frac{n}{\int n d\underline{x}}\gamma$ with the rest. The boundary conditions on g and γ are therefore for $t=0$,

$$g = \delta(\underline{V}-\underline{V}_1) \qquad (3\text{-}10)$$

$$\gamma = 0$$

The equation satisfied by the distribution function associated with the incoming molecule is then

$$\frac{Dng}{Dt} = [ng, f^{(0)}+f'] \;, \qquad (3\text{-}11)$$

and so the equation satisfied by the function γ is

$$\frac{Dn\gamma}{Dt} = [n\gamma, f^{(0)}+f'] + [f^{(0)}+f', n\gamma] + [f^{(0)}+f', ng] \,.$$

For $t=0$ we have defined $\underline{V}_1$ by

$$\underline{V}_1 = \underline{Y}_1 - \underline{u}(\underline{x}, 0) \,,$$

and so for all t we may take either $\underline{V}_1 = \underline{Y}_1 - \underline{u}(\underline{x}, t)$ or $\underline{V}_1 = \underline{Y}_1 - \underline{u}(\underline{x}, 0)$ whichever is the more convenient, as each definition must produce equivalent distribution functions.

3-3 FORWARD EQUATIONS FOR TEMPERATURE AND NUMBER DENSITY GRADIENTS

Equation (3-11) above is solved in the same manner as the full Boltzmann equation via the Chapman-Enskog method (e.g. see C.C. Chapter 7).

The derivatives of the macroscopic parameters T, n and $\underline{u}$ are eliminated by using the macroscopic equations of motion;

$$\frac{dn}{dt} \equiv \left(\frac{\partial}{\partial t} + \underline{u}\cdot\frac{\partial}{\partial \underline{x}}\right)n = -n\left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right) \qquad (3\text{-}12a)$$

$$\frac{d\underline{u}}{dt} = -\frac{1}{\rho}\frac{\partial p}{\partial \underline{x}} \qquad (3\text{-}12b)$$

$$\frac{dT}{dt} = -\frac{2}{3}T\left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right)$$

where ρ = density = mn, p = pressure = nkT, and there are no external forces. Using these equations and the fact that we are taking the mass velocity gradient, $\frac{\partial \underline{u}}{\partial \underline{x}}$, as zero, equation (3-11) becomes

$$n\frac{\partial g}{\partial t}_{\exp} + \underline{w}\cdot\frac{\partial ng}{\partial \underline{x}} + \frac{n}{\rho}\frac{\partial p}{\partial \underline{x}}\cdot\frac{\partial g}{\partial \underline{w}} = [ng, f^{(0)} + f'] \qquad (3\text{-}13)$$

where f' is linear in the temperature gradient but does not involve the number density gradient (see C.C. Chapter 7).

(a) Terms involving the temperature gradient.

The terms in the function g which involve the temperature gradient are first found. In this case equation (3-13) becomes,

$$\frac{\partial g}{\partial t}_{\exp} + \underline{w}.\frac{\partial g}{\partial \underline{x}} + \frac{1}{\beta m}\,\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}.\frac{\partial g}{\partial \underline{w}} = [g,f^{(o)}+f'] \quad (3\text{-}14)$$

In the case of terms involving the number density and temperature gradients it is convenient to define $\underline{w}_t$ for all t by $\underline{w}_t=\underline{v}_t-\underline{u}(\underline{x},o)$ and, since $\frac{\partial \underline{u}}{\partial \underline{x}} = o$, then $\underline{u}(\underline{x},o)$ is a constant vector.

The equation (3-14) is solved by the usual perturbation method. Owing to the temperature gradient, the equilibrium solution given by equation (2-13) will be perturbed so that

$$g = g_e + G \qquad (3\text{-}15)$$

where g_e does not involve $\frac{\partial T}{\partial \underline{x}}$

and G is linear in $\frac{\partial T}{\partial \underline{x}}$.

Substituting (3-15) into (3-14) and equating terms linear in, or not involving the temperature gradient, it is found, of course, that g_e satisfies equation (3-5) i.e. the equation solved in the previous chapter, and G satisfies

$$\frac{\partial G}{\partial t}_{\exp} - [G, f^{(o)}] = -\underline{w}\cdot\frac{\partial g_e}{\partial \underline{x}} - \frac{1}{\beta m}\,\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial g_e}{\partial \underline{w}} + [g_e, f'] \qquad (3\text{-}16)$$

Now, equation (3-16) is linear and so may be divided into;

$$\frac{\partial G}{\partial t}_{\exp} - [G, f^{(o)}] = -\underline{w}\cdot\frac{\partial g_e}{\partial \underline{x}} - \frac{1}{\beta m}\,\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial g_e}{\partial \underline{w}} \qquad (3\text{-}17)$$

$$\frac{\partial G}{\partial t}_{\exp} - [G, f^{(o)}] = [g_e, f'] \qquad (3\text{-}18)$$

$$\frac{\partial G}{\partial t}_{\exp} - [G, f^{(o)}] = 0 \, . \qquad (3\text{-}19)$$

The distribution function, $g_e + G$, must satisfy the boundary condition (3-10) for t=o, and this is only possible if, for t=o,

$$G = 0 \, . \qquad (3\text{-}20)$$

The solution of the above equations is of considerable length and so will not be given in this chapter but is given in Appendix B.

(b) Terms involving the number density gradient.

With the temperature gradient taken as zero in equation (3-13) we obtain,

$$n\,\frac{\partial g}{\partial t}_{\exp} + \underline{w}\cdot\frac{\partial ng}{\partial \underline{x}} + \frac{1}{\beta m}\,\frac{\partial n}{\partial \underline{x}}\cdot\frac{\partial g}{\partial \underline{w}} = [ng, f^{(o)}] \qquad (3\text{-}21)$$

The solution may be written in the form

$$g = g_e + H,$$

where g_e is the zero order solution as above, and H is linear in the number density gradient and satisfies,

$$\frac{\partial H}{\partial t}_{\exp} - [H, f^{(0)}] = -\frac{w}{n} \cdot \frac{\partial n g_e}{\partial x} - \frac{1}{\beta m} \frac{1}{n} \frac{\partial n}{\partial x} \cdot \frac{\partial g_e}{\partial w} \qquad (3\text{-}22)$$

$$\frac{\partial H}{\partial t}_{\exp} - [H, f^{(0)}] = 0.$$

The boundary condition is for t=o,

$$H = 0. \qquad (3\text{-}23)$$

The solution of these equations is also given in Appendix B.

The complete solution when considering a system in which there exists a temperature gradient with the mass velocity gradient zero is given by the addition of the above solutions i.e. g_e+G+H. If the pressure is uniform, then the following relation exists between the two gradients,

$$\frac{1}{n}\frac{\partial n}{\partial x} = \frac{1}{T}\frac{\partial T}{\partial x}. \qquad (3\text{-}24)$$

However, in general, there is not a definite relation between these gradients.

3-4 FORWARD EQUATION FOR VELOCITY GRADIENT

The above solutions apply to a system in which there are gradients of temperature and number density only i.e. we have taken the mass velocity gradient as zero. Physically, this means that we were considering the distinguished molecule in a system in which the mass velocity, at any given instant, is constant over the whole volume. Hence, when considering a molecule surrounded by a general gas in "steady" state non-equilibrium in which all gradients may exist, we must add, to the above solutions, terms which involve the gradient of the mass velocity.

The spatial delta function in the velocity distribution function for time $t=0$ has been replaced by the factor $\frac{n}{\int n\underline{dx}}$. This factor is, to some extent, arbitrary depending on the region of integration used in the integral in the denominator. To remove this arbitrariness we shall suppose that the region, Rm, is such that each point on the boundary surface, S, moves with the mass velocity at that point, then,

$$\frac{\partial}{\partial t}\int_{Rm} n\underline{dx} = \int_{Rm}\frac{\partial n}{\partial t}\,\underline{dx} + \int_{S} n\,\underline{u}\cdot\underline{dS}$$

$$= \int_{Rm}\left(\frac{\partial n}{\partial t} + \frac{\partial}{\partial \underline{x}}\cdot n\underline{u}\right)\underline{dx}$$

$$= 0,$$

from the conservation equation. The effects of volume viscosity are known to be comparatively small and can be neglected for a dilute gas. Therefore, when considering terms in the distribution function involving the mass velocity gradient we may, without risk of error, discard terms in the solution which involve the divergence of the mass velocity, i.e. we may consider a pure shearing motion of the gas.

When calculating the terms in the distribution function which involve the mass velocity gradient, it is found more convenient to take $\underline{w}_1 = \underline{v}_1 - \underline{u}(\underline{x}, t)$ for all t. When the gradients of temperature and number density are taken as zero, equation (3-11) becomes, using equations (3-12)

$$\frac{\partial g}{\partial t}\,\mathrm{exp} - \left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right)\frac{\partial ng}{\partial n} - \frac{2}{3}\,T\left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right)\frac{\partial g}{\partial T} - \frac{\partial g}{\partial \underline{w}}\,\underline{w}:\frac{\partial \underline{u}}{\partial \underline{x}} - \frac{\partial g}{\partial \underline{w}_1}\,\underline{W}:\frac{\partial \underline{u}}{\partial \underline{x}}$$

$$= [g, f^{(0)} + f^{\circ}] \qquad (3\text{-}25)$$

Following the perturbation technique used above, then the zero order is as above (except that $\underline{w}_1$ is defined slightly differently) and the terms linear in the mass velocity gradient, denoted by U, satisfies the following equations;

$$\frac{\partial U}{\partial t}_{\exp} - [U, f^{(0)}] = [g_e, f'] \tag{3-26}$$

$$\frac{\partial U}{\partial t}_{\exp} - [U, f^{(0)}] = \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right) \frac{\partial n g_e}{\partial n} + \frac{2}{3} T \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right) \frac{\partial g_e}{\partial T}$$

$$+ \frac{\partial g_e}{\partial \underline{W}} \underline{W} : \frac{\partial \underline{u}}{\partial \underline{x}} + \frac{\partial g_e}{\partial \underline{W}_1} \underline{W} : \frac{\partial \underline{u}}{\partial \underline{x}} \tag{3-27}$$

$$\frac{\partial U}{\partial t}_{\exp} - [U, f^{(0)}] = 0 \tag{3-28}$$

together with the boundary condition for t=o,

$$U = 0. \tag{3-29}$$

The solution to these equations are found in Appendix B.

This completes the discussion of the forward equations for the distinguished molecule in the "steady" state non-equilibrium gas in which all gradients are present.

3-5 BACKWARD BOLTZMANN EQUATION

In the case of the forward Boltzmann equation, in the collision integral one assumes that the velocities are uncorrelated before a collision and so correlated after the collision. However, in the backward Boltzmann equation the velocities are uncorrelated "after" the collision (in the backward time sense), and correlated "before" the collision, and this leads to the sign of the collision integral being changed. The forward distribution will, of course, differ from the backward distribution. Hence the backward equation corresponding to the forward equation (3-11) will be

$$\frac{Dng_b}{Dt} = -[ng_b, f^{(0)}-f'] \qquad (3\text{-}30)$$

where the change in sign of the first order perturbation f' is due to the change in the sign of the collision integral in the full Boltzmann equation for a general dilute gas in "steady" state non-equilibrium. In the equilibrium case, equation (3-30) reduces to the backward equation found in the previous chapter.

Hence, for the backward distributions, equations (3-14), (3-21) and (3-25) become respectively;

$$\frac{\partial g_b}{\partial t}_{\exp} + \underline{W}\cdot\frac{\partial g_b}{\partial \underline{x}} + \frac{1}{\beta m}\,\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial g_b}{\partial \underline{W}} = -[g_b, f^{(0)}-f'] \qquad (3\text{-}31)$$

$$n\frac{\partial g_b}{\partial t}_{\exp} + \underline{W}\cdot\frac{\partial n g_b}{\partial \underline{x}} + \frac{1}{\beta mn}\,\frac{\partial n}{\partial \underline{x}}\cdot\frac{\partial n g_b}{\partial \underline{W}} = -[ng_b, f^{(0)}] \qquad (3\text{-}32)$$

$$\frac{\partial g_b}{\partial t}_{\exp} - \left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right)\frac{\partial n g_b}{\partial n} - \frac{2}{3}\,T\left(\frac{\partial}{\partial \underline{x}}\cdot\underline{u}\right)\frac{\partial g_b}{\partial T} - \frac{\partial g_b}{\partial \underline{W}}\,\underline{W}:\frac{\partial \underline{u}}{\partial \underline{x}} - \frac{\partial g_b}{\partial \underline{W}_1}\,\underline{W}:\frac{\partial \underline{u}}{\partial \underline{x}}$$

$$= -[g_b, f^{(0)}-f'] \,. \qquad (3\text{-}33)$$

The boundary condition on g_b is for $t=o$,

$$g_b = \delta(\underline{w}-\underline{w}') . \qquad (3\text{-}34)$$

These equations are solved in exactly the same manner as the corresponding forward equations and the solutions will differ from the corresponding solutions of the latter only in the signs of certain terms. For these reasons the formal solutions will be presented only for Maxwellian molecules for the terms used in the calculation of the mean accelerations of the distinguished molecule - see Chapter V.

3-6 MAXWELLIAN MOLECULES

As pointed out in Chapter II, the exact eigenfunctions of the collision operator are not known for any molecular model except the Maxwellian molecules which are defined by the force law $F = \frac{\kappa}{r^5}$.

In Appendix B it is shown that for Maxwellian molecules the forward distribution function tends to the following value as $t \to \infty$,

$$g = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}\left[1 - \frac{a'}{n}\left(\tfrac{1}{2}\beta m w^2 - 5/2\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}} - \frac{1}{2}\,\frac{b'}{n}\left(\underline{w}\,\underline{w} - \tfrac{1}{3}w^2\,\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}\right]$$

(3-35)

As this is the usual distribution function given by the Chapman-Enskog theory, this clearly shows that the distinguished molecule has become indistinguishable from the rest.

The backward distribution tends to the following value as t->-∞ ,

$$g_b = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{\frac{1}{2}\beta m w^2}\left[1 + \frac{a'}{n}\left(\tfrac{1}{2}\beta m w^2 - {}^{5}\!/_{2}\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}} + \frac{1}{2}\frac{b'}{n}\left(\underline{w}\,\underline{w} - \tfrac{1}{3}w^2\,\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}\right].$$

3-7 ALTERNATIVE APPROACH TO BACKWARD EQUATION

In the discussion of the backward equation (3-30) above, we have, in effect, completely time reversed the situation as a whole, i.e. not only have we considered the behaviour of the distinguished molecule as anticausal but the other surrounding molecules. An alternative approach would be to introduce a time reversal only of the motion of the distinguished molecule. In this case equation (3-30) is replaced by,

$$-\frac{\partial n g_b}{\partial t}_{\exp} + \frac{\partial n g_b}{\partial t}_{\mathrm{imp}} + \underline{v}\cdot\frac{\partial n g_b}{\partial \underline{x}} = [g_b, f^{(0)} + f'] , \qquad (3\text{-}36)$$

and as t->-∞,

$$g_b = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}\left[1 - \frac{a'}{n}\left(\tfrac{1}{2}\beta m w^2 - {}^{5}\!/_{2}\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}} - \frac{1}{2}\frac{b'}{n}\left(\underline{w}\,\underline{w} - \tfrac{1}{3}w^2\,\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}\right]$$

as in the case of 3-35 above.

Following section 5-3, we define

$$\underline{\Pi} = \left\{\frac{D'}{D,t}\left[\frac{\int n g_b \underline{V} d\underline{V}}{\int n g_b d\underline{V}}\right]\right\}_{t=0},$$

where to be consistent with (3-36), we must take

$$\frac{D'}{D,t} = \frac{\partial}{\partial t}_{\text{exp}} - \frac{\partial}{\partial t}_{\text{imp}} - \underline{V}_1 \cdot \frac{\partial}{\partial \underline{x}}.$$

It is found from (3-36) that

$$\underline{\Pi} = -\left\{\frac{1}{n}\int \underline{V}[n g_b, f^{(0)}]\underline{dV}\right\}_{t=0}$$

$$= -\left\{\frac{1}{n}\int \underline{V}[n\,\delta(\underline{V}-\underline{V}_1), f^{(0)}]\underline{dV}\right\},$$

which is the value (5-22a) found in Chapter V.

3-8 EXPERIMENTAL VERIFICATION

A direct verification of the above results by experiment appears possible.

A small beam of radioactive particles could be injected or allowed to diffuse into a gas in equilibrium and, at a certain time, the momentum distribution of the subsequent β-decay could be observed. The experiment could then be repeated for a gas in non-equilibrium. Probably the best way to carry out this experiment is with uniform pressure throughout the gas e.g. no mass velocity with no external forces. Hence we have the relation

$$-\frac{1}{n}\frac{\partial n}{\partial x} = \frac{1}{T}\frac{\partial T}{\partial x},$$

and so the distribution functions above do not contain the number density gradient.

The choice of radioactive particles and gas molecules should be such that their chemical and physical properties are similar so that the particles can be regarded as indistinguishable from the gas molecules. The momentum distribution should be observed before the steady-state has been reached, although allowances should be made so that incoming particles have lost their original momentum, i.e. had at least one collision. At N.T.P. the mean collision time between successive collisions in hydrogen is 6.6×10^{-11} secs., although, if the density is decreased, this time is increased. If the eigenvalue λ_{01}, for Maxwellian molecules, is calculated approximately for Hydrogen at N.T.P., it is found that it has the value of about three or four times that of the collision time. It appears from this that the steady-state is reached after only a few collisions and so the observation would have to be made a very short time after the particles enter the gas.

The theory is as follows: suppose the beam enters with (peculiar) velocity $\underline{w}_1$ into the gas. Consider the differential cross-section $I(m\,\underline{v},\underline{p})d\underline{p}$, normalized so that $I\,d\underline{p}$ is the probability that a particle with momentum $m\underline{v}$ emits an electron with momentum in the range $\underline{p},\underline{p}+d\underline{p}$. Since $g(t_1,\underline{w},\underline{w}_1)\underline{dw}$ is the probability of a particle having peculiar velocity in the range $\underline{w},\underline{w}+\underline{dw}$ at time t_1 when its peculiar velocity was $\underline{w}_1$ at time $t=0$, the momentum distribution at time t_1 of the β-radiation is given by

$$P\,\underline{dp} = \underline{dp}\int g(t_1,\underline{w},\underline{w}_1)\,I\,\underline{dw}\,.$$

The velocity distribution function, g, for the equilibrium and non-equilibrium cases is given by the above sections, and will produce a different momentum distribution in each case. Actually, the correct distribution applying to the above would be that defined in equation (3-1).

However, one would expect that the distribution would not depend critically on the simplification introduced by replacing the spatial delta function by the factor $\frac{n}{\int n dz}$.

Footnote:- Van Hove$^{(1)}$ has pointed out that the incoherent radiation in the neutron diffraction in fluids gives information concerning the time dependent correlation functions, and so this may be able to be used to demonstrate experimentally the difference between the "equilibrium" and "non-equilibrium" functions defined above.

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CHAPTER IV KUBO-TYPE TRANSPORT COEFFICIENTS

4-1 INTRODUCTION

The exact theory of transport phenomena in dilute gases was developed independently by Chapman and Enskog nearly 50 years ago. This was preceded by the mean free path theory(1) which was not exact, but certainly gave a good physical picture and qualitative results for the transport processes. One of the deficiencies of this theory was the fact that the persistence of velocities in the collision processes was not fully accounted for. Yang(2) and, Furry and Pitkannen(3) improved the theory by extending the theory to follow statistically the motion of a molecule in a gas through a large number of collisions so that the persistence could be accounted for. However, their results have been applied to the various diffusion coefficients and not to the coefficients of viscosity and thermal conduction. Another application, where the mean-free-path theory has been successfully employed, is to the properties of free electrons moving in a gas to which an electric field has been applied. Huxley(4) has calculated the coefficient of diffusion and drift velocity of the free electrons. Monchick(5) has shown the equivalence between an extension of the mean-free-path theory and the Chapman-Enskog theory by using a Liouville-

Neumann series for the first order solution of the Boltzmann equation. "Unfortunately, in the process an *effective* transition probability" (Monchick's emphasis) has been introduced.

Considerable interest has lately been shown in the Kubo-type transport coefficients introduced by Kubo's electrical conductivity formula(7) and by other authors(8-11) who recognised the application of this type of formula to the other coefficients. Actually, M.S. Green(6) had obtained similar results a few years previous to Kubo's independent derivation. Various authors(12-14) have calculated these expressions for dilute gases and demonstrated that they were equivalent to those obtained via the Chapman-Enskog method. This was done by Green(14) by considering from the complete ensemble of statistical equilibrium, a sub-ensemble in which the velocity, $\mathbf{v}_i$, of the i^{th} molecule has a specified value $\mathbf{v}_i$ at time $t=0$. It has been shown in Chapters I and II that, in dilute gases, this is equivalent to considering a system in equilibrium into which a molecule has been injected with velocity $\mathbf{v}_i$ at any point in this system. Using this comparatively simple non-equilibrium system, Green(14) has shown that it is possible to calculate all the transport coefficients for dilute gases.

In this chapter, we apply the various distribution functions (calculated in Chapter II) associated with the complete system of a molecule entering similar molecules which form a system in equilibrium, to the calculations of the transport coefficients of the Kubo-type for viscosity and thermal conduction.

4-2 GENERAL EXPRESSIONS

The general expression for the Kubo-type transport coefficient is$^{(14)}$

$$I = a\langle\tau(\underline{w}_i)\int_0^\infty \Sigma_j\ \tau(\underline{w}_j')dt'\rangle_i^e \qquad (4\text{-}1)$$

where the values of "$\tau(\underline{w})$" and "a" depend on the particular coefficient being considered; Σ_j is a summation over all the molecules in the system; $\underline{w}_j'$ is the velocity of the j^{th} molecule at time t'. $\langle\text{---}\rangle_i^e$ is an average with an equilibrium distribution function. In the case of viscosity $\tau(\underline{w})$ is given by $\tau(\underline{w}) = \underline{w}\,\underline{w}-\frac{1}{3}w^2\underline{\underline{\delta}}$, and is $\tau(\underline{w})=(\frac{1}{2}\beta m w^2-{}^5/2)\underline{w}$ for thermal conduction.

We may now divide the coefficient into two separate parts so that,

$$I = a\langle\tau(\underline{w}_i)\int_0^\infty \tau(\underline{w}_i')dt'\rangle_i^e + a\langle\tau(\underline{w}_i)\int_0^\infty \sum_{j\neq i}\ \tau(\underline{w}_j')dt'\rangle_i^e$$

$$= I_i + I_r \qquad (4\text{-}2)$$

where the first term, I_i, gives the contribution from the

i^{th} molecule, and the second term, I_r, the contribution from the rest. Therefore, using the subensemble for which the velocity, $\underline{w}_i$, of the i^{th} molecule has the value $\underline{w}_1$ at t=0, (4-2) may be expressed in the following manner,

$$I_l = a \int f^{(0)}(w_1^2)\ \tau(\underline{w}_1) \int_0^\infty \int g(t,\underline{w},\underline{w}_1)\tau(\underline{w})\underline{dw}\ dt\ \underline{dw}_1 \quad (4\text{-}3)$$

and

$$I_r = a \int f^{(0)}(w_1^2)\tau(\underline{w}_1) \int_0^\infty \int \gamma(t,\underline{w},\underline{w}_1)\tau(\underline{w})\underline{dw}\ dt\ \underline{dw}_1 \quad (4\text{-}4)$$

where g is the distribution function associated with the motion of the "incoming" molecule, and γ is the function associated with all the molecules excluding this distinguished molecule, (see Chapter II). In equation (4-4), we have taken

$$\int f^{(0)}\tau(\underline{w})\underline{dw} = 0$$

as I_r is volume independent.

Therefore, I_l is the part of the transport coefficient obtained by following statistically the motion of a molecule moving with initial velocity $\underline{w}_1$ in the gas. By defining I_l in this manner, we may identify this coefficient with the mean-free-path transport coefficient in which the persistence of velocities has been accounted for exactly.

Hence, using equations (4-3) and (4-4), and the solutions g and γ from Chapter II, the "mean-free-path" contribution I_l, and the remaining contribution, I_r, to the transport coefficients may be calculated for Maxwellian molecules. As we have considered the problem with only one type of molecule we are not in the position to calculate the various diffusion coefficients. However, the theory involving more than one type of molecule could be obtained by an extension of the theory presented in Chapter II, and the diffusion coefficients calculated in the same manner as those calculated below.

4-2-1 THE COEFFICIENT OF THERMAL CONDUCTION K

In the case of thermal conduction, equations (4-3) and (4-4) become,

$$K_t = \frac{1}{3}\int f^{(0)}(w_1^2)\tfrac{1}{2}mw_1^2\underline{W}_1 \cdot \iint g(t,\underline{W},\underline{W}_1)(\tfrac{1}{2}\beta mw^2 - 5/2)\underline{W}\,\underline{dW}\,dt\,\underline{dW}_1$$

and

$$K_r = \frac{1}{3}\int f^{(0)}(w_1^2)\,\tfrac{1}{2}mw_1^2\underline{W}_1 \cdot \iint \gamma(t,\underline{W},\underline{W}_1)(\tfrac{1}{2}\beta mw^2 - 5/2)\underline{W}\,\underline{dW}\,dt\,\underline{dW}_1 .$$

If we use equations (2-30) and (2-32) and the orthogonality relations, we find for Maxwellian molecules,

$$K_t = \frac{5}{\beta^2 m}\;\frac{1}{\pi[2A_1(5)+A_2(5)]}\left(\frac{m}{2K}\right)^{\frac{1}{2}}$$

$$K_r = \frac{5}{\beta^2 m}\;\frac{2A_1(5) - A_2(5)}{2\pi A_2(5)[2A_1(5)+A_2(5)]}\left(\frac{m}{2K}\right)^{\frac{1}{2}} . \qquad (4\text{-}6)$$

Then the coefficient of thermal conduction, K, is given by

$$K = K_t + K_r = \frac{5}{2\pi A_2(5)} \left(\frac{m}{2\kappa}\right)^{\frac{1}{2}} \frac{1}{\beta^2 m}, \qquad (4\text{-}7)$$

which is the value given by the Chapman-Enskog method - see C.C. page 174.

4-2-2 THE COEFFICIENT OF VISCOSITY

I_t and I_r take the following form in the case of viscosity,

$$\eta_t = \frac{1}{10}\,\beta m \int f^{(0)}(w_1^2)\underline{W}_1\underline{W}_1 : \iint m\, g(t,\underline{W},\underline{W}_1)\ (\underline{W}\,\underline{W} - \tfrac{1}{3}W^2\underline{\underline{\delta}})\underline{dW}\ dt\ \underline{dW}_1$$

and

$$\eta_r = \frac{1}{10}\,\beta m \int f^{(0)}(w_1^2)\underline{W}_1\underline{W}_1 : \iint m\, \gamma(t,\underline{W},\underline{W}_1)(\underline{W}\,\underline{W} - \tfrac{1}{3}W^2\underline{\underline{\delta}})\underline{dW}\ dt\ \underline{dW}_1.$$

For Maxwellian molecules, the results obtained are,

$$\eta_t = \frac{4}{\pi[4A_1(5)+3A_2(5)]}\left(\frac{m}{2\kappa}\right)^{\frac{1}{2}}\frac{1}{\beta}$$

and

$$\eta_r = \frac{2}{3\pi}\,\frac{[4A_1(5) - 3A_2(5)]}{A_2(5)[4A_1(5)+3A_2(5)]}\left(\frac{m}{2\kappa}\right)^{\frac{1}{2}}\frac{1}{\beta}. \qquad (4\text{-}8)$$

Hence the coefficient of viscosity, η is given by,

$$\eta = \eta_t + \eta_r = \frac{2}{3\pi A_2(5)}\left(\frac{m}{2\kappa}\right)^{\frac{1}{2}}\frac{1}{\beta}, \qquad (4\text{-}9)$$

which is in agreement with the Chapman-Enskog result.

4-3 CONCLUSIONS

Using the solution obtained from the full linear Boltzmann equation for Maxwellian molecules, we have calculated the transport coefficients for thermal conduction and viscosity, via the Kubo-type method of Green. As expected, these results agree with those of the Chapman-Enskog method.

If the values of the constants, $A_1(5) = 0.422$ and $A_2(5) = 0.436$, are substituted in equations (4-6) and (4-8), then the following results are obtained for the ratios of the two contributions,

$$\frac{K_t}{K_r} = 2.14$$

and

$$\frac{\eta_t}{\eta_r} = 6.88 \quad .$$

As was previously pointed out, the contributions K_t and η_t correspond to the exact mean-free-path coefficients.
From the ratios above, it is seen that, in both cases, the greater contribution to the exact Chapman-Enskog coefficient comes from this mean-free-path coefficient.

A vague concept of relaxation time associated with transport phenomena has been introduced by replacing the collision integral in the Boltzmann equation by the approximation,

$$L_1 f \approx \frac{f-f^{(0)}}{-\tau}$$

where τ is the relaxation time. This relaxation time has been taken as a mean collision time, and has produced results which give approximate values, involving this relaxation time, for the coefficients of viscosity and thermal conduction.(15,16)

From the above theory, for Maxwellian molecules we may define a microscopic relaxation time, associated with each of the irreversible processes, as the inverse of the eigenvalue of the full Boltzmann collision operator (see Chapter II) corresponding to the particular mode of relaxation for the process. Hence the relaxation times for viscosity and thermal conduction for Maxwellian molecules forming a dilute gas are respectively,

$$\tau_v = \frac{1}{\mu_{02}} = [\,{}^3/2\; n\pi A_2(5) \left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}]^{-1} \qquad (4\text{-}10)$$

and

$$\tau_c = \frac{1}{\mu_{11}} = [n\pi A_2(5) \left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}]^{-1} , \qquad (4\text{-}11)$$

where μ_{02} and μ_{11} are the eigenvalues given in section 2-5, and in each case correspond to the value of $\tau(\underline{w})$ appearing in equation (4-1). The values given by (4-10) and (4-11) were obtained by Mori(12) by a similar method using the eigenvalues of the master and binary collision operators.

Also

$$\eta = \tau_v nkT = \tau_v p$$

and

$$K = \tau_c \, {}^5\!/_2 \, \frac{n}{\beta^2 m}$$

which agree with Mori.(12) Storer and Green(17,18) have also obtained similar results using a similar, but not exact, concept of relaxation time. However, their results apply to dense gases and liquids as well as dilute gases.

In the above theory, we have two relaxation times for each process. The first, the eigenvalue of the half Boltzmann collision operator, corresponds to the mode of relaxation of the incoming molecule. The other is the relaxation time for the corresponding mode of the complete system of the incoming molecule and the molecules into which it enters. The latter times are given by the eigenvalues of the full Boltzmann collision operator.

In the case of thermal conduction, the two relaxation times for the particular mode is given by (4-11) above, and by

$$\tau_c^{\lambda} = \frac{1}{\lambda_{11}} = \left[n\sigma\left(A_1(5)+\tfrac{1}{2}A_2(5)\right)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\right]^{-1} \qquad (4\text{-}12)$$

Therefore the relaxation time associated with the incoming molecule is less than the corresponding relaxation time for the complete system. This means that the particular mode of relaxation of the incoming molecule reaches completion before the mode of the complete system. Hence for this particular process in which we are concerned with transfer of energy, the incoming molecule attains the mode of the complete system before the transfer is completed.

In the case of viscosity, the two relaxation times are given by (4-10) above, and by

$$\tau_{v}^{\lambda} = \frac{1}{\lambda_{02}} = \left[n\pi\left(A_{1}(5) + \frac{3}{4} A_{2}(5)\right) \left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} \right]^{-1} . \qquad (4\text{-}13)$$

Hence, as in the case of thermal conduction, the relaxation time for the incoming molecule is less than the corresponding relaxation time for the complete system. So, in this process of momentum transfer, we again have the incoming molecule attaining the mode of the complete system before this transfer is exhausted.

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CHAPTER V MEAN ACCELERATIONS USING THE CORRELATION FUNCTIONS.

5-1 INTRODUCTION

In this chapter, we introduce the definitions of various mean accelerations of a molecule moving in a gas by using the velocity distribution functions that were defined and calculated in chapters II and III. These mean accelerations correspond to those defined in the theory of Kirkwood$^{(1)}$ and O'Toole and Dahler$^{(2)}$ (see General Introduction), and we show that the mean acceleration defined by O'Toole and Dahler is equivalent to that defined below. In section (5-4) the equivalence of our definitions and of Kirkwood's is discussed.

5-2 "FORWARD" AND "BACKWARD" MEAN ACCELERATIONS.

In the theory of Kirkwood the mean acceleration $\underline{a}_K(t,\underline{x}^{(1)},\underline{v}^{(1)})$ of a molecule moving with velocity $\underline{v}^{(1)}$ at the point $\underline{x}^{(1)}$ for both equilibrium and non-equilibrium is given by equation (7), i.e.

$$\underline{a}_K = \frac{1}{2\tau} \langle \underline{\tilde{p}}_0{}^{(1)} + \underline{\tilde{p}}^{(1)} \rangle \qquad (5-1)$$

where, in the average <...> , the position and velocity of the molecule 1 is fixed at time t. Another mean acceleration $\underline{\eta}_{+}$ was also introduced and is given by

$$\underline{\eta}_{+} = \frac{\langle \underline{\varphi}^{(1)} \rangle}{\tau} \quad . \tag{5-2}$$

This mean acceleration may be considered as a "forward" acceleration as the velocity and position of the molecule are specified at the beginning, viz. time t, of the time interval and the subsequent average change of velocity is computed during the following time interval from t to t+τ.

In the same manner, we may define a mean acceleration $\underline{\eta}_{-}$ given by

$$\underline{\eta}_{-} = \frac{\langle \underline{\varphi}_{o}^{(1)} \rangle}{\tau} \quad , \tag{5-3}$$

and so we consider $\underline{\eta}_{-}$ as a "backward" acceleration in the sense that the velocity and position of the molecule 1 are specified at the end, viz. time t, of the time interval and the average change in velocity is computed during the past time interval from t-τ to t. Hence, the mean acceleration $\underline{\eta}_{K}$ may be expressed in terms of $\underline{\eta}_{+}$ and $\underline{\eta}_{-}$ by using (5-1) i.e.

$$\underline{\eta}_{K} = \tfrac{1}{2}(\underline{\eta}_{+} + \underline{\eta}_{-}) \quad . \tag{5-4}$$

5-3 DEFINITIONS USING THE CORRELATION FUNCTIONS.

Using the distribution functions introduced in chapters II and III, we define the various mean accelerations corresponding to (5-2) and (5-3).

(1) "Forward" mean acceleration

If $\langle \underline{v} \rangle(\tau)$ is the mean value at time τ of the velocity of the distinguished molecule which has velocity $\underline{v}_1$ at time t=o – this mean value being taken with the forward distribution function associated with this molecule and defined in chapter I, then the forward mean acceleration is defined as follows;

$$\underline{\Pi}_+ (\underline{v}_1) = \lim_{\tau \to o^+} \frac{\langle \underline{v} \rangle(\tau) - \underline{v}_1}{\tau} \quad . \tag{5-5}$$

We are therefore not taking the average with respect to the grand ensemble but with respect to the fluctuation ensemble.

Using the distribution functions defined in chapters II and III, formula (5-5) becomes,[+]

$$\underline{\Pi}_+ = \lim_{\tau \to o^+} \frac{1}{\tau} \left\{ \frac{\int n(\underline{x}+\underline{v}\tau,\tau) g(\tau,\underline{v}_1,\underline{x}+\underline{v}\tau) \underline{v} d\underline{v}}{\int n(\underline{x}+\underline{v}\tau,\tau) g(\tau,\underline{v}_1,\underline{x}+\underline{v}\tau) d\underline{v}} - \frac{\int n(\underline{x},o) g(o,\underline{v}_1,\underline{x}) \underline{v} d\underline{v}}{\int n(\underline{x},o) g(o,\underline{v}_1,\underline{x}) d\underline{v}} \right\} \tag{5-6}$$

[+] Alternatively we may take

$$\left\{ \frac{D}{Dt} \left[\frac{\int n g \underline{v} d\underline{v}}{\int n g d\underline{v}} \right] \right\}_{t=o} , \text{ where } \frac{D}{Dt} = \frac{\partial}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}} ,$$

i.e. differentiation following the motion. This also reduces to (5-8).

where $g(o,\underline{V},\underline{V}) = \delta(\underline{V}-\underline{V}_1)$. (5-7)

This reduces to,

$$\underline{\eta}_+ (\underline{V}_1) = \left\{\frac{1}{n} \frac{\partial}{\partial t} \int n g \underline{V} d\underline{V} - \frac{\underline{V}_1}{n} \frac{\partial}{\partial t} \int n g d\underline{V}\right\}_{t=o} . \quad (5\text{-}8)$$

<u>In uniform equilibrium</u>, formula (5-8) reduces to

$$\underline{\eta}_+^{(0)} (\underline{V}_1) = \left\{\frac{\partial}{\partial t} \int g \underline{V} d\underline{V}\right\}_{t=o} . \quad (5\text{-}9)$$

The work of O'Toole and Dahler has been discussed in the General Introduction. These authors defined the mean acceleration $\underline{\eta}_+^{(0)}$ as follows,

$$\underline{\eta}_+^{(0)} = \iint f^{(0)}(w') \, (\underline{V}_f-\underline{V}_1) \, \sigma \, \underline{db} \, \underline{dV}' , \quad (5\text{-}10)$$

when considering the collision process $(\underline{V}_1,\underline{V}') \to (\underline{V}_f,\underline{V}_f')$. The definitions (5-10) and (5-9) are, in fact, equivalent. This is shown as follows: The equation satisfied by the distribution function $g(t,\underline{V},\underline{V}_1)$ is (2-2), i.e.

$$\frac{\partial g}{\partial t} = [g,f^{(0)}] . \quad (5\text{-}11)$$

Hence,

$$\left\{\frac{\partial}{\partial t} \int g \underline{V} d\underline{V}\right\}_{t=o} = \left\{ \int \underline{V}[g,f^{(0)}]d\underline{V}\right\}_{t=o}$$

$$= \left\{ \int \underline{V}[g,f^{(0)}]d\underline{V}\right\}_{t=o}$$

$$= \int \underline{W} \iint \{ g(0,\underline{W}_0,\underline{W}_1) f^{(0)}(w_0') - g(0,\underline{W},\underline{W}_1) f^{(0)}(w') \} \sigma\, \underline{db}\, \underline{dW'}\, \underline{dW},$$

but $g(0,\underline{W},\underline{W}_1) = \delta(\underline{W}-\underline{W}_1)$, (5-12)

and so

$$\left\{ \frac{\partial}{\partial t} \int g\underline{Y} d\underline{Y} \right\}_{t=0} = \int \underline{W} \iint \left\{ \delta(\underline{W}_0-\underline{W}_1) f^{(0)}(w_0') - \delta(\underline{W}-\underline{W}_1) f^{(0)}(w') \right\} \sigma\, \underline{db}\, \underline{dW'}\, \underline{dW} \quad (5\text{-}13)$$

when considering the collision process $(\underline{W}_0,\underline{W}_0') \to (\underline{W},\underline{W}')$. Considering each term separately in the right hand side of (5-13), and following the procedure used on page 2-8, we find;

$$\iiint \underline{W}\, \delta(\underline{W}_0-\underline{W}_1) f^{(0)}(w_0') \sigma\, \underline{db}\, \underline{dW'}\, \underline{dW}$$

$$= \iint \underline{W}\, f^{(0)}(w_0')\, \sigma\, \underline{db}\, \underline{dW_0'}$$

for the collision process $(\underline{W}_1,\underline{W}_0') \to (\underline{W},\underline{W}')$,

and

$$\iiint \underline{W}\, \delta(\underline{W}-\underline{W}_1) f^{(0)}(w') \sigma\, \underline{db}\, \underline{dW'}\, \underline{dW}$$

$$= \iint \underline{W}_1 f^{(0)}(w_0')\, \sigma\, \underline{db}\, \underline{dW_0'}\ ,$$

also for the collision process $(\underline{W}_1,\underline{W}_0') \to (\underline{W},\underline{W}')$. Combining these results, we finally obtain,

$$\left\{\frac{\partial}{\partial t}\int \underline{g}\underline{v}d\underline{v}\right\}_{t=o} = \iint f^{(0)}(w_o')(\underline{w}-\underline{w}_1)\sigma\, \underline{db}\ \underline{dw_o}'$$

for the collision process $(\underline{w}_1,\underline{w}_o')\to(\underline{w},\underline{w}')$, which is the expression (5-10) of O'Toole and Dahler. However, as already pointed out in the General Introduction, O'Toole and Dahler found it necessary to introduce a "plateau-time". In the definition (5-5) such a concept is not introduced.

Using the distribution function (2-30), $\underline{\eta}_+^{(0)}$ has the following value for Maxwellian molecules

$$\underline{\eta}_+^{(0)}(\underline{w}) = -n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\underline{w} \qquad (5\text{-}14)$$

which is the value obtained by O'Toole and Dahler.† Hence

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† O'Toole and Dahler also calculate the average power consumption, P. Using the distribution function (2-30) P is defined by

$$P = \left\{\frac{\partial}{\partial t}\langle\tfrac{1}{2}mv^2\rangle^g\right\}_{t=o} = \tfrac{1}{2}m\left\{\frac{\partial}{\partial t}\int v^2\underline{g}d\underline{v}\right\}_{t=o}$$

$$= n\,\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}[{}^3/2\ kT-\tfrac{1}{2}m\ v_1^2]$$

if $\underline{u}=o$, which is agreement with their result. If $\underline{u}\neq o$, the average power consumption is given by

$$P = n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}[{}^3/2\ kT-\tfrac{1}{2}m\ v_1^2+\tfrac{1}{2}m\ u^2]\ .$$

the friction coefficient for Maxwellian molecules is given by,

$$\zeta = n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}} .$$

For the general molecular model $\underline{\eta}_+^{(0)}$ will have the following form,

$$\underline{\eta}_+^{(0)}(\underline{v}) = -\zeta\underline{v}$$

where ζ is not necessarily a constant but may be velocity dependent. In fact, ζ has been found velocity dependent by O'Toole and Dahler for a number of molecular models.

<u>In non-equilibrium</u>, the distribution function ng satisfies the following equation (see Chapter III),

$$\frac{\partial ng}{\partial t} + \underline{v}\cdot\frac{\partial ng}{\partial \underline{x}} = [ng, f^{(0)}] + [ng, f'] . \qquad (5\text{-}15)$$

Hence from (5-8), using (5-15) and

$$\left\{\int [ng, f^{(0)}]\underline{dv}\right\}_{t=0} = 0,$$

the following expression for the mean acceleration in non-equilibrium is found,

$$\underline{\eta}_+ = \left\{\frac{1}{n}\int\underline{v}[ng, f^{(0)}]\underline{dv}\right\}_{t=0} + \left\{\frac{1}{n}\int\underline{v}[ng, f']\underline{dv}\right\}_{t=0} .$$

For Maxwellian molecules it is found that the second term does not contribute, and so we finally obtain the result for this force law,

$$\underline{\eta}_+(\underline{w}_1) = \left\{\frac{1}{n}\int \underline{v}[ng, f^{(o)}]d\underline{v}\right\}_{t=0} .$$

Therefore, from the condition (5-12), we see that the non-equilibrium part of the distribution function does not contribute, and so in this case $\underline{\eta}_+$ has the value,

$$\underline{\eta}_+(\underline{w}) = -n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\underline{w} \qquad (5\text{-}16)$$

for both equilibrium and non-equilibrium. In Appendix B, $\underline{\eta}_+$ is calculated using the distribution function ng for Maxwellian molecules and the result (5-16) is obtained as expected.

(2) "Backward" mean acceleration.

The "backward" mean acceleration is defined similarly to (5-5), but the mean velocity at time τ, $\langle v\rangle(\tau)$, is now calculated using the backward distribution function associated with the distinguished molecule. The "backward" mean acceleration is defined by,

$$\underline{\eta}_- = \lim_{\tau \to 0^-} \frac{\langle\underline{v}\rangle(\tau) - \underline{v}_1}{\tau} . \qquad (5\text{-}17)$$

Hence using the backward distribution function ng_b, as in the forward case we obtain,

$$\underline{\eta}_-(\underline{V}_1) = \left\{\frac{1}{n}\frac{\partial}{\partial t}\int ng_b(t,\underline{V},\underline{V}_1)\underline{V}d\underline{V} - \frac{\underline{V}_1}{n}\frac{\partial}{\partial t}\int ng_b d\underline{V}\right\}_{t=0}, \qquad (5\text{-}18)$$

where $ng_b(0,\underline{V},\underline{V}_1) = n\,\delta(\underline{V}-\underline{V}_1)$. $\qquad$ (5-19)

<u>In equilibrium</u>, using the backward distribution function for Maxwellian molecules given by (2-31), we obtain

$$\underline{\eta}_-^{(0)}(\underline{V}) = +\,n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\underline{V}\,, \qquad (5\text{-}20)$$

and for the general molecular model $\underline{\eta}_-^{(0)}(\underline{V})$ will have the form

$$\underline{\eta}_-^{(0)}(\underline{V}) = +\,\zeta\underline{V}.$$

Hence, the mean acceleration $\underline{\eta}$ in equilibrium has the following value,

$$\underline{\eta} = \tfrac{1}{2}(\underline{\eta}_+ + \underline{\eta}_-) = 0\,, \qquad (5\text{-}21)$$

which one would expect as the mean force acting on a molecule in a system in statistical equilibrium is zero.

<u>In non-equilibrium</u>, the backward equation has the form (see Chapter III),

$$-\frac{\partial ng_b}{\partial t} - \underline{v}\cdot\frac{\partial ng_b}{\partial \underline{x}} = [ng_b, f^{(0)}] - [ng_b, f'] ,$$

and so using the same method as in the forward case, we finally obtain the following result for Maxwellian molecules,

$$\underline{\eta}_- = -\left\{\frac{1}{n}\int \underline{v}[ng_b, f^{(0)}]d\underline{v}\right\}_{t=0} .$$

Hence $\underline{\eta}_-$ has the equilibrium value of (5-20), viz.

$$\underline{\eta}_- = + n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\underline{w} ,$$

and so in non-equilibrium

$$\underline{\eta} = \tfrac{1}{2}(\underline{\eta}_+ + \underline{\eta}_-) = 0. \qquad (5\text{-}22)$$

5-4 EQUIVALENCE OF MEAN ACCELERATIONS

From (5-22), we see that in non-equilibrium the mean acceleration, $\underline{\eta}$, vanishes as in the equilibrium case - a result one would not expect if we identify it with the mean accelerations of Kirkwood and the Liouville equation ($\underline{\eta}_K$ and $\underline{\eta}_L$), as from equations (6) and (14) it is seen that these accelerations must involve the gradients of the macroscopic parameters. We may therefore ask whether the mean accelerations defined using the fluctuation ensemble (and so also that mean acceleration of O'Toole and Dahler) are equivalent to those defined by Kirkwood.

(1) η_K and η_L.

In the limit of small values of τ, the η_K of Kirkwood has the form from (11) and (8),

$$mf\eta_K = -\sum_N \int \cdots \int F_{N+1} \frac{\partial \Phi_{N+1}}{\partial \underline{x}^{(1)}} \, d\underline{x}^{(2)} d\underline{y}^{(2)} \cdots d\underline{x}^{(N+1)} d\underline{y}^{(N+1)} / N!$$

$$mf\eta_K(t,\underline{x},\underline{y}) = -\sum_N \int \cdots \int F_{N+1} \Sigma_\ell \frac{\partial \Phi_{N+1}}{\partial \underline{x}^{(\ell)}} \; \delta(\underline{x}-\underline{x}^{(\ell)})\delta(\underline{y}-\underline{y}^{(\ell)})$$

$$d\underline{x}^{(1)} d\underline{y}^{(1)} \cdots d\underline{x}^{(N+1)} d\underline{y}^{(N+1)} / (N+1)!$$

Now, assuming additive two body forces,

$$mf\eta_K = -\Sigma_N \int \cdots \int F_{N+1} \Sigma_\ell \; \delta(\underline{x}-\underline{x}^{(\ell)})\delta(\underline{y}-\underline{y}^{(\ell)}) \Sigma_{j\neq l} \frac{\partial \phi^{(\ell j)}}{\partial \underline{x}^{(\ell)}} \; d\Omega_{N+1}$$

$$= -\Sigma_N \int \cdots \int F_{N+1} \Sigma_\ell \delta(\underline{x}-\underline{x}^{(\ell)})\delta(\underline{y}-\underline{y}^{(\ell)}) \Sigma_{j\neq l} \delta(\underline{x}'-\underline{x}^{(j)})\delta(\underline{y}'-\underline{y}^{(j)})$$

$$\frac{\partial \phi^{(\ell j)}}{\partial \underline{x}^{(\ell)}} \quad d\underline{x}' d\underline{y}' d\Omega_{N+1}$$

$$= -\iint f_2(t,\underline{x},\underline{y},\underline{x}',\underline{y}') \frac{\partial \phi(|\underline{x}-\underline{x}'|)}{\partial \underline{x}} \; d\underline{x}' d\underline{y}' \, .$$

Hence

$$\eta_K(\lim \tau \to 0) = -\frac{1}{m} \iint \frac{f_2(t,\underline{x},\underline{y},\underline{x}',\underline{y}')}{f(t,\underline{x},\underline{y})} \; \frac{\partial \phi(|\underline{x}-\underline{x}'|)}{\partial \underline{x}} \, d\underline{x}' d\underline{y}'$$

$$= \eta_L \, . \qquad (5\text{-}23)$$

However, to order τ - the order to which Kirkwood works - $\underline{\eta}_L$ and $\underline{\eta}_K$ are equivalent. This may be shown as follows; from equation (11)

$$m\,\underline{\eta}_K = \frac{1}{2\tau} \left< \int_{t-\tau}^{t+\tau} \underline{F}_1(t')dt' \right>$$

$$\equiv \frac{1}{2\tau} \left< \int_{-\tau}^{+\tau} \underline{F}_1(t+s)ds \right>.$$

Now using a Taylor expansion about $\underline{F}_1(t)$, s being considered macroscopically small, we obtain,

$$\underline{\eta}_K = \frac{1}{2\tau} \left< \frac{1}{m} \int_{-\tau}^{\tau} \left\{ \underline{F}_1(t) + s\frac{d}{dt}\underline{F}_1(t) + O(s^2) \right\} \right.$$

$$= \left< \frac{1}{m}\underline{F}_1(t) + O(\tau^2) \right> ,$$

which, to order τ, is the instantaneous mean acceleration $\underline{\eta}_L$. Green(3) assumes this, of course, when $\underline{\eta}_K$ replaces $\underline{\eta}_L$ in the Liouville equation, as he does not introduce the time smoothed distribution function used by Kirkwood(1), viz.

$$\bar{f} = \frac{1}{\tau} \int_0^\tau f(t+s)ds.$$

This concept of time smoothing is usually introduced to allow for the experimental inaccuracy of the physical measurements.

and serves a useful purpose in the macroscopic theory of the Brownian movement. However, in other physical theories lack of precision does not normally require the introduction of a parameter such as τ, and it is presumably unnecessary in a rigorous molecular theory.

(2) The definitions introduced above and those of Kirkwood.

From the General Introduction, $\underline{n}_{+}^{(0)}$ of Kirkwood has the exact form,

$$m\underline{n}_{+}^{(0)}=\Sigma_N\int\cdots\int\frac{F^{0}_{N+1}}{f^{(0)}}\;\frac{1}{\tau}\int_t^{t+\tau}\left(-\frac{\partial\Phi_{N+1}}{\partial\underline{x}^{(1)}}\right)dt'\,\underline{dx}^{(2)}\underline{dy}^{(2)}\cdots\underline{dx}^{(N+1)}\underline{dy}^{(N+1)}/$$

$$m\underline{n}_{+}^{(0)}(t,\underline{x}_1,\underline{y}_1)=\Sigma_N\int\cdots\int\frac{F^{0}_{N+1}}{f^{(0)}}\Sigma_l\,\delta(\underline{x}_1-\underline{x}^{(l)})\,\delta(\underline{y}_1-\underline{y}^{(l)})\,\Sigma_j\frac{1}{\tau}\int_t^{t+\tau}$$

$$\left(-\frac{\partial\phi^{lj}}{\partial\underline{x}^{(l)}}\right)dt'\;\underline{dx}^{(1)}\underline{dy}^{(1)}\cdots\underline{dx}^{(N+1)}\underline{dy}^{(N+1)}/(N+1)!$$

$$=\Sigma_N\int\cdots\int\frac{F^{0}_{N+1}}{f^{(0)}}\Sigma_l\,\delta(\underline{x}_1-\underline{x}^{(l)})\,\delta(\underline{y}_1-\underline{y}^{(l)})\,\Sigma_j\,\frac{1}{\tau}\int_0^{\tau}\underline{F}_l^{\,j}(t+s)\,ds\;d\Omega_{N+1}.$$

(5-24)

where $\underline{F}_l^{\,j}$ is the force* on the l^{th} molecule due to its interaction with the j^{th} molecule. We recognize the distribution,

$$\frac{F^{0}_{N+1}}{f^{(0)}}\;\Sigma_l\,\delta(\underline{x}_1-\underline{x}^{(l)})\,\delta(\underline{y}_1-\underline{y}^{(l)})$$

---

* $\underline{F}_l^{\,l}=0$.

as the initial value of the phase space distribution function corresponding to the special sub-ensemble of the grand ensemble of statistical equilibrium that was introduced in Chapter I, i.e. from equation (1-5),

$$\chi_N^o\,(t+s) = \frac{F^o_{N+1}}{f^{(o)}}\,\Sigma_l\,\delta(\underline{x}_1-\underline{x}^{(l)})\,\delta(\underline{v}_1-\underline{v}^{(l)}),\ \text{for } s=o.$$

In this subensemble, the ith molecule in each configuration at time t is distinguished by having specified velocity and position, $\underline{v}_1$ and $\underline{x}_1$ respectively. Hence we may write (5-24) as,

$$\underline{\Pi}_+^{(o)} = \frac{1}{\tau}\int_o^\tau \Sigma_N \int\cdots\int \chi^o_{N+1}(t+s)\,\Sigma_j\frac{\underline{F}_1{}^{j}}{m}(t+s)\,ds\; d\Omega_{N+1}. \quad (5\text{-}25)$$

and so in going from (5-24) to (5-25) we have replaced the time independent equilibrium ensemble by the time dependent fluctuation ensemble.

To compare the $\underline{\Pi}_+^{(o)}$ above with that introduced in section (5-3), we wish to take the average using the one-particle velocity distribution function associated with the distinguished molecule. This function was defined in Chapter I and is given by

$$g(t+s,\underline{x},\underline{v};\underline{x}_1,\underline{v}_1) = \langle\delta(\underline{x}-\underline{x}_s)\,\delta(\underline{v}-\underline{v}_s)\rangle_\chi$$

where $\underline{x}_s$,$\underline{v}_s$ are the position and velocity of the molecule whose position and velocity at time s=o is $\underline{x}_1$ and $\underline{v}_1$.

We may write (5-25) as,

$$m\underline{\eta}_+^{(o)} = \frac{1}{\tau}\int_0^{\tau} \Sigma_N \int\int\cdot\cdot\int \chi^{o}_{N+1}(t+s)\,\delta(\underline{x}-\underline{x}_s)\,\delta(\underline{v}-\underline{v}_s)$$

$$\Sigma_j\, \underline{F}_1^{\,j}(t+s)\; ds\; d\Omega_{N+1}\, \underline{dx}\; \underline{dv}$$

which is equivalent to

$$\underline{\eta}_+^{(o)} = \frac{1}{\tau}\int_0^{\tau} \langle \underline{\eta}_1 \rangle^{g}(t+s)\,ds, \qquad (5\text{-}26)$$

where $\underline{\eta}_1$ is the instantaneous mean acceleration of the distinguished molecule and the distribution function g is associated with the motion of the distinguished molecule. However, if the limit from the formula (5-9) is omitted, then definition (5-9) is equivalent to

$$\frac{\langle \underline{v} \rangle^{g}\,(t+\tau) - \langle \underline{v} \rangle^{g}\,(t)}{\tau}\,, \qquad (5\text{-}27)$$

where the distinguished molecule has velocity $\underline{v}_1$ at time t. Formula (5-27) may be written as

$$\frac{1}{\tau}\int_t^{t+\tau} \frac{d}{dt'}\,\langle \underline{v} \rangle^{g} dt' \qquad (5\text{-}28)$$

and so we see the important difference between our definition

(5-28) (and therefore that of O'Toole and Dahler) and that of Kirkwood. In (5-26), we are essentially differentiating before the average with the special ensemble is taken. In the limit of small $\tau \to 0^+$, we may proceed as we have in the derivation of (5-23), and so $\eta_+^{(0)}$ will have the equilibrium form of η_K, i.e. $\eta_+^{(0)} = 0$. However, in (5-28) the average is taken with the special ensemble <u>before</u> the differentiation and so is not equivalent to (5-25) as the distribution function is time dependent. Because of this difference, when we take the limit as $\tau \to 0^+$ as we have in (5-9), the equilibrium value, viz. $\eta_+^{(0)} = 0$, is not obtained. The plateau time τ plays no essential part in the present theory and the limit $\tau \to 0^+$ is implied.

The same arguments apply of course, to the backward accelerations and the "non-equilibrium" accelerations.

5-5. THE MEAN RATE OF CHANGE OF ENERGY, ENERGY FLUX, MOMENTUM AND MOMENTUM FLUX AT TIME t=0 USING THE CORRELATION FUNCTION.

(1) Momentum

In section (5-3) above, we have calculated for Maxwellian molecules the mean rate of change of momentum for the distinguished molecule at time t=o, and shown that the values for "equilibrium" and "non-equilibrium" are the same i.e.

$$m\left\{\frac{D}{Dt}\langle\underline{V}\rangle^{g}\right\}_{t=0}$$

$$= m\left\{\frac{1}{n}\frac{\partial}{\partial t}\int ng\,\underline{V}\,\underline{dv} - \frac{\underline{V}_1}{n}\frac{\partial}{\partial t}\int ng\,\underline{dv}\right\}_{t=0}$$

$$= -m\, n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\underline{V}_1 \;.$$

(2) Kinetic Energy

A similar result[†] is found for the mean rate of change of the kinetic energy at time t=0 (called the power consumption(2)) for Maxwellian molecules, viz.

$$\left\{\frac{D}{Dt}\langle\tfrac{1}{2}mv^2\rangle^{g}\right\}_{t=0}$$

$$= \tfrac{1}{2}m\left\{\frac{1}{n}\frac{\partial}{\partial t}\int ng\,v^2\,\underline{dv} - \frac{\underline{V}_1^{\,2}}{n}\frac{\partial}{\partial t}\int ng\,\underline{dv}\right\}_{t=0}$$

$$= n\pi A_1(5)\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\left[{}^3/2\;kT-\tfrac{1}{2}mv_1^{\,2}+\tfrac{1}{2}mu^2\right] ,$$

for both "equilibrium" and "non-equilibrium".

[†] Note footnote page 5.6

(3) Momentum Flux

The mean rate of change of the total momentum flux at time t=o in "equilibrium" is given by,

$$m\left\{\frac{\partial}{\partial t}\langle \underline{V}\,\underline{V}\rangle^{g}\right\}_{t=o}$$

$$= m\left\{\int \underline{V}\,\underline{V}[g,f^{(0)}]\underline{dv}\right\}_{t=o} .$$

For Maxwellian molecules this gives,

$$mn\pi\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\left[\frac{A_1(5)}{\beta m}\left(1-\frac{1}{3}\beta m w_1^{2}\right)\underline{\underline{\delta}} - \left(A_1(5)+\frac{3}{4}A_2(5)\right)\left(\underline{W}_1\underline{W}_1-\frac{1}{3}w_1^{2}\underline{\underline{\delta}}\right)\right.$$

$$\left. - A_1(5)\underline{u}\,\underline{W}_1 - A_1(5)\underline{W}_1\underline{u}\right] .$$

In non-equilibrium the above becomes,

$$m\left\{\frac{D}{Dt}\langle \underline{V}\,\underline{V}\rangle^{g}\right\}_{t=o}$$

$$= m\left\{\frac{1}{n}\int \underline{V}\,\underline{V}[ng,f^{(0)}]\underline{dv}\right\}_{t=o} + m\left\{\frac{1}{n}\int \underline{W}\,\underline{W}[ng,f']\underline{dw}\right\}_{t=o} .$$

For Maxwellian molecules we obtain,

$$mn\pi\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\left[\frac{A_1(5)}{\beta m}\left(1-\frac{1}{3}\beta m w_1^2\right)\underline{\underline{\delta}}-\left(A_1(5)+\frac{3}{4}A_2(5)\right)\left(\underline{w}_1\underline{w}_1-\frac{1}{3}w_1^2\underline{\underline{\delta}}\right)\right.$$

$$\left.-A_1(5)\underline{u}\,\underline{w}_1-A_1(5)\underline{w}_1\underline{u}\right]-\frac{1}{\beta}\left(\frac{4}{3}\frac{A_1(5)}{A_2(5)}-1\right)\frac{\partial_{\rho}\underline{u}}{\underline{\partial x}}\,.$$

(4) Energy Flux

The mean rate of change of the total energy flux at time t=o is given by,

$$\tfrac{1}{2}m\left\{\frac{\partial}{\partial t}\langle v^2\,\underline{v}\rangle^g\right\}_{t=o}$$

$$=\tfrac{1}{2}m\left\{\int v^2\,\underline{v}\,[g,f^{(0)}]\,d\underline{v}\right\}_{t=o}\,.$$

For Maxwellian molecules this gives,

$$\tfrac{1}{2}mn\pi\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\left[\frac{5}{2\beta m}A_2\underline{w}_1+\frac{5}{\beta m}A_1\underline{u}+\left(\tfrac{1}{2}A_2-A_1\right)w_1^2\underline{u}-A_1u^2\underline{w}_1\right.$$

$$\left.-\left(2A_1+\frac{3}{2}A_2\right)\underline{w}_1\underline{w}_1\cdot\underline{u}-2A_1\,\underline{u}\,\underline{u}\cdot\underline{w}_1\right].$$

In "non-equilibrium", the mean rate of change of the total energy flux at time $t=0$ is given by,

$$\tfrac{1}{2}m\left\{\frac{D}{Dt}\langle v^2\underline{v}\rangle^g\right\}_{t=0}$$

$$=\tfrac{1}{2}m\left\{\int v^2\underline{v}[g,f^{(0)}]d\underline{v}\right\}_{t=0}+\left\{\frac{1}{n}\int\tfrac{1}{2}mv^2\underline{v}[ng,f']d\underline{v}\right\}_{t=0}.$$

For Maxwellian molecules this gives,

$$\tfrac{1}{2}mn\pi\left(\frac{2\kappa}{m}\right)^{\frac{1}{2}}\left[\frac{5}{2\beta m}A_2\underline{W}_1+\frac{5}{\beta m}A_1\underline{u}+(\tfrac{1}{2}A_2-A_1)W_1^2\underline{u}-A_1u^2\underline{W}_1\right.$$

$$\left.-(2A_1+\frac{3}{2}A_2)\underline{W}_1\underline{W}_1\cdot\underline{u}-2A_1\underline{u}\,\underline{u}\cdot\underline{W}_1\right]-\frac{1}{\beta}\left(\frac{4}{3}\frac{A_1}{A_2}-1\right)\underline{u}\cdot\frac{\partial_s\underline{u}}{\partial\underline{x}}$$

$$-\frac{5}{2}\frac{1}{\beta^2m}\left(\frac{A_1}{A_2}-\tfrac{1}{2}\right)\frac{1}{T}\frac{\partial T}{\partial\underline{x}}.$$

From the above we see that there are differences in the expressions between the "equilibrium" and "non-equilibrium" momentum and energy fluxes which involve the velocity and temperature gradients. This is probably what an experimentalist could look for.

REFERENCES

(1) J.G. Kirkwood, J. Chem. Phys. <u>14</u>, 180 (1946)

(2) J.T. O'Toole and J.S. Dahler, J. Chem. Phys. <u>33</u>, 1496 (1960)

(3) H.S. Green, "Handbuch der Physik" (Springer-Verlag, Berlin, 1960) Vol.10 p112 and following.

APPENDIX A.

In the Appendices we are concerned with the evaluations used in Chapters 11, 111, and V. The algebra is heavy and so for this reason only final results are usually given.

A.1 Eigenfunctions of the half-Boltzmann collision operator.

The half-Boltzmann collision operator was defined in Chapter 11 and is given by

$$L g \equiv [g, f^{(0)}] = \iiint \{ g(\underline{w}_0) f^{(0)}(w_0') - g(\underline{w}) f^{(0)}(w') \} \sigma \, \underline{db} \, \underline{dw}', \tag{1}$$

and so the following relation for Maxwellian molecules, quoted in section 2.5, is to be verified;

$$- \lambda_{r\ell} \, e^{-\frac{1}{2}\beta m w^2} S^{(r)}_{\ell+\frac{1}{2}} (\tfrac{1}{2}\beta m w^2) P_\ell(\cos\theta) \, w^\ell$$
$$= \left[e^{-\frac{1}{2}\beta m w^2} S^{(r)}_{\ell+\frac{1}{2}} (\tfrac{1}{2}\beta m w^2) P_\ell(\cos\theta) \, w^\ell , f^{(0)} \right], \tag{2}$$

where;

$S^{(r)}_{\ell+\frac{1}{2}}(\frac{1}{2}\beta m w^2)$ are the Sonine polynomials given by the coefficient of s^n in the expansion of

$$(1-s)^{-\ell-3/2} \, e^{-\frac{1}{2}\beta m w^2 s/1-s}, \tag{3}$$

$P_\ell(\cos\theta)$ are the Legendre polynomials,

$\lambda_{r\ell}$ are the eigenvalues (independent of the molecular velocity w).

Now let us take,

$$\begin{aligned} h &= [e^{-\frac{1}{2}\beta m w^2} L_0(\tfrac{1}{2}\beta m w^2), f^{(0)}], \\ \underline{h} &= [e^{-\frac{1}{2}\beta m w^2} L_1\, \underline{w}, f^{(0)}], \\ \underline{\underline{h}} &= [e^{-\frac{1}{2}\beta m w^2} L_2 (\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}), f^{(0)}], \\ &\vdots \qquad\qquad \vdots \end{aligned} \tag{4}$$

then, since the functions $\underline{w}, \underline{w}\,\underline{w} - \frac{1}{3}w^2\underline{\underline{\delta}}, \ldots$ are unique[+],

$$\begin{aligned} h &\equiv h_0(\tfrac{1}{2}\beta m w^2), \\ \underline{h} &\equiv h_1(\tfrac{1}{2}\beta m w^2)\, \underline{w}, \\ \underline{\underline{h}} &\equiv h_2(\tfrac{1}{2}\beta m w^2)(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}), \\ &\vdots \qquad\qquad \vdots \end{aligned} \tag{5}$$

[+] i.e. $\underline{w}$ is the only vector that can be formed.

$(\underline{w}\,\underline{w} - \frac{1}{3}w^2\underline{\underline{\delta}})_{ij} \equiv w_i w_j - \frac{1}{3} w^2 \delta_{ij}$ is unique in the sense that it is the only second order tensor that can be formed with zero trace (i.e. $i = j$).

$$(\underline{w}\,\underline{w}\,\underline{w} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}\,\underline{w} - \tfrac{1}{5} w^2 \underline{w}\,\underline{\underline{\delta}} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}'\underline{w})_{ijk}$$

$\equiv w_i w_j w_k - \frac{1}{5} w^2 \delta_{ij} w_k - \frac{1}{5} w^2 \delta_{jk} w_i - \frac{1}{5} w^2 \delta_{ik} w_j$ is unique in the sense that it is the only third order tensor that can be formed with zero trace (viz. $i = j$ and $j = k$), and so on.

where

$$h_1(\tfrac{1}{2}\beta m w^2) = [e^{-\frac{1}{2}\beta m w^2} L_1 \underline{w}, f^{(0)}] \cdot \underline{w}/w^2 ,$$

$$h_2(\tfrac{1}{2}\beta m w^2) = [e^{-\frac{1}{2}\beta m w^2} L_2 (\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}), f^{(0)}] : \underline{w}\,\underline{w}/\tfrac{2}{3} w^4 ,$$

(6)

Therefore if the components of the vector w are taken in (5) in the polar angle form, viz. ($w\sin\theta\cos\phi$, $w\sin\theta\sin\phi$, $w\cos\theta$), then the eigenfunctions involve $P_\ell^m(\cos\theta)\, e^{im\phi}$. The eigenvalues below will, of course, be independent of m.

So from (4), (5) and (6), let $L_{r0}(\tfrac{1}{2}\beta m w^2)$, $L_{r1}(\tfrac{1}{2}\beta m w^2)$, ... be the solutions of the integral equations,

$$[e^{-\frac{1}{2}\beta m w^2} L_{r0}, f^{(0)}] = -\lambda_{r0} L_{r0}\, e^{-\frac{1}{2}\beta m w^2} ,$$

$$[e^{-\frac{1}{2}\beta m w^2} L_{r1} \underline{w}, f^{(0)}] \cdot \underline{w}/w^2 = -\lambda_{r1} L_{r1}\, e^{-\frac{1}{2}\beta m w^2} ,$$

$$\vdots$$

(7)

and so on,

where the $\lambda_{r0}, \lambda_{r1}, \ldots$ are the corresponding eigenvalues. In the case of Maxwellian molecules, these eigenfunctions are shown below to be the Sonine polynomials.

The Sonine polynomials will now be shown to be the eigenfunctions for the Maxwellian molecules corresponding to each value of in the above.

The polynomials corresponding to $\ell = 0$ are the polynomials $S^{(r)}_{1/2}(\tfrac{1}{2}\beta m w^2)$. This is shown by using the orthogonality relation

$$\int e^{-x}\, S_{1/2}^{(k)}(x)\, S_{1/2}^{(l)}(x)\, x^{1/2}\, dx = c_k\, \delta_{kl}.$$

So if $S_{1/2}^{(k)}$ are the eigenfunctions, then from (1)

$$\iiint e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w') \; S_{1/2}^{(l)}(\tfrac{1}{2}\beta m w^2) \left[S_{1/2}^{(k)}(\tfrac{1}{2}\beta m w_0^2) - S_{1/2}^{(k)}(\tfrac{1}{2}\beta m w^2) \right] \sigma\, \underline{db}\, \underline{dw'}\, \underline{dw} = c_k\, \delta_{kl}. \qquad (8)$$

Using the generating function (3), for relation (8) to hold, if

$$F(s,t) = \frac{1}{(1-s)^{3/2}(1-t)^{3/2}} \iiint e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w')\, e^{-\frac{1}{2}\beta m T w^2} \left[e^{-\frac{1}{2}\beta m S w_0^2} - e^{-\frac{1}{2}\beta m S w^2} \right] \sigma\, \underline{db}\, \underline{dw'}\, \underline{dw},$$

$$\left(T \equiv \frac{t}{1-t}, \; S \equiv \frac{s}{1-s} \right), \qquad (9)$$

F(s,t) must be a function of (st) alone. This is proved in a method similar to that used by Chapman and Cowling (C.C.) section 9.3.

If $\underline{\sigma}_0 = \underline{w}_0' - \underline{w}_0$ and $\underline{\sigma} = \underline{w}' - \underline{w}$ and $\underline{\sigma} \cdot \underline{\sigma}_0 = \sigma^2 \cos\chi$ then for Maxwellian molecules[+] formula (9) may be written as

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[+] Note Chapman and Cowling (C.C.) page 174.

$$F(s,t) = \frac{1}{(1-s)^{3/2}(1-t)^{3/2}} \int (H(x) - H(0))\, \sigma\, \underline{db},$$

where

$$H(x) = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \iint e^{-\frac{1}{2}\beta m (w^2 + w'^2 + Tw^2 + Sw_0^2)}\, \underline{dw'}\,\underline{dw}. \qquad (10)$$

Now, if $\underline{G} = \underline{w} + \underline{w}'$, $\underline{v} = \underline{G} - \frac{1}{a}(T\underline{\sigma} + S\underline{\sigma}_0)$, $a = S + T + 2$, and $b = a - \frac{1}{a}(S^2 + T^2 + 2ST\cos x)$, then (10) takes the simpler form

$$H(x) = n\left(\frac{\beta m}{2\pi}\right)^{3/2} \iint \exp\left(-\tfrac{1}{8}\beta m[av^2 + b\sigma^2]\right) \underline{dv}\,\underline{d\sigma}$$

$$= n\left(\frac{\beta m}{2\pi}\right)^{3/2} \left(\frac{8\pi}{\beta m}\right)^{3} \frac{1}{a^{3/2}\, b^{3/2}}.$$

Hence, finally we obtain

$$F(s,t) = A \int \left\{ [2 - st(1 + \cos x)]^{-3/2} - [2 - 2st]^{-3/2} \right\} \sigma\, \underline{db}$$

(A = constant)

and so when the integration over the cross section is performed we will have a function of st alone.

Similarly to prove that the polynomials corresponding to the value $\ell = 1$ are $S_{3/2}^{(r)}(\frac{1}{2}\beta m w^2)$, we must prove that

$$F_1(s,t) = \frac{1}{(1-s)^{5/2}(1-t)^{5/2}} \iiint e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w') \, e^{-\frac{1}{2}\beta m T w^2}$$

$$\left[e^{-\frac{1}{2}\beta m S w_0^2}\, \underline{w}\cdot\underline{w}_0 - e^{-\frac{1}{2}\beta m S w^2}\, w^2 \right] \sigma\, \underline{db}\, \underline{dw'}\,\underline{dw}$$

is a function of (st) alone. Using the above method we finally obtain

$$F_1(s,t) = \; , A\int\left\{\left[2-st(1+\cos\chi)\right]^{-5/2}(1+\cos\chi) - \left[2-st\right]^{-5/2}\right\}\sigma\, d\underline{b}_s$$

which is also a function of (st) alone, thus proving the orthogonality.

A similar result may be found by the same method for $\ell=2$.

The method could be used for higher ℓ, but the algebra becomes very long, and so we assume that the Sonine polynomials are the eigenfunctions for higher values of ℓ. Actually all the calculations used in the thesis only require the Sonine polynomials for the above values of ℓ, and the higher values are not required.

A.2 Eigenvalues.

The eigenvalues corresponding to the above eigenfunctions may be found by direct substitution into the collision integral and then by direct calculation. The calculations follow those of Chapman and Cowling (C.C.) page 175, and so only the calculation of λ_{01} will be given here briefly.

We wish to find the eigenvalue corresponding to the eigenfunction $e^{-\frac{1}{2}\beta m w^2}\underline{w}$. Substituting in the collision integral (1),

$$-\lambda_{01}\, e^{-\frac{1}{2}\beta m w^2}\underline{w} = \iint e^{-\frac{1}{2}\beta m w^2}(\underline{w}_0-\underline{w})\, e^{-\frac{1}{2}\beta m w'^2} n\left(\frac{\beta m}{2\pi}\right)^{3/2}\sigma\, d\underline{b}\, d\underline{w}'$$

$$= \frac{1}{2}\iint e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w') \, (\underline{\sigma} - \underline{\sigma}_0) \, \sigma \, d\underline{b} \, d\underline{w}'$$

$$= \frac{1}{2}\iiint e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w') \left[\underline{\sigma}(1-\cos\chi) - \sigma \underline{h} \sin\chi \cos\epsilon - \sigma \underline{i} \sin\chi \sin\epsilon \right] \sigma \, db \, d\epsilon \, d\underline{w}'$$

$$= \pi \int e^{-\frac{1}{2}\beta m w^2} f^{(0)}(w') \left(\frac{2K}{m}\right)^{1/2} A_1(s) \, \underline{\sigma} \, d\underline{w}',$$

where $2\pi \left(\frac{2K}{m}\right)^{1/2} A_\ell(s) = \int (1-\cos^\ell \chi) \, \sigma \, db,$

and $A_\ell(s)$ are tabulated p.172 C.C.

This gives $\lambda_{01} = n\pi A_1(s) \left(\frac{2K}{m}\right)^{1/2}.$

Using the same method the following eigenvalues, used in the thesis, were calculated;

$$\lambda_{00} = 0 \qquad \lambda_{10} = n\pi A_1(s) \left(\frac{2K}{m}\right)^{1/2} \qquad \lambda_{20} = n\pi (A_1(s) + A_2(s)) \left(\frac{2K}{m}\right)^{1/2}$$

$$\lambda_{01} = \lambda_{10} \qquad \lambda_{11} = n\pi \left(A_1(s) + \frac{1}{2} A_2(s)\right) \left(\frac{2K}{m}\right)^{1/2}$$

$$\lambda_{02} = n\pi \left(A_1(s) + \frac{3}{4} A_2(s)\right) \left(\frac{2K}{m}\right)^{1/2}.$$

A.3 Miscellaneous.

For the evaluations in Appendix B we need the values of $\left[g_e, e^{-\frac{1}{2}\beta m w^2} (\underline{w}\underline{w} - \frac{1}{3} w^2 \underline{\underline{S}})\right]$ and $\left[g_e, e^{-\frac{1}{2}\beta m w^2} S^{(1)}_{3/2} \underline{w}\right].$
By using the method of A.1(b), we can show, after heavy algebra, that

$$\iiint f^{(0)} f^{(0)}(w') \, S^{(\ell)}_{3/2}(\tfrac{1}{2}\beta m w^2) \Big\{ S^{(k)}_{1/2}(\tfrac{1}{2}\beta m w_0'^2) \, \underline{w}_0' \cdot \underline{w} \, (\tfrac{1}{2}\beta m w_0'^2 - \tfrac{5}{2})$$

$$- S^{(k)}_{1/2}(\tfrac{1}{2}\beta m w'^2) \, \underline{w}' \cdot \underline{w} \, (\tfrac{1}{2}\beta m w'^2 - \tfrac{5}{2}) \Big\} \sigma \, d\underline{b} \, d\underline{w}' d\underline{w}$$

$$= c_k \, \delta_{\ell+1,k}, \tag{11}$$

i.e. it is found that,

$$F_2(s,t) = \frac{1}{(1-s)^{3/2}(1-t)^{5/2}} \iiint f^{(0)} f^{(0)}(w') \, e^{-\frac{1}{2}\beta m T w^2} \Big\{ e^{-\frac{1}{2}\beta m S w_0^2}$$

$$(\tfrac{1}{2}\beta m w_0'^2 - 5/2)\, \underline{w}_0' \cdot \underline{w} - e^{-\frac{1}{2}\beta m S w^2} (\tfrac{1}{2}\beta m w'^2 - 5/2)\, \underline{w}' \cdot \underline{w} \Big\} \sigma \, \underline{db}\, \underline{dw'}\, \underline{dw}$$

$$= {}_2A \int t \, [1 - st(1+\cos\chi)]^{-7/2} \left[(1-\cos^2\chi) - 2(1-\cos\chi) \right] \sigma \, \underline{db} \, ,$$

$$({}_2A = \text{constant})$$

i.e. $F_2(s,t) = t \, F_3(st)$, which establishes (11).

Also, using the method of A.2 it is found, after heavy algebra, that

$$\left[e^{-\frac{1}{2}\beta m w^2} \underline{w} \, , \, e^{-\frac{1}{2}\beta m w^2} S_{3/2}^{(1)}(\tfrac{1}{2}\beta m w^2) \underline{w} \right]$$

$$= -\frac{\pi}{24} \left(A_3(5) + A_2(5) - A_1(5) \right) \left(\frac{2K}{m} \right)^{1/2} e^{-\frac{1}{2}\beta m w^2} S_{5/2}^{(1)}(\tfrac{1}{2}\beta m w^2)$$

$$\left(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}} \right).$$

We therefore assume that if

$$g_e = e^{-\frac{1}{2}\beta m w^2} \sum_{r} \Big\{ S_{1/2}^{(r)}(\tfrac{1}{2}\beta m w^2) + S_{3/2}^{(r)}(\tfrac{1}{2}\beta m w^2)\, \underline{a} \cdot \underline{w} + \ldots \Big\} \qquad (12)$$

then

$$\left[g_e , e^{-\frac{1}{2}\beta m w^2} (\tfrac{5}{2} - \tfrac{1}{2}\beta m w^2) \underline{w} \right]$$

$$= e^{-\frac{1}{2}\beta m w^2} \sum_r \Big[a_r^{(0)} \; S_{3/2}^{(r+1)}(\tfrac{1}{2}\beta m w^2)\, \underline{w}$$

$$+ a_r^{(1)} \; S_{5/2}^{(r+1)}(\tfrac{1}{2}\beta m w^2)\, \underline{a}\cdot(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}})$$

$$+ \ldots \Big].$$

Similarly, since

$$\big[f^{(0)}, e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}})\big] + \big[e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}), f^{(0)}\big]$$

$$= -\mu_{02}\, e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}),$$

i.e.

$$\big[f^{(0)}, e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}})\big] = (\lambda_{02} - \mu_{02})\, e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}),$$

then we make a similar assumption to the above, i.e. using (12)

$$\big[g_e, e^{-\frac{1}{2}\beta m w^2}(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}})\big]$$

$$= e^{-\frac{1}{2}\beta m w^2} \sum_r \Big[b_r^{(0)} \; S_{5/2}^{(r)}(\tfrac{1}{2}\beta m w^2)\, (\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}})$$

$$+ b_r^{(1)} \; S_{7/2}^{(r)}\, \underline{a}\cdot(\underline{w}\,\underline{w}\,\underline{w} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}\,\underline{w} - \tfrac{1}{5} w^2 \underline{w}\,\underline{\underline{\delta}} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}'\underline{w})$$

$$+ \ldots \Big].$$

APPENDIX B: Calculations involved in Chapters 111 and V.

In this appendix, the calculations involved in the solution of the half Boltzmann equation for non-equilibrium discussed in Chapter 111 are given. In the first part the equations are solved for the general gas-model with a temperature gradient, number density gradient and mass velocity gradient.

In the second part certain results are obtained using the solution for Maxwellian molecules. These results are quoted in Chapters 111 and V.

1. GENERAL MOLECULAR MODEL.

B.1 Solution involving Temperature Gradient - solution of equation (3.14).

The linear equation [+](3.16) has been divided into,

$$\frac{\partial G}{\partial t_{exp}} - [G, f^{(0)}] = -\underline{w} \cdot \frac{\partial g_e}{\partial \underline{x}} - \frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}}, \qquad (1)$$

$$\frac{\partial G}{\partial t_{exp}} - [G, f^{(0)}] = [g_e, f'], \qquad (2)$$

$$\frac{\partial G}{\partial t_{exp}} - [G, f^{(0)}] = 0, \qquad (3)$$

[+] If the definition $\underline{w}_1 = \underline{v}_1 - \underline{u}(\underline{x}, t)$ is used, an extra term "$-\frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}_1}$" must be added to the right hand side of equation (1).

where g_e is given by the equilibrium solution (2.13). We therefore wish to solve (1), (2) and (3) with the boundary condition given by (3.20), viz.

$$G = 0. \tag{4}$$

In the solution of these equations the temperature gradient will be resolved into two components - one component parallel to the velocity $\underline{w}_1$ and the other perpendicular to $\underline{w}_1$ in the plane containing $\underline{w}_1$ and $\frac{\partial T}{\partial \underline{x}}$, i.e.

$$\begin{aligned}\frac{\partial T}{\partial \underline{x}} &= \hat{\underline{w}}_1 \cdot \frac{\partial T}{\partial \underline{x}}\, \hat{\underline{w}}_1 + \hat{\underline{w}}_1 \times \left(\frac{\partial T}{\partial \underline{x}} \times \hat{\underline{w}}_1\right) \\ &\equiv \frac{\partial T}{\partial x_{\parallel}}\, \hat{\underline{w}}_1 + \frac{\partial T}{\partial x_{\perp}}\, \hat{\underline{a}}\,, \end{aligned} \tag{5}$$

and we will take $\underline{w} \cdot \hat{\underline{w}}_1 = w \cos\theta$ and $\underline{w} \cdot \hat{\underline{a}} = w \sin\theta \cos\phi$.

Firstly, consider terms in G that involve $\frac{\partial T}{\partial x_{\parallel}}$ - terms containing $\frac{\partial T}{\partial x_{\perp}}$ will be similar but will involve terms in the associated Legendre polynomial $P_\ell^1(\cos\theta)$.

(a) Solution of (1):-

If the recurrence relations, etc. of the $L_{r\ell}$ polynomials, and the relations,

$$\begin{aligned}(2\ell+1)x P_\ell(x) &= (\ell+1) P_{\ell+1} + \ell P_{\ell-1} \\ (2\ell+1)(1-x^2) P_\ell'(x) &= \ell(\ell+1)\left[P_{\ell-1} - P_{\ell+1}\right], \end{aligned} \tag{6}$$

are used, the following expansion may be employed in (1);

$$
\begin{aligned}
&-\underline{w}\cdot\frac{\partial g_e}{\partial \underline{x}}-\frac{1}{\beta m}\frac{1}{T}\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial g_e}{\partial \underline{w}}\\
&= e^{-\frac{1}{2}\beta m w^2}\sum_{rli}\Big\{F^{(1)}_{rli}\;L_{il+1}w^{l+1}P_{l+1}(\cos\theta)\,e^{-\lambda_{rl}t}\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}\\
&\qquad + F^{(2)}_{rli}\;L_{il-1}w^{l-1}P_{l-1}(\cos\theta)\,e^{-\lambda_{rl}t}\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}\\
&\qquad + F^{(3)}_{rli}\;L_{il+1}w^{l+1}P_{l+1}(\cos\theta)\,te^{-\lambda_{rl}t}\frac{\partial \lambda_{rl}}{\partial T}\frac{\partial T}{\partial x_{\parallel}}\\
&\qquad + F^{(4)}_{rli}\;L_{il-1}w^{l-1}P_{l-1}(\cos\theta)\,te^{-\lambda_{rl}t}\frac{\partial \lambda_{rl}}{\partial T}\frac{\partial T}{\partial x_{\parallel}}\Big\},
\end{aligned}
\tag{6a}
$$

where L_{il+1} is always taken as a function of $\frac{1}{2}\beta m w^2$ unless otherwise indicated, and $F^{(j)}_{rli}$ are all functions of $w_{\parallel}$. In the solution we must consider the possibility of degenerate eigenvalues. We make the assumption that we may have equal eigenvalues only for different values of "l" in λ_{rl} i.e. in the expansion (6a) above for each particular value of r, l, we may have

$$\lambda_{a,l+1}=\lambda_{rl} \quad \text{or} \quad \lambda_{b,l-1}=\lambda_{rl}\ , \tag{7}$$

for only one value of "a" and "b". However, if this assumption is not valid then further summations must be introduced. For all values of r, l, there may be certain values a(r,e) and b(r,l) for which relation (7) holds - these values are considered separately in the solution.

Take

$$G=\sum_{rli}\left(G^{(0)}_{rli}\,e^{-\lambda_{rl}t}+G^{(1)}_{rli}\,te^{-\lambda_{rl}t}+G^{(2)}_{rli}\,t^2e^{-\lambda_{rl}t}\right). \tag{8}$$

If (7) holds and if $G^{(1)}_{rla}$ has the form

$$G^{(1)}_{rla} = F_1(w_1)\, L_{al+1}\, w^{l+1}\, P_{l+1}\, \frac{1}{T}\frac{\partial T}{\partial x_{\parallel}},$$

then for this value of r,l

$$-\lambda_{rl}\, G^{(1)}_{rla} - [G^{(1)}_{rla}, f^{(0)}] = 0 .$$

Similarly, if $G^{(1)}_{rlb}$ has the form

$$G^{(1)}_{rlb} = F_2(w_1)\, L_{bl-1}\, w^{l-1}\, P_{l-1}\, \frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}$$

then

$$-\lambda_{rl}\, G^{(1)}_{rlb} - [G^{(1)}_{rlb}, f^{(0)}] = 0.$$

Hence we must take the following contributions

$$G^{(2)}_{rla} = \frac{1}{2}\, e^{-\frac{1}{2}\beta m w^2}\, \frac{\partial T}{\partial x_{\parallel}}\, \frac{\partial \lambda_{rl}}{\partial T} \left\{ F^{(3)}_{rla}\, L_{al+1}\, w^{l+1}\, P_{l+1} \right\} \qquad (9)$$

and

$$G^{(1)}_{rlb} = \frac{1}{2}\, e^{-\frac{1}{2}\beta m w^2}\, \frac{\partial T}{\partial x_{\parallel}}\, \frac{\partial \lambda_{rl}}{\partial T} \left\{ F^{(4)}_{rlb}\, L_{bl-1}\, w^{l-1}\, P_{l-1} \right\}, \qquad (10)$$

and for all other values of i, $G^{(2)}_{rli} = 0.$

For $i \neq a$ the contribution from $F^{(3)}_{rli}$ is

$$G^{(1)}_{rli} = e^{-\frac{1}{2}\beta m w^2}\, \frac{\partial T}{\partial x_{\parallel}}\, \frac{\partial \lambda_{rl}}{\partial T} \left\{ \frac{1}{(\lambda_{il+1} - \lambda_{rl})}\, F^{(3)}_{rli}\, L_{il+1}\, w^{l+1}\, P_{l+1} \right\}, \qquad (11)$$

and for $i \neq b$ the contribution from $F^{(4)}_{rli}$ is

$$G^{(1)}_{rli} = e^{-\frac{1}{2}\beta m w^2}\, \frac{\partial T}{\partial x_{\parallel}}\, \frac{\partial \lambda_{rl}}{\partial T} \left\{ \frac{1}{(\lambda_{il-1} - \lambda_{rl})}\, F^{(4)}_{rli}\, L_{il-1}\, w^{l-1}\, P_{l-1} \right\}. \qquad (12)$$

When $i = a$, $i = b$ (relation (7) holds) contributions from $F^{(1)}_{r\ell i}$ and $F^{(2)}_{r\ell i}$ are,

$$G^{(1)}_{r\ell a} = F^{(1)}_{r\ell a} \, L_{a\ell+1} \, w^{\ell+1} \, P_{\ell+1} \, \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} \qquad (13)$$

and

$$G^{(1)}_{r\ell b} = F^{(2)}_{r\ell b} \, L_{b\ell-1} \, w^{\ell-1} \, P_{\ell-1} \, \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \, . \qquad (14)$$

For unequal eigenvalues,

$$\underset{i \neq a}{G^{(0)}_{r\ell i}} = e^{-\frac{1}{2}\beta m w^2} \frac{\partial T}{\partial x_{\parallel}} \left[\frac{F^{(1)}_{r\ell i}}{T(\lambda_{i\ell+1} - \lambda_{r\ell})} - \frac{\partial \lambda_{r\ell}}{\partial T} \frac{F^{(3)}_{r\ell i}}{(\lambda_{i\ell+1} - \lambda_{r\ell})^2} \right] L_{i\ell+1} \, w^{\ell+1} \, P_{\ell+1} \qquad (15)$$

and

$$\underset{i \neq b}{G^{(0)}_{r\ell i}} = e^{-\frac{1}{2}\beta m w^2} \frac{\partial T}{\partial x_{\parallel}} \left[\frac{F^{(2)}_{r\ell i}}{T(\lambda_{i\ell-1} - \lambda_{r\ell})} - \frac{\partial \lambda_{r\ell}}{\partial T} \frac{F^{(4)}_{r\ell i}}{(\lambda_{i\ell-1} - \lambda_{r\ell})^2} \right] L_{i\ell-1} \, w^{\ell-1} \, P_{\ell-1} \qquad (16)$$

This completes the solution of equation (1).

(b) Solution of (2):-

The first order perturbation to the equilibrium distribution for a dilute gas for the general model, as given by the Chapman-Enskog theory, has the form,

$$f' = f^{(0)} A(w) \frac{\underline{w}}{T} \cdot \frac{\partial T}{\partial \underline{x}}$$

$$= f^{(0)} A(w) \, w \cos\theta \, \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} + f^{(0)} A(w) \, w \sin\theta \cos\phi \, \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \, .$$

We therefore assume that the collision term may be expanded in the eigenfunctions used in the equilibrium solution in the following way,

$$[g_e, f^1] = e^{-\frac{1}{2}\beta m w^2} \sum_{r,l,i,j} \left[\frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} a_{rlij} P_j + \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} b_{rlij} P_j^1 \cos\phi \right] L_{ij} w^j e^{-\lambda_{rl} t}, \tag{17}$$

where a_{rlij} and b_{rlij} are functions of w_1.

Take

$$G = \sum_{r,l,i,j} \left(G^{(0)}_{rlij} e^{-\lambda_{rl} t} + G^{(1)}_{rlij} t e^{-\lambda_{rl} t} \right), \tag{18}$$

and so, by substitution into equation (2), it is found that

$$G^{(0)}_{rlij} = e^{-\frac{1}{2}\beta m w^2} \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} \frac{1}{\lambda_{ij} - \lambda_{rl}} a_{rlij} L_{ij} P_j w^j \tag{19}$$

if $\lambda_{ij} \neq \lambda_{rl}$,

$$= 0 \qquad \text{otherwise}. \tag{20}$$

If $\lambda_{ab} = \lambda_{rl}$ then

$$G^{(1)}_{rlab} = e^{-\frac{1}{2}\beta m w^2} \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} a_{rlab} L_{ab} w^b P_b ; \tag{21}$$

and for general $i \neq a$, $j \neq b$

$$G^{(1)}_{rlij} = 0. \tag{22}$$

Equations (19), (20), (21) and (22) determine the functions involved in (18), and so complete the solution of equation (2).

(c) Solution of (3):-

The solution of this homogeneous equation ensures that the boundary condition (4) holds. Hence, by taking t = 0 in the above solutions (15), (16) and (19), the following result is obtained for the solution of (3),

$$G = e^{-\frac{1}{2}\beta m w^2} \frac{\partial T}{\partial x_{\parallel}} \Bigg\{ \sum_{\substack{r\ell i \\ i \neq a}} \Bigg(\Bigg[\frac{F^{(1)}_{r\ell i}}{T(\lambda_{i\ell+1} - \lambda_{r\ell})} - \frac{\partial \lambda_{r\ell}}{\partial T} \frac{F^{(3)}_{r\ell i}}{(\lambda_{i\ell+1} - \lambda_{r\ell})^2} \Bigg]$$

$$L_{i\ell+1} w^{\ell+1} P_{\ell+1} e^{-\lambda_{i\ell+1} t} + \sum_{\substack{r\ell i \\ i \neq b}} \Bigg[\frac{F^{(2)}_{r\ell i}}{T(\lambda_{i\ell-1} - \lambda_{r\ell})} - \frac{\partial \lambda_{r\ell}}{\partial T} \frac{F^{(4)}_{r\ell i}}{(\lambda_{i\ell-1} - \lambda_{r\ell})^2} \Bigg]$$

$$L_{i\ell-1} w^{\ell-1} P_{\ell-1} e^{-\lambda_{i\ell-1} t} \Bigg) \Bigg\} - e^{-\frac{1}{2}\beta m w^2} \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} \sum_{\substack{r,\ell,i,j \\ i \neq a,\, j \neq b}} \frac{1}{(\lambda_{ij} - \lambda_{r\ell})} a_{r\ell ij}$$

$$L_{ij} P_j w^j e^{-\lambda_{ij} t} . \qquad (22)$$

This completes the part of the solution which involves the component $\frac{\partial T}{\partial x_{\parallel}}$. The terms in the solution which involve the perpendicular component $\frac{\partial T}{\partial x_{\perp}}$ are obtained in the same manner as the solutions above, and so will not be repeated. The results obtained are as follows:

If the terms involving $\frac{\partial T}{\partial x_{\perp}}$ in the expansion of

$$- \underline{w} \cdot \frac{\partial g_e}{\partial \underline{x}} - \frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}}$$

$$= e^{-\frac{1}{2}\beta m w^2} \frac{\partial T}{\partial x_{\perp}} \sum_{r,\ell,i} \Big\{ \frac{1}{T} J^{(1)}_{r\ell i} L_{i\ell+1} w^{\ell+1} P^{1}_{\ell+1}(\cos\theta) \cos\phi \, e^{-\lambda_{r\ell} t}$$

$$+ \frac{1}{T} J^{(2)}_{\tau \ell i} L_{i\ell-1} w^{\ell-1} P^{1}_{\ell-1} \cos\phi \, e^{-\lambda_{\tau\ell} t}$$

$$+ \frac{\partial \lambda_{\tau\ell}}{\partial T} J^{(3)}_{\tau \ell i} L_{i\ell+1} w^{\ell+1} P^{1}_{\ell+1} \cos\phi \, t e^{-\lambda_{\tau\ell} t}$$

$$+ \frac{\partial \lambda_{\tau\ell}}{\partial T} J^{(4)}_{\tau \ell i} L_{i\ell-1} w^{\ell-1} P^{1}_{\ell-1} \cos\phi \, t e^{-\lambda_{\tau\ell} t} \Big] \Big\}_{s}$$

(23)

where $J^{(j)}_{\tau \ell i}$ are functions of w_1. Then the full solution of equations (1), (2) and (3) is as follows,

$$e^{\frac{1}{2}\beta m w^2} G = \sum_{\substack{\tau, \ell, i \\ (\lambda_{i\ell+1} \neq \lambda_{\tau\ell})}} \Bigg[\frac{\partial \lambda_{\tau\ell}}{\partial T} t e^{-\lambda_{\tau\ell} t} L_{i\ell+1} \frac{w^{\ell+1}}{(\lambda_{i\ell+1} - \lambda_{\tau\ell})}$$

$$\left\{ F^{(3)}_{\tau \ell i} P_{\ell+1} \frac{\partial T}{\partial x_{\parallel}} + J^{(3)}_{\tau \ell i} P^{1}_{\ell+1} \cos\phi \frac{\partial T}{\partial x_{\perp}} \right\} + \left(e^{-\lambda_{\tau\ell} t} - e^{-\lambda_{i\ell+1} t}\right)$$

$$L_{i\ell+1} w^{\ell+1} \left\{ \left(\frac{F^{(1)}_{\tau \ell i}}{T(\lambda_{i\ell+1} - \lambda_{\tau\ell})} - \frac{\partial \lambda_{\tau\ell}}{\partial T} \frac{F^{(3)}_{\tau \ell i}}{(\lambda_{i\ell+1} - \lambda_{\tau\ell})^2} \right) P_{\ell+1} \frac{\partial T}{\partial x_{\parallel}} \right.$$

$$\left. + \left(\frac{J^{(1)}_{\tau \ell i}}{T(\lambda_{i\ell+1} - \lambda_{\tau\ell})} - \frac{\partial \lambda_{\tau\ell}}{\partial T} \frac{J^{(3)}_{\tau \ell i}}{(\lambda_{i\ell+1} - \lambda_{\tau\ell})^2} \right) P^{1}_{\ell+1} \cos\phi \frac{\partial T}{\partial x_{\perp}} \right\} \Bigg]$$

$$+\sum_{\substack{\tau,\ell,i \\ (\lambda_{i\ell-1}\neq\lambda_{\tau\ell})}} \Bigg[\frac{\partial\lambda_{\tau\ell}}{\partial T}\, t e^{-\lambda_{\tau\ell}t}\, \frac{L_{i\ell-1}\, w^{\ell-1}}{(\lambda_{i\ell-1}-\lambda_{\tau\ell})} \left\{ F^{(4)}_{\tau\ell i}\, P_{\ell-1}\, \frac{\partial T}{\partial x_{\parallel}} + J^{(4)}_{\tau\ell i}\, P^{1}_{\ell-1} \cos\phi\, \frac{\partial T}{\partial x_{\perp}} \right\}$$

$$+\left(e^{-\lambda_{\tau\ell}t}-e^{-\lambda_{i\ell-1}t}\right) L_{i\ell-1}\, w^{\ell-1} \Bigg\{ \Bigg(\frac{F^{(2)}_{\tau\ell i}}{T(\lambda_{i\ell-1}-\lambda_{\tau\ell})} - \frac{\partial\lambda_{\tau\ell}}{\partial T} \frac{F^{(4)}_{\tau\ell i}}{(\lambda_{i\ell-1}-\lambda_{\tau\ell})^{2}} \Bigg)$$

$$P_{\ell-1}\, \frac{\partial T}{\partial x_{\parallel}} + \Bigg(\frac{J^{(2)}_{\tau\ell i}}{T(\lambda_{i\ell-1}-\lambda_{\tau\ell})} - \frac{\partial\lambda_{\tau\ell}}{\partial T} \frac{J^{(4)}_{\tau\ell i}}{(\lambda_{i\ell-1}-\lambda_{\tau\ell})^{2}} \Bigg) P^{1}_{\ell-1} \cos\phi\, \frac{\partial T}{\partial x_{\perp}} \Bigg\} \Bigg]$$

$$+\sum_{\substack{\tau,\ell,[a(\tau,\ell),\, b(\tau,\ell)] \\ \left(\begin{smallmatrix}\lambda_{a\ell+1}=\lambda_{\tau\ell} \\ \lambda_{b\ell-1}=\lambda_{\tau\ell}\end{smallmatrix}\right)}} \Bigg[t^{2} e^{-\lambda_{\tau\ell}t}\, \frac{1}{2}\, \frac{\partial\lambda_{\tau\ell}}{\partial T} \Bigg(w^{\ell+1} L_{a\ell+1} \left\{ F^{(3)}_{\tau\ell a}\, P_{\ell+1}\, \frac{\partial T}{\partial x_{\parallel}} + J^{(3)}_{\tau\ell a}\, P^{1}_{\ell+1}\right.$$

$$\left.\cos\phi\, \frac{\partial T}{\partial x_{\perp}} \right\} + w^{\ell} L_{b\ell-1} \left\{ F^{(4)}_{\tau\ell b}\, P_{\ell-1}\, \frac{\partial T}{\partial x_{\parallel}} + J^{(4)}_{\tau\ell b}\, P^{1}_{\ell-1} \cos\phi\, \frac{\partial T}{\partial x_{\perp}} \right\} \Bigg) + t e^{-\lambda_{\tau\ell}t}\, w^{\ell+1}$$

$$L_{a\ell+1} \left\{ F^{(1)}_{\tau\ell a}\, P_{\ell+1}\, \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} + J^{(1)}_{\tau\ell a}\, P^{1}_{\ell+1} \cos\phi\, \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \right\} + t e^{-\lambda_{\tau\ell}t}\, w^{\ell-1} L_{b\ell-1}$$

$$\left\{ F^{(2)}_{\tau\ell b}\, P_{\ell-1}\, \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} + J^{(2)}_{\tau\ell b}\, P^{1}_{\ell-1} \cos\phi\, \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \right\} \Bigg] + \sum_{\substack{\tau,\ell,i,j \\ \lambda_{ij}\neq\lambda_{\tau\ell}}} \left(e^{-\lambda_{\tau\ell}t}-e^{-\lambda_{ij}t}\right)$$

$$\frac{w^{j} L_{ij}}{(\lambda_{ij}-\lambda_{\tau\ell})} \left\{ a_{\tau\ell ij}\, \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}}\, P_{j} + b_{\tau\ell ij}\, P^{1}_{j} \cos\phi\, \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \right\}$$

$$+\sum_{\substack{\tau,\ell,a(\tau,\ell),\, b(\tau,\ell) \\ \lambda_{ab}=\lambda_{\tau\ell}}} \left\{ \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}}\, a_{\tau\ell ab}\, L_{ab}\, P_{b}\, w^{b}\, t e^{-\lambda_{ab}t} + \frac{1}{T} \frac{\partial T}{\partial x_{\perp}}\, b_{\tau\ell ab}\, L_{ab}\right.$$

$$\left. P^{1}_{b} \cos\phi\, w^{b}\, t e^{-\lambda_{ab}t} \right\}.$$

(24)

B.2 Solution involving number density gradient - solution of equation (3.21).

The equations[+] to be solved are,

$$\frac{\partial H}{\partial t_{exp}} - [H, f^{(0)}] = -\frac{\underline{w}}{n}\cdot\frac{\partial n g_e}{\underline{\partial x}} - \frac{1}{\beta m}\frac{1}{n}\frac{\partial n}{\underline{\partial x}}\cdot\frac{\partial g_e}{\underline{\partial w}} \qquad (25)$$

$$\frac{\partial H}{\partial t_{exp}} - [H, f^{(0)}] = 0 \, , \qquad (26)$$

with the boundary condition for t = o, H = 0.

Then, if the number density gradient is expressed in the manner of (5) above, i.e.

$$\frac{\partial n}{\underline{\partial x}} = \hat{\underline{w}}_i \circ \frac{\partial n}{\underline{\partial x}}\,\hat{\underline{w}}_i + \hat{\underline{w}}_i \times \left(\frac{\partial n}{\underline{\partial x}} \times \hat{\underline{w}}_i\right)$$

$$= \frac{\partial n}{\partial x_{\parallel}}\,\hat{\underline{w}}_i + \frac{\partial n}{\partial x_{\perp}}\,\hat{\underline{a}}_i \qquad (27)$$

where we take $\underline{w}\cdot\hat{\underline{a}}_i = w \sin\theta \cos\phi_1$ we may proceed in the same way as we have with terms involving the temperature gradient in B.1 above.

Therefore, expanding the right hand side of (25) using the recurrence relations, etc. for the polynomials, we may express it as follows;

$$-\frac{\underline{w}}{n}\circ\frac{\partial n g_e}{\underline{\partial x}} - \frac{1}{\beta m}\frac{1}{n}\frac{\partial n}{\underline{\partial x}}\circ\frac{\partial g_e}{\underline{\partial w}}$$

[+] If the definition $\underline{w}_1 = \underline{v}_1 - \underline{u}(\underline{x}, t)$ is used, an extra term "$-\frac{1}{\beta m}\frac{1}{n}\frac{\partial n}{\underline{\partial x}}\cdot\frac{\partial g_e}{\underline{\partial w}_i}$" must be added to the right hand side of equation (25).

$$= e^{-\frac{1}{2}\beta m w^2} \sum_{r,l,i} \Big\{ \Big(F^{(5)}_{rli} P_{l+1}(\cos\theta) \frac{\partial n}{\partial x_{\parallel}} + J^{(5)}_{rli} P^{1}_{l+1}(\cos\theta) \cos\phi_1 \frac{\partial n}{\partial x_{\perp}} \Big) \frac{1}{n} L_{il+1} w^{l+1} e^{-\lambda_{rl} t}$$

$$+ \Big(F^{(6)}_{rli} P_{l-1} \frac{\partial n}{\partial x_{\parallel}} + J^{(6)}_{rli} P^{1}_{l-1} \cos\phi_1 \frac{\partial n}{\partial x_{\perp}} \Big) \frac{1}{n} L_{il-1} w^{l-1} e^{-\lambda_{rl} t}$$

$$+ \Big(F^{(7)}_{rli} P_{l+1} \frac{\partial n}{\partial x_{\parallel}} + J^{(7)}_{rli} P^{1}_{l+1} \cos\phi_1 \frac{\partial n}{\partial x_{\perp}} \Big) \frac{\partial \lambda_{rl}}{\partial n} L_{il+1} w^{l+1} t e^{-\lambda_{rl} t}$$

$$+ \Big(F^{(8)}_{rli} P_{l-1} \frac{\partial n}{\partial x_{\parallel}} + J^{(8)}_{rli} P^{1}_{l-1} \cos\phi_1 \frac{\partial n}{\partial x_{\perp}} \Big) \frac{\partial \lambda_{rl}}{\partial n} L_{il-1} w^{l-1} t e^{-\lambda_{rl} t} \Big\},$$

(28)

where $F^{(j)}_{rli}$ and $J^{(j)}_{rli}$ are functions of w_1. Using the same method employed in sections (a) and (c) above, we finally obtain the following as the solution to (25) and (26) with the boundary condition;

$$e^{\frac{1}{2}\beta m w^2} H = \sum_{\substack{r,l,i \\ (\lambda_{il+1} = \lambda_{rl})}} \Big[\frac{\partial \lambda_{rl}}{\partial n} t e^{-\lambda_{rl} t} L_{il+1} \frac{w^{l+1}}{(\lambda_{il+1} - \lambda_{rl})} \Big\{ F^{(7)}_{rli} P_{l+1} \frac{\partial n}{\partial x_{\parallel}}$$

$$+ J^{(7)}_{rli} P^{1}_{l+1} \cos\phi_1 \frac{\partial n}{\partial x_{\perp}} \Big\} + \left(e^{-\lambda_{rl} t} - e^{-\lambda_{il+1} t} \right) L_{il+1} w^{l+1}$$

$$\Big\{ \Big(\frac{F^{(5)}_{rli}}{\pi(\lambda_{il+1} - \lambda_{rl})} - \frac{\partial \lambda_{rl}}{\partial n} \frac{F^{(7)}_{rli}}{(\lambda_{il+1} - \lambda_{rl})^2} \Big) P_{l+1} \frac{\partial n}{\partial x_{\parallel}}$$

$$+\left(\frac{J^{(5)}_{r\ell i}}{n(\lambda_{i\ell+1}-\lambda_{r\ell})}-\frac{\partial\lambda_{r\ell}}{\partial n}\frac{J^{(7)}_{r\ell i}}{(\lambda_{i\ell+1}-\lambda_{r\ell})^2}\right)P^1_{\ell+1}\cos\phi_1\frac{\partial n}{\partial x_\perp}\Bigg\}\Bigg]+\sum_{\substack{r,\ell,i\\(\lambda_{i\ell-1}\neq\lambda_{r\ell})}}$$

$$\Bigg[\frac{\partial\lambda_{r\ell}}{\partial n}te^{-\lambda_{r\ell}t}L_{i\ell-1}\frac{w^{\ell-1}}{(\lambda_{i\ell-1}-\lambda_{r\ell})}\left\{F^{(8)}_{r\ell i}P_{\ell-1}\frac{\partial n}{\partial x_{\parallel}}+J^{(8)}_{r\ell i}P^1_{\ell-1}\cos\phi_1\frac{\partial n}{\partial x_\perp}\right\}$$

$$+\left(e^{-\lambda_{r\ell}t}-e^{-\lambda_{i\ell-1}t}\right)L_{i\ell-1}w^{\ell-1}\Bigg\{\left(\frac{F^{(6)}_{r\ell i}}{n(\lambda_{i\ell-1}-\lambda_{r\ell})}-\frac{\partial\lambda_{r\ell}}{\partial n}\frac{F^{(8)}_{r\ell i}}{(\lambda_{i\ell-1}-\lambda_{r\ell})^2}\right)$$

$$P_{\ell-1}\frac{\partial n}{\partial x_{\parallel}}+\left(\frac{J^{(6)}_{r\ell i}}{n(\lambda_{i\ell-1}-\lambda_{r\ell})}-\frac{\partial\lambda_{r\ell}}{\partial n}\frac{J^{(8)}_{r\ell i}}{(\lambda_{i\ell-1}-\lambda_{r\ell})^2}\right)P^1_{\ell-1}\cos\phi_1\frac{\partial n}{\partial x_\perp}\Bigg\}\Bigg]$$

$$+\sum_{\substack{r,\ell,[a(r,\ell),\,b(r,\ell)]\\ \left(\begin{smallmatrix}\lambda_{a\ell+1}=\lambda_{r\ell}\\ \lambda_{b\ell-1}=\lambda_{r\ell}\end{smallmatrix}\right)}}\Bigg[t^2e^{-\lambda_{r\ell}t}\frac{1}{2}\frac{\partial\lambda_{r\ell}}{\partial n}\Bigg(w^{\ell+1}L_{a\ell+1}\left\{F^{(7)}_{r\ell i}P_{\ell+1}\frac{\partial n}{\partial x_{\parallel}}\right.$$

$$\left.+J^{(7)}_{r\ell i}P^1_{\ell+1}\cos\phi_1\frac{\partial n}{\partial x_\perp}\right\}+w^{\ell-1}L_{b\ell-1}\left\{F^{(8)}_{r\ell b}P_{\ell-1}\frac{\partial n}{\partial x_{\parallel}}+J^{(8)}_{r\ell b}P^1_{\ell-1}\cos\phi_1\frac{\partial n}{\partial x_\perp}\right\}\Bigg)$$

$$+te^{-\lambda_{r\ell}t}w^{\ell+1}L_{a\ell+1}\left\{F^{(5)}_{r\ell a}P_{\ell+1}\frac{1}{n}\frac{\partial n}{\partial x_{\parallel}}+J^{(5)}_{r\ell a}P^1_{\ell+1}\cos\phi_1\frac{1}{n}\frac{\partial n}{\partial x_\perp}\right\}$$

$$+te^{-\lambda_{r\ell}t}w^{\ell-1}L_{b\ell-1}\left\{F^{(6)}_{r\ell b}P_{\ell-1}\frac{1}{n}\frac{\partial n}{\partial x_{\parallel}}+J^{(6)}_{r\ell b}P^1_{\ell-1}\cos\phi_1\frac{1}{n}\frac{\partial n}{\partial x_\perp}\right\}\Bigg].\qquad(29)$$

B.3 Solution involving mass velocity gradient - solution of equation (3.25)

The equations to be solved are,

$$\frac{\partial U}{\partial t_{exp}} - [U, f^{(0)}] = \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right) \frac{\partial n g_e}{\partial n} + \frac{2}{3} T \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right) \frac{\partial g_e}{\partial T} + \frac{\partial g_e}{\partial \underline{w}} \underline{w} : \frac{\partial \underline{u}}{\partial \underline{x}} + \frac{\partial g_e}{\partial \underline{w}_1} \underline{w} : \frac{\partial \underline{u}}{\partial \underline{x}} , \qquad (30)$$

$$\frac{\partial U}{\partial t_{exp}} - [U, f^{(0)}] = [g_e, f'] , \qquad (31)$$

$$\frac{\partial U}{\partial t_{exp}} - [U, f^{(0)}] = 0 , \qquad (32)$$

together with the boundary condition for t = o

$$U = 0 .$$

Take

$$\underline{w} = w \sin\theta \cos\phi \, \underline{i} + w \sin\theta \sin\phi \, \underline{j} + w \cos\theta \, \underset{\sim}{h} , \qquad (33)$$

where

$$\underset{\sim}{h} = \frac{\underline{w}_1}{w_1} .$$

(a) Solution of (30):-

As we are neglecting terms in $\left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u}\right)$ in the distribution function (see section 3.4), (30) becomes,

$$\frac{\partial U}{\partial t_{exp}} - [U, f^{(0)}] = \frac{\partial g_e}{\partial \underline{w}} \underline{w} : \frac{\partial \underline{u}}{\partial \underline{x}} + \frac{\partial g_e}{\partial \underline{w}_1} \underline{w} : \frac{\partial \underline{u}}{\partial \underline{x}} . \qquad (34)$$

From (33), putting $\frac{\partial u_j}{\partial x_i} = A_{ij}$,

$$\underline{w}\circ\frac{\partial u}{\partial x}\circ\underline{w} = w^2\Big\{\sin^2\theta\Big[\tfrac{1}{2}(2\cos^2\phi-1)A_{11}+\tfrac{1}{2}A_{11}+\sin\phi\cos\phi\,(A_{12}+A_{21})-\tfrac{1}{2}(1-2\sin^2\phi)A_{22}+\tfrac{1}{2}A_{22}\Big]+\cos\theta\sin\theta\,\Big[\cos\phi(A_{13}+A_{31})+\sin\phi\,(A_{23}+A_{32})\Big]+\cos^2\phi\,\Big[A_{33}\Big]\Big\},$$

(35)

and

$$\underline{w}\circ\frac{\partial u}{\partial x}\circ\underline{w}_1 = w w_1\Big\{\sin\theta\,[\cos\phi\,A_{13}+\sin\phi\,A_{23}]+\cos\theta\,A_{33}\Big\}. \qquad (36)$$

Now, using the recurrence relations, etc. for the L_{rl} polynomials and the $P_l^m(\cos\theta)$ (e.g. reference (1) p. 1325-1326), the right hand side of (34) may be expanded. We assume here the most general expansion, i.e.

$$\underline{w}\cdot\frac{\partial u}{\partial x}\circ\frac{\partial g_e}{\partial \underline{w}}+\underline{w}\circ\frac{\partial u}{\partial x}\circ\frac{\partial g_e}{\partial \underline{w}_1}$$

$$\begin{aligned}
= \sum_{imrl}\Big\{ & K^{(1)}_{imrl}(w_1)\;L_{im}\,w^m\,P_m\,e^{-\lambda_{rl}t}\,[A_{11}+A_{22}] \\
& + K^{(2)}_{imrl}(w_1)\;L_{im}\,w^m\,P_m\,e^{-\lambda_{rl}t}\,[A_{33}] \\
& + K^{(3)}_{imrl}(w_1)\;L_{im}\,w^m\,P_m^1\,e^{-\lambda_{rl}t}\,[\cos\phi(A_{13}+A_{31})+\sin\phi(A_{23}+A_{32})] \\
& + K^{(4)}_{imrl}(w_1)\;L_{im}\,w^m\,P_m^1\,e^{-\lambda_{rl}t}\,[\cos\phi\,A_{13}+\sin\phi\,A_{23}] \\
& + K^{(5)}_{imrl}(w_1)\;L_{im}\,w^m\,P_m^2\,e^{-\lambda_{rl}t}\Big[\tfrac{1}{2}(2\cos^2\phi-1)A_{11}-\tfrac{1}{2}(1-2\sin^2\phi)A_{22} \\
& \qquad +\sin\phi\cos\phi\,(A_{12}+A_{21})\Big]\Big\},
\end{aligned}$$

(37)

where $L_{im} \equiv L_{im}(\tfrac{1}{2}\beta m w^2)$ and $P_m^n \equiv P_m^n(\cos\theta)$.

Formula (37) is the most general expansion - it is to be hoped that for specific models the expansion is simpler than the above. In fact, below we see that the expansion for the Maxwellian model is simpler. However, expansion (37) is sufficient to show the most general method of obtaining the solution.

Now take,

$$U = \sum_{imrl} \left\{ U_{imrl}\, e^{-\lambda_{rl} t} + U^{(1)}_{imrl}\, t e^{-\lambda_{rl} t} \right\}. \tag{38}$$

The first term in (38), viz. U_{imrl} takes account of all terms in the expansion (37) in which $\lambda_{im} \neq \lambda_{rl}$. When

then we must use the second term

Hence;

$$\begin{aligned} \underset{\lambda_{im} \neq \lambda_{rl}}{U_{imrl}} = \frac{1}{\lambda_{im} - \lambda_{rl}} L_{im} w^m \Big\{ & K^{(1)}_{imrl}\, P_m \left[A_{11} + A_{22} \right] \\ & + K^{(2)}_{imrl}\, P_m \left[A_{33} \right] \\ & + K^{(3)}_{imrl}\, P_m^1 \left[\cos\phi\,(A_{13} + A_{31}) + \sin\phi\,(A_{23} + A_{32}) \right] \\ & + K^{(4)}_{imrl}\, P_m^1 \left[\cos\phi\, A_{13} + \sin\phi\, A_{23} \right] \\ & + K^{(5)}_{imrl}\, P_m^2 \Big[\tfrac{1}{2}(2\cos^2\phi - 1)\, A_{11} - \tfrac{1}{2}(1 - 2\sin^2\phi)\, A_{22} \\ & \qquad + \sin\phi \cos\phi\,(A_{12} + A_{21}) \Big] \Big\}, \end{aligned} \tag{39}$$

$$= 0 \qquad \text{if} \quad \lambda_{im} = \lambda_{rl}.$$

Also, if $\lambda_{im} = \lambda_{rl}$ (including i = r & m = l), then

$$\begin{aligned} \underset{(\lambda_{im} = \lambda_{rl})}{U^{(1)}_{imrl}} = {} & K^{(1)}_{imrl} \, L_{im} \, w^m \, P_m \left[A_{11} + A_{22} \right] \\ & + K^{(2)}_{imrl} \, L_{im} \, w^m \, P_m \left[A_{33} \right] \\ & + K^{(3)}_{imrl} \, L_{im} \, w^m \, P_m^1 \left[\cos\phi \, (A_{13} + A_{31}) + \sin\phi \, (A_{23} + A_{32}) \right] \\ & + K^{(4)}_{imrl} \, L_{im} \, w^m \, P_m^1 \left[\cos\phi \, A_{13} + \sin\phi \, A_{23} \right] \\ & + K^{(5)}_{imrl} \, L_{im} \, w^m \, P_m^2 \left[\tfrac{1}{2} (2\cos^2\phi - 1) A_{11} - \tfrac{1}{2} (1 - 2\sin^2\phi) A_{22} \right. \\ & \qquad \left. + \sin\phi \cos\phi \, (A_{12} + A_{21}) \right]. \end{aligned} \tag{40}$$

(b) Solution of (31):-

For viscosity f' has the following form (see C.C. Chapter 7),

$$f' = -f^{(0)} \, B(w) \, (\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}) : \frac{\partial \underline{u}}{\partial \underline{x}} \, , \tag{41}$$

and so the form that the right hand side of (31) takes for the general molecular model is difficult to predict. For Maxwellian molecules, the form of (41) is simpler as B(w) is found not to depend on the molecular velocity and also the bracket is comparatively easy to evaluate. It is found that the bracket has an expansion of the following form,

$$\sum_{r} \Big[\; b_r^{(0)}(w_1) \; S^{(r)}_{5/2}\left(\tfrac{1}{2}\beta m w^2\right) \left(\underline{w}\,\underline{w} - \tfrac{1}{3} w^2 \underline{\underline{\delta}}\right) : \frac{\partial \underline{u}}{\partial \underline{x}} \; e^{-\lambda_{r0} t}$$

$$+ \; b_r^{(1)}(w_1) \; S^{(r)}_{7/2}\left(\tfrac{1}{2}\beta m w^2\right) \underline{w}_1 \cdot \left(\underline{w}\,\underline{w}\,\underline{w} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}\,\underline{w} - \tfrac{1}{5} w^2 \underline{w}\,\underline{\underline{\delta}} - \tfrac{1}{5} w^2 \underline{\underline{\delta}}'\,\underline{w}\right) : \frac{\partial \underline{u}}{\partial \underline{x}} \; e^{-\lambda_{r1}}$$

$$+ \dots \qquad\qquad \Big].$$

So, we will again assume a very general expansion in which we consider for the sake of simplicity only $\frac{\partial u_1}{\partial x_1}$ i.e. A_{11} The terms involving the other components could be considered similarly and so will not be given here.

Hence

$$[g_e, f']_{A_{11}} = A_{11} \sum_{imrl} e^{-\lambda_{rl} t} L_{im}\left(\tfrac{1}{2}\beta m w^2\right) w^m \Big\{ K^{(6)}_{imrl}(w_1)\, P_m(\cos\theta)$$

$$+ K^{(7)}_{imrl}\, P_m^1 \cos\phi + K^{(8)}_{imrl}\, P_m^1 \sin\phi + K^{(9)}_{imrl}\, P_m^2 (2\cos^2\phi - 1)$$

$$+ K^{(10)}_{imrl}\, P_m^2 \cos\phi \sin\phi + K^{(11)}_{imrl}\left(1 - 2\sin^2\phi\right)\Big\}.$$

Equation (31) is then treated in the same manner as (30) in (a) above.

(c) Solution of (32):-

The solution of (32) ensures the vanishing of U for $t=0$. Hence from (39) above we see that part of the solution of (32) is given by,

$$U = - \sum_{\substack{imr\ell \\ (\lambda_{im} \neq \lambda_{r\ell})}} \frac{e^{-\lambda_{im} t}}{\lambda_{im} - \lambda_{r\ell}} L_{im} w^m \Big\{ K^{(1)}_{imr\ell} P_m [A_{11} + A_{22}]$$

$$+ K^{(2)}_{imr\ell} P_m [A_{33}] + K^{(3)}_{imr\ell} P_m^1 [\cos\phi (A_{13} + A_{31}) + \sin\phi (A_{23} + A_{32})]$$

$$+ K^{(4)}_{imr\ell} P_m^1 [\cos\phi A_{13} + \sin\phi A_{23}] + K^{(5)}_{imr\ell} P_m^2 [\tfrac{1}{2}(2\cos^2\phi - 1) A_{11} +$$

$$\sin\phi \cos\phi (A_{21} + A_{12}) - \tfrac{1}{2}(1 - 2\sin^2\phi) A_{22}] \Big\}.$$

When $\lambda_{im} = \lambda_{r\ell}$ then (40) vanishes, and so no contribution from (32) is needed.

There will also be a similar contribution from the solution of (31).

2. MAXWELLIAN MOLECULES.

B.4 Results for Maxwellian molecules forming a dilute gas with a temperature gradient.

For Maxwellian molecules,

$$g_l = e^{-\frac{1}{2}\beta m w^2} \sum_{r,l} a_{rl} \left(\tfrac{1}{2}\beta m\right)^{l+3/2} (w w_1)^l P_l(\cos\theta) \, {}_1S^{(r)}_{l+1/2} \, S^{(r)}_{l+1/2} \, e^{-\lambda_{rl} t}, \tag{42}$$

where

$${}_1S^{(r)}_{l+1/2} \equiv S^{(r)}_{l+1/2}\left(\tfrac{1}{2}\beta m w_1^2\right),$$

$$S^{(r)}_{l+1/2} \equiv S^{(r)}_{l+1/2}\left(\tfrac{1}{2}\beta m w^2\right),$$

$$a_{rl} = \frac{1}{\pi}\left(l+\tfrac{1}{2}\right)\frac{r!}{(l+r+\frac{1}{2})!},$$

and λ_{rl} are independent of the temperature T.

Now

$$\frac{\partial g_l}{\partial \underline{w}} = \sum_{r,l} a_{rl} \left(\tfrac{1}{2}\beta m\right)^{l+3/2} {}_1S^{(r)}_{l+1/2} \, w_1{}^l \, e^{-\frac{1}{2}\beta m w^2} \Big[\beta m w^l S^{(r)\prime}_{l+1/2} P_l \underline{w}$$

$$-\beta m w^l S^{(r)}_{l+1/2} P_l \underline{w} - w^{l-1} S^{(r)}_{l+1/2} P_l' \cos\theta \, \underline{w} + l w^{l-2} S^{(r)}_{l+1/2} P_l \underline{w}$$

$$+ w^{l-1} S^{(r)}_{l+1/2} P_l' \frac{\underline{w}_1}{w_1}\Big]. \tag{42a}$$

Hence using the following relations (2);

$$S^{(r)\prime}_{l+1/2} = - S^{(r-1)}_{l+1+1/2},$$

$$x\, S^{(r)\prime}_{l+1/2}(x) + \left(l+\tfrac{1}{2}\right) S^{(r)}_{l+1/2} = \left(r+l+\tfrac{1}{2}\right) S^{(r)}_{l-1+1/2},$$

$$x\, S^{(r)}_{l+1/2}(x) = \left(r+l+\tfrac{1}{2}\right) S^{(r)}_{l-1+1/2} - (r+1)\, S^{(r+1)}_{l-1+1/2}, \tag{43}$$

$$S^{(r)}_{l+1/2} = S^{(r)}_{l+1+1/2} - S^{(r-1)}_{l+1+1/2},$$

and those of (6), and considering only the terms involving $\frac{\partial T}{\partial x_{\parallel}}$ we finally obtain;

$$\underline{w} \cdot \frac{\partial g_e}{\partial \underline{x}} + \frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}}$$

$$= e^{-\frac{1}{2}\beta m w^2} \frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} \sum_{r,l} \left(\tfrac{1}{2}\beta m\right)^{l+3/2} a_{rl}\, e^{-\lambda_{rl} t}\, w_1^{l} \Big\{ P_{l+1}\, w^{l+1} \frac{l+1}{2l+1}$$

$$\Big[\left(2r\, {}_1S^{(r)}_{l+1/2} - \tfrac{1}{2}\beta m w_1^2\, {}_1S^{(r)\prime}_{l+1/2}\right) S^{(r)}_{l+1+1/2} + \left(\tfrac{1}{2}\beta m w_1^2\, {}_1S^{(r)\prime}_{l+1/2} - r\, {}_1S^{(r)}_{l+1/2}\right)$$

$$S^{(r-1)}_{l+1+1/2} - (r+1)\, {}_1S^{(r)}_{l+1/2}\, S^{(r+1)}_{l+1+1/2} \Big] + P_{l-1}\, w^{l-1} \frac{2}{\beta m} \frac{l}{2l+1} \Big[\Big(r(r+l+1/2)\, {}_1S^{(r)}_{l+1/2}$$

$$- \tfrac{1}{2}\beta m w_1^2\, {}_1S^{(r)\prime}_{l+1/2} \Big) S^{(r)}_{l-1+1/2} + \left((r+1)(1-r)\, {}_1S^{(r)}_{l+1/2} + \tfrac{1}{2}\beta m w_1^2 (r+1)\, {}_1S^{(r)\prime}_{l+1/2} \right) S^{(r+1)}_{l-1+1/2}$$

$$+ (r+1)(r+2)\, {}_1S^{(r)}_{l+1/2}\, S^{(r+2)}_{l-1+1/2} \Big\},$$

(44)

which has the form of (6a) above.

Similarly, considering the perpendicular component we obtain;

$$\underline{w} \cdot \frac{\partial g_e}{\partial \underline{x}} + \frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}}$$

$$= e^{-\frac{1}{2}\beta m w^2} \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} \cos\phi \sum_{r,l} \left(\tfrac{1}{2}\beta m\right)^{l+3/2} a_{rl}\, e^{-\lambda_{rl} t}\, w_1^{l} \Big\{ P^1_{l+1}\, w^{l+1}$$

$$\frac{1}{2\ell+1}\Big[\big(2r\,{}_1S^{(r)}_{\ell+1/2} - \tfrac{1}{2}\beta m w_1^{2}\,{}_1S^{(r)\prime}_{\ell+1/2}\big) S^{(r)}_{\ell+1+1/2} + \big(\tfrac{1}{2}\beta m w_1^{2}\,{}_1S^{(r)\prime}_{\ell+1/2} - r\,{}_1S^{(r)}_{\ell+1/2}\big)$$

$$-(r+1)\,{}_1S^{(r)}_{\ell+1/2}\,S^{(r+1)}_{\ell+1+1/2}\Big] + P^{1}_{\ell-1}\,w^{\ell-1}\,\frac{2}{\beta m}\,\frac{1}{2\ell+1}\Big[\big(r(r+\ell+1/2)\,{}_1S^{(r)}_{\ell+1/2}$$

$$-\tfrac{1}{2}\beta m w_1^{2}\,{}_1S^{(r)\prime}_{\ell+1/2}\big) S^{(r)}_{\ell-1+1/2} + \big((r+1)(1-r)\,{}_1S^{(r)}_{\ell+1/2} + \tfrac{1}{2}\beta m w_1^{2}(r+1)\,{}_1S^{(r)\prime}_{\ell+1/2}\big)$$

$$S^{(r+1)}_{\ell-1+1/2} + (r+1)(r+1)\,{}_1S^{(r)}_{\ell+1/2}\,S^{(r+2)}_{\ell-1+1/2}\Big].$$

(45)

From (44) and (45) we see that the term involving $S^{(0)}_{3/2}\,w$ in the expansions is

$$-\tfrac{3}{2}\,a_{10}\,e^{-\lambda_{10}t}\left(\tfrac{1}{2}\beta m\right)^{3/2}\left[\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}\,P_1 + \frac{1}{T}\frac{\partial T}{\partial x_{\perp}}\,P_1^{1}\cos\phi\right] S^{(0)}_{3/2}\,w.$$

Hence the contribution from the velocity distribution function G is given by the solution of the equation,

$$\frac{\partial G}{\partial t_{exp}} - \left[G, f^{(0)}\right] = \tfrac{3}{2}\,a_{10}\,e^{-\lambda_{10}t}\left(\tfrac{1}{2}\beta m\right)^{3/2}$$

$$\left[\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}\,P_1 + \frac{1}{T}\frac{\partial T}{\partial x_{\perp}}\,P_1^{1}\cos\phi\right] S^{(0)}_{3/2}\,w.$$

This solution is

$$\tfrac{3}{2}\,a_{10}\,t\,e^{-\lambda_{10}t}\left(\tfrac{1}{2}\beta m\right)^{3/2}\left[\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}}\,P_1 + \frac{1}{T}\frac{\partial T}{\partial x_{\perp}}\,P_1^{1}\cos\phi\right] S^{(0)}_{3/2}\,w, \qquad (46)$$

and so

$$\left\{\frac{\partial}{\partial t}\int G\,\underline{w}\,d\underline{w}\right\}_{t=0} = \frac{1}{\beta m}\,\frac{1}{T}\left(\frac{\partial T}{\partial x_{\parallel}}\,\hat{\underline{w}}_1 + \frac{\partial T}{\partial x_{\perp}}\,\hat{\underline{a}}\right) = \frac{1}{\beta m}\,\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}\,. \qquad (47)$$

Because (46) vanishes identically at t = o, there will be no contribution from equation (3). Also, in Appendix A we show that

$$[g_e, f'] \equiv \left[g_e, f^{(0)}\frac{a_1}{n}\left(\tfrac{5}{2}-\tfrac{1}{2}\beta m w^2\right)\frac{\underline{\underline{w}}}{T}\cdot\frac{\partial T}{\partial \underline{x}}\right]$$

(for Maxwellian molecules)

has the form

$$e^{-\frac{1}{2}\beta m w^2}\sum_r\Big[a_r^{(0)}(w_1)\,S_{3/2}^{(r+1)}\,\frac{\underline{\underline{w}}}{T}\cdot\frac{\partial T}{\partial \underline{x}}\,e^{-\lambda_{r0}t}$$

$$+\,a_r^{(1)}(w_1)\,S_{5/2}^{(r+1)}\,\underline{w}_1\cdot\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right)\cdot\frac{1}{T}\frac{\partial T}{\partial \underline{x}}\,e^{-\lambda_{r1}t}$$

$$+\;\cdots\qquad\Big],$$

and so there will be no contribution to (47) from (2). Note that also from (45) the coefficient of $S_{1/2}^{(0)}\;P_0(\cos\theta)$ is zero, i.e. $\int G\,d\underline{w} = 0$

In the above evaluations we have taken $\underline{w}_1 = \underline{v}_1 - \underline{u}(o)$ for all t, and if we take $\underline{w}_1 = \underline{v}_1 - \underline{u}(t)$, then we must consider the term

$$\frac{1}{\beta m}\;\frac{1}{T}\,\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial g_e}{\partial \underline{w}_1} \qquad (48)$$

in the above equation (1). Since

$$\frac{\partial g_e}{\partial \underline{w}_1} = e^{-\frac{1}{2}\beta m w^2}\sum_{r,\ell} C_{r\ell}\,e^{-\lambda_{r\ell}t}\,S_{\ell+1/2}^{(r)}\,w^{\ell}\left[\beta m\,w_1\,\ell\,,S_{\ell+1/2}^{(r)\prime}\,P_\ell\,\underline{w}_1\right.$$

$$+ \ell w_1^{\ell-2}\, {}_1S^{(\tau)}_{\ell+1/2}\, P_\ell\, \underline{w}_1 - w_1^{\ell-2}\, {}_1S^{(\tau)}_{\ell+1/2}\, P_\ell' \cos\theta\, \underline{w}_1$$

$$+ w_1^{\ell-1}\, {}_1S^{(\tau)}_{\ell+1/2}\, P_\ell' \frac{\underline{w}}{w}\Big],$$

(49)

then,

$$\frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} \cdot \frac{\partial g_\ell}{\partial \underline{w}_1}$$

$$= \frac{1}{\beta m} e^{-\frac{1}{2}\beta m w^2} \sum_{\tau,\ell} C_{\tau\ell}\, e^{-\lambda_{\tau\ell} t}\, w^\ell S^{(\tau)}_{\ell+1/2} \Big\{\Big[\beta m\, w_1^{\ell+1}$$

$${}_1S^{(\tau)\prime}_{\ell+1/2}\, P_\ell + \ell w_1^{\ell-1}\, {}_1S^{(\tau)}_{\ell+1/2}\Big] \frac{1}{T}\frac{\partial T}{\partial x_{\parallel}} P_\ell + w_1^{\ell-1}\, {}_1S^{(\tau)}_{\ell+1/2}\, \frac{1}{T}\frac{\partial T}{\partial x_{\perp}} \cos\phi\, P_\ell^1\Big\}.$$

(50)

Therefore, the coefficient $S^{(0)}_{1/2}\, P_0(\cos\theta)$ is zero, and the term involving $S^{(0)}_{3/2}\, w$ is as follows,

$$\frac{1}{\beta m} e^{-\frac{1}{2}\beta m w^2} C_{01}\, e^{-\lambda_{01} t}\, S^{(0)}_{3/2}\, w \Big\{\frac{1}{T}\frac{\partial T}{\partial x_{\parallel}} P_1 + \frac{1}{T}\frac{\partial T}{\partial x_{\perp}} P_1^1 \cos\phi\Big\}.$$

From (1), the contribution from this extra term to $\Big\{\frac{\partial}{\partial t}\int G\underline{w}\, d\underline{w}\Big\}_{t=0}$ is,

$$-\frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}}. \qquad (51)$$

In the case of equation (25) a term

$$\frac{1}{\beta m} \frac{1}{n} \frac{\partial n}{\partial \underline{x}} \cdot \frac{\partial g_\ell}{\partial \underline{w}_1}$$

must be considered, and so the same results are obtained, i.e. replacing T by n in (51).

With the backward equation, we have to solve

$$\frac{\partial G_b}{\partial t_{exp}} + \left[G_b, f^{(0)}\right] = \frac{3}{2} a_{10} e^{+\lambda_{10} t} \left(\tfrac{1}{2}\beta m\right)^{3/2} \left[\frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} P_1 + \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} P_1^1 \cos\phi\right] S^{(0)}_{3/2}\, w,$$

and so the solution is

$$\frac{3}{2} a_{10}\, t e^{+\lambda_{10} t} \left(\tfrac{1}{2}\beta m\right)^{3/2} \left[\frac{1}{T} \frac{\partial T}{\partial x_{\parallel}} P_1 + \frac{1}{T} \frac{\partial T}{\partial x_{\perp}} P_1^1 \cos\phi\right] S^{(0)}_{3/2}\, w$$

as in (46). Correspondingly similar results can be found in all the other cases.

B.5 Terms involving the number density gradient.

From (42a), in equation (25),

$$\frac{\underline{w}}{n} \circ \frac{\partial n g_e}{\partial \underline{x}} + \frac{1}{\beta m} \frac{1}{n} \frac{\partial n}{\partial \underline{x}} \circ \frac{\partial g_e}{\partial \underline{w}}$$

$$= - e^{-\frac{1}{2}\beta m w^2} \frac{1}{n} \frac{\partial n}{\partial x_{\parallel}} \sum_{r,\ell} c_{r\ell}\, e^{-\lambda_{r\ell} t} w_1 \ell\, {}_1S^{(r)}_{\ell+1/2} \frac{2}{\beta m} \frac{1}{2\ell+1} \Big(\Big\{ -\lambda_{r\ell} t \left(\tfrac{1}{2}\beta m\right) \left[S^{(r)}_{\ell+1+1/2} - S^{(r-1)}_{\ell+1+1/2}\right] - \left(\tfrac{1}{2}\beta m\right) S^{(r-1)}_{\ell+1+1/2} \Big\} (\ell+1) P_{\ell+1} w^{\ell+1} + \Big\{ -\lambda_{r\ell} t \left[(r+\ell+\tfrac{1}{2}) S^{(r)}_{\ell-1+1/2} - (r+1) S^{(r+1)}_{\ell-1+1/2} \right] + \ell (r+\ell+\tfrac{1}{2}) S^{(r)}_{\ell-1+1/2} \Big\} \ell P_{\ell-1} w^{\ell-1} \Big) + e^{-\frac{1}{2}\beta m w^2} \frac{1}{n} \frac{\partial n}{\partial x_{\perp}} \cos\phi$$

$$\sum_{r,\ell} c_{r\ell}\, e^{-\lambda_{r\ell} t} w_1 \ell\, {}_1S^{(r)}_{\ell+1/2} \frac{2}{\beta m} \frac{1}{2\ell+1} \Big(\Big\{ -\lambda_{r\ell} t \left(\tfrac{1}{2}\beta m\right) \left[S^{(r)}_{\ell+1+1/2} - S^{(r-1)}_{\ell+1+1/2}\right] - \tfrac{1}{2}\beta m\, S^{(r-1)}_{\ell+1+1/2} \Big\} P^1_{\ell+1} w^{\ell+1} - \Big\{ -\lambda_{r\ell} t \left[(r+\ell+\tfrac{1}{2}) S^{(r)}_{\ell-1+1/2} - (r+1) S^{(r+1)}_{\ell-1+1/2} \right] + (r+\ell+\tfrac{1}{2}) S^{(r)}_{\ell-1+1/2} \Big\} P^1_{\ell-1} w^{\ell-1} \Big).$$

(52)

To calculate terms in H from equation (25) which involve $S^{(0)}_{3/2}$ w, from the above expansion, we must solve

$$\frac{\partial H}{\partial t} - \left[H, f^{(0)}\right] = -e^{-\frac{1}{2}\beta m w^2}\frac{1}{n}\frac{\partial n}{\partial x_{\parallel}} S^{(0)}_{3/2}\, w\, P_1 \Big[C_{10}\lambda_{10} t e^{-\lambda_{10}t}\, {}_{1}S^{(1)}_{1/2}$$

$$- C_{10} e^{-\lambda_{10}t}\, {}_{1}S^{(1)}_{1/2} - C_{02}\lambda_{02} t e^{-\lambda_{02}t} w_1{}^2 - 2C_{02} e^{-\lambda_{02}t} w_1{}^2 \Big]$$

$$- e^{-\frac{1}{2}\beta m w^2}\frac{1}{n}\frac{\partial n}{\partial x_{\perp}} \cos\phi_1\, S^{(0)}_{3/2}\, w\, P_1^1 \Big[C_{10}\lambda_{10} t e^{-\lambda_{10}t}\, {}_{1}S^{(1)}_{1/2} - C_{10} e^{-\lambda_{10}t}\, {}_{1}S^{(1)}_{1/2}$$

$$+ C_{02}\lambda_{02} t e^{-\lambda_{02}t}\frac{1}{\beta m} w_1{}^2 - C_{02} e^{-\lambda_{02}t}\frac{1}{\beta m} w_1{}^2 \Big].$$

The solution is found to be (using equation (26) also);

$$H = \left(\frac{\beta m}{2\pi}\right)^{3/2}\frac{1}{n}\frac{\partial n}{\partial x_{\parallel}} e^{-\frac{1}{2}\beta m w^2} S^{(0)}_{3/2}\, w\, P_1 \Big[-\frac{\lambda_{10}}{3}\, {}_{1}S^{(1)}_{1/2}\, t^2 e^{-\lambda_{10}t}$$

$$+ \frac{2}{3}\, {}_{1}S^{(1)}_{1/2}\, t e^{-\lambda_{10}t} + \frac{\lambda_{02}}{\lambda_{01}-\lambda_{02}}\,\frac{4}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) t e^{-\lambda_{02}t}$$

$$- \frac{\lambda_{01}}{(\lambda_{01}-\lambda_{02})^2}\,\frac{4}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) e^{-\lambda_{02}t} + \frac{\lambda_{01}}{(\lambda_{01}-\lambda_{02})^2}\,\frac{4}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) e^{-\lambda_{01}t} \Big]$$

$$+ \left(\frac{\beta m}{2\pi}\right)^{3/2}\frac{1}{n}\frac{\partial n}{\partial x_{\perp}} e^{-\frac{1}{2}\beta m w^2} S^{(0)}_{3/2}\, w\, P_1^1 \cos\phi_1 \Big[-\frac{\lambda_{10}}{3}\, {}_{1}S^{(1)}_{1/2}\, t^2 e^{-\lambda_{10}t} + \frac{2}{3}\, {}_{1}S^{(1)}_{1/2}\, t e^{-\lambda_{01}t}$$

$$- \frac{\lambda_{02}}{\lambda_{01}-\lambda_{02}}\,\frac{2}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) t e^{-\lambda_{02}t} + \frac{\lambda_{01}}{(\lambda_{01}-\lambda_{02})^2}\,\frac{2}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) e^{-\lambda_{02}t}$$

$$- \frac{\lambda_{01}}{(\lambda_{01}-\lambda_{02})^2}\,\frac{2}{3}\left(\tfrac{1}{2}\beta m w_1{}^2\right) e^{-\lambda_{01}t} \Big].$$

Hence, we finally obtain

$$\left\{ \frac{\partial}{\partial t} \int H \underline{w} \, d\underline{w} \right\}_{t=0} = \frac{1}{\beta m} \frac{1}{n} \frac{\partial n}{\partial \underline{x}} - \underline{w}_1 \cdot \frac{\partial n}{\partial \underline{x}} \, \underline{w}_1 . \tag{53}$$

Also, from (52), the terms involving are the following,

$$e^{-\frac{1}{2}\beta m w^2} \frac{1}{n} \frac{\partial n}{\partial x_{\parallel}} w_1 \frac{1}{\beta m} \left[c_{01} e^{-\lambda_{01} t} - c_{01} \lambda_{01} t e^{-\lambda_{01} t} \right] S_{1/2}^{(0)} P_0(\cos\theta) ,$$

and so this gives the following term in H from equation (25),

$$-\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2} \underline{w}_1 \cdot \frac{\partial n}{\partial \underline{x}} \, S_{1/2}^{(0)} P_0(\cos\theta) \, t e^{-\lambda_{01} t}$$

Therefore we have the following,

$$\left\{ \frac{\partial}{\partial t} \int H \, d\underline{w} \right\}_{t=0} = -\underline{w}_1 \cdot \frac{\partial n}{\partial \underline{x}} . \tag{54}$$

<u>Mean acceleration</u>

From chapter V,

$$\begin{aligned} f_+ &= \left\{ \frac{1}{n} \frac{\partial}{\partial t} \int n g \, \underline{v} \, d\underline{v} - \frac{\underline{v}_1}{n} \frac{\partial}{\partial t} \int n g \, d\underline{v} \right\}_{t=0} \\ &= \left\{ \frac{1}{n} \frac{\partial}{\partial t} \int n g_e \, \underline{w} \, d\underline{w} + \frac{1}{n} \frac{\partial}{\partial t} \int n g_e \, \underline{u} \, d\underline{w} - \frac{\underline{v}_1}{n} \frac{\partial}{\partial t} \int n g_e \, d\underline{w} \right. \\ &\quad \left. + \frac{\partial}{\partial t} \int H \underline{w} \, d\underline{w} + \frac{\partial}{\partial t} \int G \, \underline{w} \, d\underline{w} - \underline{v}_1 \frac{\partial}{\partial t} \int H \, d\underline{w} \right\}_{t=0} . \end{aligned}$$

From (47), (51), (53) and (54) above, this expression gives

$$\begin{aligned} f_+ &= -n\pi A_1(5) \left(\frac{2K}{m}\right)^{1/2} \underline{w}_1 + \frac{1}{\beta m} \frac{1}{T} \frac{\partial T}{\partial \underline{x}} + \frac{1}{\beta m} \frac{1}{n} \frac{\partial n}{\partial \underline{x}} + \frac{\partial \underline{u}}{\partial t} \\ &= -n\pi A_1(5) \left(\frac{2K}{m}\right)^{1/2} \underline{w}_1 . \end{aligned}$$

As expected, this value is obtained in the both cases of taking

$$\underline{w}_1 = \underline{v}_1 - \underline{u}(0)$$

and $\underline{w}_1 = \underline{v}_1 - \underline{u}(t)$.

<u>Solution as $t \to \infty$</u>

As $t \to \infty$ the only terms that remain in G are those which are time independent, and these terms must involve λ_{00} since $\lambda_{00} = 0$. Hence contribution from (1) is given by the solution of

$$\frac{\partial G}{\partial t_{exp}} - [G, f^{(0)}] = -\underline{w}\cdot\frac{\partial}{\partial \underline{x}}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2} - \frac{1}{\beta m}\frac{1}{T}\frac{\partial T}{\partial \underline{x}}\cdot\frac{\partial}{\partial \underline{w}}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}$$

$$= \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}\left(\frac{5}{2} - \frac{1}{2}\beta m w^2\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}} .$$

So the contribution to G is

$$\frac{1}{\lambda_{11}}\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}\left(\frac{5}{2} - \frac{1}{2}\beta m w^2\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}} . \tag{55}$$

There is no contribution from (3) as the coefficient of the terms of G in (1) involving $S^{(0)}_{1/2} P_0(\cos\theta)$ is zero. However, there is a contribution from equation (2) given by the solution of

$$\frac{\partial G}{\partial t_{exp}} - [G, f^{(0)}] = \left[e^{-\frac{1}{2}\beta m w^2}\left(\frac{\beta m}{2\pi}\right)^{3/2}, f'\right]$$

$$= \left[e^{-\frac{1}{2}\beta m w^2}\left(\frac{\beta m}{2\pi}\right)^{3/2}, f^{(0)}\frac{a_1}{n}\left(\frac{5}{2} - \frac{1}{2}\beta m w^2\right)\frac{\underline{w}}{T}\cdot\frac{\partial T}{\partial \underline{x}}\right] \tag{56}$$

for Maxwellian molecules, where

$$a_1 = \frac{1}{\pi A_2(5)\left(\frac{2K}{m}\right)^{1/2}} .$$

Equation (56) reduces to,

$$\frac{\partial G}{\partial t_{exp}} - \left[G, f^{(0)}\right] = \left(\lambda_{11} - \mu_{11}\right)\left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2} \frac{a_1}{n}$$

$$\left(\tfrac{5}{2} - \tfrac{1}{2}\beta m w^2\right) \frac{\underline{\underline{w}}}{T} \cdot \frac{\partial T}{\underline{\partial x}} ,$$

and so gives the contribution

$$\frac{\left(\lambda_{11} - \mu_{11}\right)}{\lambda_{11}} \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2} \frac{a_1}{n} \left(\tfrac{5}{2} - \tfrac{1}{2}\beta m w^2\right) \frac{\underline{\underline{w}}}{T} \cdot \frac{\partial T}{\underline{\partial x}} . \tag{57}$$

Combining (55) and (57), we finally obtain

$$G(t \to \infty) = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m} \frac{a_1}{n} \left(\tfrac{5}{2} - \tfrac{1}{2}\beta m w^2\right) \frac{\underline{\underline{w}}}{T} \cdot \frac{\partial T}{\underline{\partial x}} . \tag{58}$$

The term (48) does not contribute to (58).

The right hand side of (25) vanishes when we take $g_e = \left(\frac{\beta m}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\beta m w^2}$. Also we have shown above that there are no terms of the type $S_{1/2}^{(0)} P_0(\cos\theta)\, e^{-\lambda t}$ in the expansion (52) and so

$$H(t \to \infty) = 0 .$$

B.6 Terms involving the mass velocity gradient.

From (35), (36), (42a) and (50), using the relations given by (43), we obtain;

$$\underline{w} \cdot \frac{\partial \underline{u}}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}} + \underline{w} \cdot \frac{\partial \underline{u}}{\partial \underline{x}} \cdot \frac{\partial g_e}{\partial \underline{w}_1}$$

$$= \sum_{r,l} C_{rl} e^{-\lambda_{rl} t} e^{-\frac{1}{2}\beta m w^2} \Big\{ {}_1S^{(r)}_{l+1/2}\, w_1^{\,l} w^{l} \Big[\Big(2\big[(r+1)\, S^{(r+1)}_{l+1/2} -$$

$$(r+l+3/2)\, S^{(r)}_{l+1/2} \big] + l\, S^{(r)}_{l+1/2} \Big) \Big(P_l \sin^2\theta \,[\cos^2\phi\, A_{11} + \sin\phi\cos\phi\,(A_{12}+A_{21})$$

$$+ \sin^2\phi\, A_{22}] + P_l \cos^2\theta\, A_{33} + P_l \sin\theta\cos\theta\,[\sin\phi\,(A_{23}+A_{32}) +$$

$$\cos\phi\,(A_{31}+A_{13})]\Big) - S^{(r)}_{l+1/2} \Big(P_l' \cos\theta \sin^2\theta\,[\cos^2\phi\, A_{11} + \sin\phi\cos\phi\,(A_{12}+A_{21})$$

$$+ \sin^2\phi\, A_{22}] + P_l' \cos^3\theta\, A_{33} + P_l' \cos^2\theta\sin\theta\,[\sin\phi\,(A_{23}+A_{32}) + \cos\phi\,(A_{31} +$$

$$A_{13})]\Big) + S^{(r)}_{l+1/2} \Big(P_l' \sin\theta\,[\cos\phi\, A_{13} + \sin\phi\, A_{23}] + P_l' \cos\theta\, A_{33} \Big) \Big]$$

$$+ S^{(r)}_{l+1/2}\, w_1^{\,l-1} w^{l+1} \Big[{}_1S^{(r)}_{l+1/2} \Big(P_l' \sin^2\theta\,[\cos^2\phi\, A_{11} + \sin\phi\cos\phi\,(A_{12}+A_{21})$$

$$+ \sin^2\phi\, A_{22}] + P_l' \cos\theta\sin\theta\,[\cos\phi\, A_{31} + \sin\phi\, A_{32}] \Big) + \beta m w_1^{\,2}\, {}_1S^{(r)\prime}_{l+1/2}$$

$$\Big([P_l \sin\theta\,(\cos\phi\, A_{13} + \sin\phi\, A_{23})] + P_l \cos\theta\, A_{33} \Big) + l\, {}_1S^{(r)}_{l+1/2} \Big([P_l \sin\theta$$

$$(\cos\phi\, A_{13} + \sin\phi\, A_{23})] + P_l \cos\theta\, A_{33} \Big) \Big].$$

We could use the relations for the Legendre polynomials and Sonine polynomials, and arrange (59) in the form of (52) above.

However, we wish only to calculate $\int U \underline{w}\, d\underline{w}$ and so need terms in (59) which involve $P_1(\cos\theta)\, S^{(0)}_{3/2}\, w$, $P_1^1 \sin\phi\, S^{(0)}_{3/2}\, w$ or $P_1^1 \cos\phi\, S^{(0)}_{3/2}\, w$ The final result is

$$\frac{\partial U}{\partial t} - \left[U, f^{(0)}\right] = A_{33}\, S^{(0)}_{3/2}\, w\, P_1(\cos\theta)\left[c_{02}\, e^{-\lambda_{02}t}\frac{1}{\beta m} + c_{10}\, e^{-\lambda_{10}t}\beta m - c_{01}\, e^{-\lambda_{01}t}\right] + (\cos\phi\, A_{31} + \sin\phi\, A_{32})\, S^{(0)}_{3/2}\, w_1 w\, P_1^1(\cos\theta)\left[c_{02}\, e^{-\lambda_{02}t}\frac{3}{\beta m} - c_{01}\, e^{-\lambda_{01}t}\right] + (\cos\phi\, A_{13} + \sin\phi\, A_{23})\, S^{(0)}_{3/2}\, w_1 w\, P_1^1(\cos\theta)\left[c_{10}\, e^{-\lambda_{10}t}\beta m - c_{02}\, e^{-\lambda_{02}t}\frac{2}{\beta m}\right].$$

Hence, the terms involving in the distribution function are;

$$c_{02}\,\frac{e^{-\lambda_{02}t} - e^{-\lambda_{01}t}}{\lambda_{01} - \lambda_{02}}\,\frac{1}{\beta m}\, w_1\, S^{(0)}_{3/2}\, w\left[3 P_1^1(\cos\phi\, A_{31} + \sin\phi\, A_{32}) + P_1 A_{33} - 2 P_1^1(\cos\phi\, A_{13} + \sin\phi\, A_{23})\right] + c_{10}\,\beta m\, w_1\, S^{(0)}_{3/2}\, w\left[P_1^1(\cos\phi\, A_{13} + \sin\phi\, A_{23}) + P_1 A_{33}\right] t e^{-\lambda_{10}t} - c_{01}\, w_1\, S^{(0)}_{3/2}\, w\left[P_1 A_{33} + P_1^1(\sin\phi\, A_{32} + \cos\phi\, A_{31})\right] t e^{-\lambda_{01}t}.$$

Hence we finally obtain,

$$\left\{\frac{\partial}{\partial t}\int U \underline{w}\, d\underline{w}\right\}_{t=0} = 0. \qquad (60)$$

We find similarly that no terms in U involve $S_{1/2}^{(0)}\, P_0(\cos\theta)$ and so

$$\int U \, d\underline{w} = 0 . \tag{61}$$

Hence the mean acceleration η_+ is given by

$$\eta_+ = \left\{ \frac{1}{n}\frac{\partial}{\partial t}\int n g \, \underline{v} \, d\underline{v} - \frac{\underline{v}_1}{n}\frac{\partial}{\partial t}\int n g \, d\underline{v} \right\}_{t=0}$$

$$= \left\{ \frac{1}{n}\frac{\partial}{\partial t}\int n g_e \, \underline{w} \, d\underline{w} + \frac{\partial}{\partial t}\int U \underline{w} \, d\underline{w} + \frac{1}{n}\frac{\partial}{\partial t}\int n g_e \, \underline{u} \, d\underline{w} \right\}_{t=0}$$

$$= \left\{ \frac{\partial}{\partial t}\left(\underline{w}_1 \, e^{-\lambda_{01} t} \right) + \frac{\partial \underline{u}}{\partial t} \right\}_{t=0}$$

$$= -n\pi \, A_1(5) \left(\frac{2K}{m} \right)^{1/2} \underline{w}_1 ,$$

since we are taking $\underline{w}_1 = \underline{v}_1 - \underline{u}(\underline{x},t)$.

Solution as t → ∞

As t → ∞ the only terms that contribute to U are those not involving t explicitly. Hence the contribution from (31) is obtained from the solution of

$$\frac{\partial U}{\partial t_{exp}} - \left[U, f^{(0)} \right] = \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u} \right) \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{1}{2}\beta m w^2} + \frac{2}{3} T \left(\frac{\partial}{\partial \underline{x}} \cdot \underline{u} \right) \frac{\partial}{\partial T}\left(\left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{1}{2}\beta m}\right.$$

$$+ \underline{w} \cdot \frac{\partial \underline{u}}{\partial \underline{x}} \cdot \frac{\partial}{\partial \underline{w}} \left(\left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{1}{2}\beta m w^2} \right) ,$$

$$= -\beta m \, e^{-\frac{1}{2}\beta m w^2} \left(\frac{\beta m}{2\pi} \right)^{3/2} \left(\underline{w}\,\underline{w} - \frac{1}{3} w^2 \underline{\underline{\delta}} \right) : \frac{\partial \underline{u}}{\partial \underline{x}} .$$

Therefore the contribution to U is

$$-\frac{1}{\lambda_{02}}\beta m \; e^{-\frac{1}{2}\beta m w^2}\left(\frac{\beta m}{2\pi}\right)^{3/2}\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}. \tag{62}$$

From (61) above there will be no contribution from (32). However, there will be a contribution from (30), which is given by the solution of,

$$\frac{\partial U}{\partial t_{exp}} - \left[U, f^{(0)}\right] = \left[e^{-\frac{1}{2}\beta m w^2}\left(\frac{\beta m}{2\pi}\right)^{3/2}, f'\right]$$

$$= -\left[e^{-\frac{1}{2}\beta m w^2}\left(\frac{\beta m}{2\pi}\right)^{3/2}, f^{(0)}\frac{1}{2}\frac{b_1}{n}\beta m\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}\right] \tag{63}$$

for Maxwellian molecules, where

$$b_1 = \frac{4}{3}\,\frac{1}{\pi A_2(5)\left(\frac{2\kappa}{m}\right)^{1/2}}.$$

Equation (63) reduces to

$$\frac{\partial U}{\partial t_{exp}} - \left[U, f^{(0)}\right] = -\left(\lambda_{02}-\mu_{02}\right)\frac{1}{2}\left(\frac{\beta m}{2\pi}\right)^{3/2}\beta m\, e^{-\frac{1}{2}\beta m w^2}\frac{b_1}{n}\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}},$$

and so the contribution from this equation is given by,

$$-\frac{\left(\lambda_{02}-\mu_{02}\right)}{\lambda_{02}}\,\frac{1}{2}\left(\frac{\beta m}{2\pi}\right)^{3/2}e^{-\frac{1}{2}\beta m w^2}\beta m\,\frac{b_1}{n}\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}.$$

Adding to this the contribution (62), we finally obtain

$$U(t\to\infty) = \frac{-1}{2}\,\frac{b_1}{n}\left(\frac{\beta m}{2\pi}\right)^{3/2}e^{-\frac{1}{2}\beta m w^2}\beta m\left(\underline{w}\,\underline{w}-\tfrac{1}{3}w^2\underline{\underline{\delta}}\right):\frac{\partial \underline{u}}{\partial \underline{x}}.$$

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(1) P.M. Morse and H. Feshbach, "Methods of Theoretical Physics". (McGraw-Hill Book Co., New York, 1953) Part 11.

(2) "Higher Transcendental Functions". Bateman Manuscript Project, Volume 2, p.188.

APPENDIX C:

The purpose of this Appendix is to resolve the apparent conflict between the results of Chapter V and the work of O'Toole and Dahler, who do not, of course, take the limit $\tau \to 0$.

From page 5.13, the expression for the mean acceleration $\eta_+^{(0)}$ from the theory of Kirkwood is given by,

$$m\,\eta_+^{(0)} = \sum_N \int \frac{\overset{\circ}{F}_{N+1}}{f^{(0)}} \sum_i \delta(\underline{x}_1 - \underline{x}^{(i)})\,\delta(\underline{v}_1 - \underline{v}^{(i)})\,\frac{1}{\tau}\int_0^{\tau} \sum_{j \neq i} \underset{\sim}{F}_i^{j}(t+s)\,ds\,d\Omega_{N+1} \tag{1}$$

$$= \sum_N \int \frac{\overset{\circ}{F}_{N+1}}{f^{(0)}} \sum_i \delta(\underline{x}_1 - \underline{x}^{(i)})\,\delta(\underline{v}_1 - \underline{v}^{(i)})\;\frac{\underline{v}_\tau^{(i)} - \underline{v}^{(i)}}{\tau}\,d\Omega_{N+1}$$

$$= \sum_N \iiint \frac{\overset{\circ}{F}_{N+1}}{f^{(0)}} \sum_i \delta(\underline{x}_1 - \underline{x}^{(i)})\,\delta(\underline{v}_1 - \underline{v}^{(i)})\,\delta(\underline{x}_\tau - \underline{x}_\tau^{(i)})\,\delta(\underline{v}_\tau - \underline{v}_\tau^{(i)})\,\frac{\underline{v}_\tau^{(i)} - \underline{v}^{(i)}}{\tau}\,d\Omega_{N+1}\,\underline{dx}_\tau\,\underline{dv}_\tau$$

$$= \frac{1}{\tau} \iint g_x^{\circ}(\tau)\,(\underline{v}_\tau - \underline{v}_1)\,\underline{dx}_\tau\,\underline{dv}_\tau\,. \tag{2}$$

From (1), if the limit is taken as $\tau \to 0$, then the equilibrium value of the mean acceleration, i.e. $\eta = 0$, is obtained. However, in (2), it has been found that the limit produces a value different from zero, viz. "$-\zeta\underline{v}_1$".

It is difficult to prove that this argument is a fallacy. Such fallacies are well-known to arise in theoretical physics where two delta functions appear under the same integral. An example of this is the critique of Schwinger's quantum electrodynamics made in Pauli's well-known letter to Schwinger (dated January 24th, 1949). Pauli remarks "Every 'evaluation' of expressions of this type is not a 'computation' in the ordinary sense, but rather a new _definition_, which can only be made precise by referring to a certain limiting process, in the course of which the singular functions are first replaced by regular functions ...... The uniqueness of sensible rules for these definitions has to be particularly investigated."

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