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QUANTUM THEORY OF DENSITY CORRECTIONS
TO THE GASEOUS TRANSPORT COEFFICIENTS

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by

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ABSTRACT

The first density corrections to the transport coefficients are investigated for the case of a quantum gas of spherical particles. The development is based upon a truncation of the quantum mechanical BBGKY equations. For this purpose, the pair distribution function is expressed in terms of singlet distribution functions through the definition of a quantity Y . The BBGKY hierarchy is then truncated by the approximation that Y may be replaced by its equilibrium value. The first of the BBGKY equations is shown, on the basis of a pair distribution function obtained in this manner, to lead to a quantum mechanical Boltzmann equation which is generalized to include both collisional transfer and three-body contributions. This equation is solved by the method of Chapman and Enskog and expressions obtained for the transport coefficients.

Numerical computations for the two-body contributions to the first transport virial coefficients are presented for a quantum gas of rigid spheres. The three-body terms are shown to lead, in the classical limit, to the results of Hoffman.

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CHAPTER I

INTRODUCTION

Statistical mechanics has as its goal the prediction of the macroscopic behavior of large aggregates of matter in terms of the dynamical properties of the constituent particles. The field divides logically into two branches: equilibrium and non-equilibrium statistical mechanics. The former is concerned with those thermodynamic properties which characterize the equilibrium state; the latter deals primarily with the interpretation of the transport phenomena observed in non-equilibrium systems.

The first mathematically rigorous kinetic theory investigations began in 1872 with the development, by Boltzmann[1], of an integro-differential equation governing the time evolution of a singlet distribution function for a gas displaced from equilibrium. The original Boltzmann equation, while valid only for dilute, classical gases of spherical particles, is not further restricted as to the exact form of the molecular interaction. No solution to the Boltzmann equation for an arbitrary intermolecular potential appeared for nearly half a century after its introduction. Finally, in the period 1916-1917, Chapman[2] and Enskog[3] independently developed methods of solution which produced identical results. These led to expressions for the transport coefficients which were in good agreement with experiment[4].

Massey and Mohr[5] were the first investigators to attempt to generalize the results of Chapman and Enskog to include quantum effects. On an intuitive basis, they replaced the classical differential cross-section with its quantum analogue in the expressions for the transport coefficients. In a more rigorous treatment, Uehling and Uhlenbeck[6] subsequently confirmed that this simple modification correctly took into account quantum mechanical diffraction effects. Their results further extended the theory to include gross statistics effects. At this point, the kinetic theory of dilute gases is in substantial agreement with experiment, except for inadequacies in our knowledge of intermolecular forces[4].

The task of generalizing the Boltzmann equation to a consideration of moderately dense gases is far more difficult. Enskog[7] presented the first such treatment. With an intuitive modification of the Boltzmann equation, Enskog succeeded in deriving expressions for the transport coefficients of a moderately dense classical gas of rigid spheres that took into account both the finite size of the spheres and three-body effects.

Since the techniques Enskog applied to rigid spheres were not readily extended to the treatment of soft potentials, it became necessary to consider a more general approach. Bogolubov[8], Born and Green[9], Kirkwood[10], and Yvon[11], by formally integrating the Liouville equation, obtained an infinite hierarchy of equations, the first of which can be shown to lead to the Boltzmann equation.

Various schemes, such as the assumption of "molecular chaos"[4], have been used to truncate the hierarchy. By solving the resulting equations, it is then possible to construct density corrections to the transport coefficients which are valid for soft potentials. Using this approach, Snider and Curtiss[12] derived first density corrections to the thermal conductivity and shear viscosity of a classical gas which took into account the effects of collisional transfer and are valid for any type of intermolecular potential. Hoffman and Curtiss[13] managed to truncate the BBGKY hierarchy with a generalization of the molecular chaos assumption to obtain a soft potential analogue of the Enskog dense gas equation which included both collisional transfer and three-body effects. Numerical computations suggest reasonable agreement with experiment[14].

Few results have, as yet, appeared for the transport coefficients of moderately dense quantum gases. Hoffman, Mueller, and Curtiss[15] have constructed a quantum analogue to the Boltzmann equation which includes collisional transfer. Imam-Rahajoe[16] solved the quantum mechanical BBGKY equations in terms of phase space transformation functions. By introducing the assumption of molecular chaos, his solution led to results for the collisional transfer contributions to the transport coefficients.

Recently, several investigators have used the correlation function approach[17] to develop expressions for the transport coefficients which are valid for moderately dense quantum gases. Herman[18] has employed this formalism to compute the collisional transfer contributions to the first density corrections to the transport coefficients of a moderately dense quantum gas of rigid spheres.

In the present study, we express the pair distribution function in terms of singlets through the definition of a quantity Y. An exact determination of Y would require a complete solution to all N equations of the hierarchy. We instead truncate the hierarchy by assuming that the non-equilibrium Y may be replaced, in approximation, by its equilibrium value in our expression for the pair distribution function. The first equation of the quantum mechanical BBGKY hierarchy is then shown, on the basis of the pair distribution function obtained in this approximation, to lead to a quantum mechanical Boltzmann equation which is generalized to include both collisional transfer and three-body effects. This approach may be regarded as a quantum mechanical generalization of that used by Hoffman[14] in a purely classical study.

A solution to this generalized Boltzmann equation, based upon a perturbation method developed by Chapman and Enskog[2,3] and discussed in detail by Chapman and Cowling[19], yields an expression for the non-equilibrium singlet distribution function which is valid in the near-equilibrium approximation. From this, the transport coefficients are obtained for a gas of particles which interact through a purely repulsive potential.

Numerical computations for the two-body contributions to the first transport virial coefficients are presented for a quantum gas of rigid spheres. The three-body terms are shown to lead, in the classical limit, to the results of Hoffman[14].

CHAPTER II

THE BOLTZMANN EQUATION

The development of classical statistical mechanics is based upon the construction of an ensemble of dynamically similar systems and a distribution function defined in a suitable phase space. These concepts are not directly applicable to the study of quantum systems, however, because the uncertainty principle prohibits assigning a system point an exact location in phase space. In this chapter, a phase space formulation of quantum mechanics based upon the Wigner distribution function is shown to lead to the quantum analogue of the BBGKY hierarchy. The formal reduction of the N-particle problem and the truncation of the hierarchy then follow from the assumption of an appropriate approximate form for the pair distribution function.

2.1 BBGKY Equations

We consider a system composed of a large number N of identical, spherical particles which interact through a potential function which is pair-wise additive, primarily repulsive, and of short range. The potential may be taken to have a weakly attractive portion, but bound states are specifically excluded.

The Hamiltonian operator appropriate to such a system is

$$\mathcal{H}_N = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\frac{d}{d\underline{r}_i}\cdot\frac{d}{d\underline{r}_i} + \sum_{i<j}^{N}\varphi(r_{ij}) \tag{2-1}$$

where r_{ij} refers to the distance between particles i and j. The form of the classical Hamiltonian function then follows directly from the correspondence principle:

$$H_N = \frac{1}{2m}\sum_{i=1}^{N} p_i^2 + \sum_{i<j}^{N}\varphi(r_{ij}) \tag{2-2}$$

The state of an N-particle quantum system is described by its density matrix ρ_N, which may be defined in terms of the system wave function Ψ_N as

$$\rho_N(\underline{r}^N;\underline{r}'^N;t) \equiv \rho_N(\underline{r}_1\ldots\underline{r}_N;\underline{r}'_1\ldots\underline{r}'_N;t)$$

$$\equiv \Psi_N(\underline{r}^N;t)\,\Psi_N^*(\underline{r}'^N;t) \tag{2-3}$$

The time development of ρ_N is then determined by the Heisenberg equation of motion:

$$i\hbar\frac{d\rho_N}{dt} = \mathcal{H}_N\rho_N - \rho_N\mathcal{H}_N \tag{2-4}$$

If we consider an ensemble consisting of a large number of dynamically similar N-particle systems, a statistical probability density matrix, $\mathcal{P}_N$, may be defined as the average over the ensemble of ρ_N. Then, according to Wigner[20], an N-particle distribution function suitable for quantum systems may be expressed as a Fourier transform of $\mathcal{P}_N$:

$$f_N(\underline{r}^N;\underline{p}^N;t) \equiv N!\left(\frac{2}{h}\right)^{3N}\int d\underline{s}^N\, e^{-\frac{2i}{\hbar}\underline{s}^N\cdot\underline{p}^N}\,\mathcal{P}_N(\underline{r}^N+\underline{s}^N;\underline{r}^N-\underline{s}^N;t) \tag{2-5}$$

Clearly, $\mathcal{P}_N$ is also a solution to equation (2-4). The normalization

$$\int d\underline{r}^N d\underline{p}^N f_N(\underline{r}^N;\underline{p}^N;t) = N! \tag{2-6}$$

follows directly from the definition of $\mathcal{P}_N$ and the normalization of the system wave functions. From a knowledge of f_N, any desired contraction may be obtained from

$$f_M(\underline{r}^M;\underline{p}^M;t) = \left[(N-M)!\right]^{-1}\int d\underline{r}^{N-M} d\underline{p}^{N-M} f_N(\underline{r}^N;\underline{p}^N;t) \tag{2-7}$$

With this definition of f_N, some average values may be calculated from formulae that are entirely analogous to those used in the classical case, although the distribution function itself cannot be interpreted in terms of probability concepts.

Moyal[21] has shown that the time evolution of the Wigner distribution function is governed by

$$\frac{\partial f_N}{\partial t} = \left[H_N, f_N\right]_{M.B.} \tag{2-8}$$

where the Moyal bracket is defined by

$$\left[H_N, f_N\right]_{M.B.} \equiv$$

$$\left\{\frac{2}{\hbar}\sin\left[\frac{\hbar}{2}\sum_{i=1}^{N}\left(\frac{\partial}{\partial \underline{r}_i^{H}}\cdot\frac{\partial}{\partial \underline{p}_i^{f}} - \frac{\partial}{\partial \underline{p}_i^{H}}\cdot\frac{\partial}{\partial \underline{r}_i^{f}}\right)\right]\right\} H_N f_N \tag{2-9}$$

Here the superscripts indicate the function on which the differential operators act. In the classical limit, the Moyal bracket becomes the Poisson bracket and equation (2-8) reduces to the Liouville equation of classical statistical mechanics.

Substitution of equation (2-2) for the classical Hamiltonian function into (2-8) leads directly to the well-known Wigner equation[22]:

$$\left\{\frac{\partial}{\partial t} + \mathcal{H}_N - \Theta_N\right\} f_N = 0 \tag{2-10}$$

where

$$\mathcal{H}_N \equiv \frac{1}{m}\sum_{i=1}^{N} \underline{p}_i \cdot \frac{\partial}{\partial \underline{r}_i}$$

$$\Theta_N \equiv -\frac{2}{\hbar}\sum_{j>i}^{N} \sin\left\{\frac{\hbar}{2}\frac{\partial \varphi}{\partial \underline{r}_{ij}} \cdot \frac{\partial}{\partial \underline{p}_{ij}}\right\} \tag{2-11}$$

$$\underline{r}_{ij} \equiv \underline{r}_j - \underline{r}_i \qquad \underline{p}_{ij} \equiv \frac{1}{2}\left(\underline{p}_j - \underline{p}_i\right)$$

The Wigner equation then equivalently determines the temporal development of the N-particle distribution function for this system.

By integrating the Wigner equation over (N-M) coordinates and momenta, we obtain the quantum analogue to the BBGKY equations of classical statistical mechanics:

$$\left\{\frac{\partial}{\partial t} + \mathcal{H}_M - \Theta_M\right\} f_M = \int d\underline{r}^{M+1} d\underline{p}^{M+1}\, \Theta_{M+1}\, f_{M+1} \tag{2-12}$$

where the operator $\mathcal{O}_{M+1}$ is defined by

$$\mathcal{O}_{M+1} \equiv \Theta_{M+1} - \Theta_{M} \tag{2-13}$$

The hierarchy of equations (2-12) then governs the time evolution of the lower order ($M < N$) distribution functions.

2.2 Truncation of the Hierarchy

In physically interesting problems, we are seldom required to know the properties of more than the very lowest order distribution functions. Unfortunately, because of the coupling between equations of the hierarchy, an exact solution of any one would require a complete solution to the N-particle Wigner equation. No completely rigorous theoretical basis for a truncation of the hierarchy has yet appeared, although numerous approximate techniques have been suggested. In this study, we truncate the hierarchy by an approximate technique which may be regarded as the quantum mechanical analogue to that used by Hoffman[14] in a purely classical treatment.

We begin by defining the operator

$$\Omega_{\infty}^{(2)}(\underline{R}\,\underline{r}\,\underline{P}\,\underline{p}|\underline{R}_o\underline{r}_o\underline{P}_o\underline{p}_o) \equiv \left(\frac{2}{h}\right)^6 \int d\underline{s}\, d\underline{\sigma}\, \delta(\underline{R}-\underline{R}_o)\,\delta(\underline{P}-\underline{P}_o)\, \times$$

$$\times\, e^{-\frac{2i}{\hbar}(\underline{s}\cdot\underline{p}+\underline{\sigma}\cdot\underline{r}_o)}\, \psi(\underline{r}+\underline{s};\underline{p}_o+\underline{\sigma})\, \psi^*(\underline{r}-\underline{s};\underline{p}_o-\underline{\sigma}) \tag{2-14}$$

where

$$\underline{R} \equiv \tfrac{1}{2}(\underline{r}_1+\underline{r}_2) \qquad \underline{r} \equiv \underline{r}_2-\underline{r}_1$$

$$\underline{P} \equiv \underline{p}_1+\underline{p}_2 \qquad \underline{p} \equiv \tfrac{1}{2}(\underline{p}_2-\underline{p}_1) \tag{2-15}$$

The wave function $\psi(\underline{r}';\underline{p}')$ is a solution to the relative motion Schrodinger equation:

$$\left\{-\frac{\hbar^2}{m}\frac{d}{d\underline{r}'}\cdot\frac{d}{d\underline{r}'} + \varphi(r')\right\}\psi = \frac{p'^2}{m}\,\psi \tag{2-16}$$

with the boundary condition that it represents asymptotically an incident plane wave of momentum $\underline{p}'$ and scattered waves.

The integral operator $\Omega_{\infty}^{(2)}$ is a phase space transformation function[21] which corresponds to the classical streaming operator $\mathcal{S}^{(2)}$. The two differ in that the $\mathcal{S}^{(2)}$ operator acts to retrace a particle back along a classical trajectory while no such well-defined trajectory exists in the quantum case.

With this, the pair distribution function may be expressed in terms of singlets through the definition of a quantity Y:

$$f_2(\underline{r}_1\underline{r}_2;\underline{p}_1\underline{p}_2;t) \equiv Y(\underline{r}_1\underline{r}_2;\underline{p}_1\underline{p}_2;t)\int d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20} \times$$

$$\times\, \Omega^{(2)}_{\infty}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20})\, f_1(\underline{r}_{10}\underline{p}_{10};t)\, f_1(\underline{r}_{20}\underline{p}_{20};t) \qquad (2\text{-}17)$$

If "molecular chaos" is assumed, Y is unity, and the pair distribution function (2-17) becomes identical to the form introduced by Imam-Rahajoe[16]. In the limit $\hbar \to 0$, Y reduces to the analogous quantity considered by Hoffman[14] for a classical system.

An exact determination of the quantity Y would require solving all N equations of the BBGKY hierarchy. We instead complete the truncation of the hierarchy with the assumption that Y may be replaced, in approximation, by its equilibrium value Y_e in our expression (2-17) for the pair distribution function. In this approximation, equation (2-17) may be substituted into the first equation of the hierarchy,

$$\left\{\frac{\partial}{\partial t} + \frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right\} f_1(\underline{r}_1;\underline{p}_1) = \int d\underline{r}_2\, d\underline{p}_2\, \Theta_2\, f_2(\underline{r}_1\underline{r}_2;\underline{p}_1\underline{p}_2) \qquad (2\text{-}18)$$

to yield:

$$\left\{\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right\}f_1(\underline{r}_1;\underline{p}_1)=\int d\underline{r}_{10}\,d\underline{r}_{20}\,d\underline{p}_{10}\,d\underline{p}_{20}\,d\underline{r}_2\,d\underline{p}_2\;\Theta_2 Y_e(\underline{r}_1\underline{r}_2;\underline{p}_1\underline{p}_2)\times$$

$$\times\,\Omega^{(2)}_{\infty}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20})\,f_1(\underline{r}_{10};\underline{p}_{10})\,f_1(\underline{r}_{20};\underline{p}_{20}) \qquad (2\text{-}19)$$

Since all quantities in equations (2-18) and (2-19) are evaluated at the same time, this dependence has been suppressed in the notation.

2.3 The Boltzmann Equation

Since the left-hand side (LHS) or "streaming" part of equation (2-19) contains only quantities localized at $\underline{r}_1$, it is evident that the right-hand side (RHS) must be similarly localized by expanding Y_e and the singlet distribution functions about their values at $\underline{r}_1$. Retaining only terms linear in the gradient $\frac{\partial}{\partial \underline{r}_1}$,

$$\left\{\frac{\partial}{\partial t} + \frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right\} f_1(\underline{p}_1) = \int d\underline{r}_2\, d\underline{p}_2\, d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \theta_2 \times$$

$$\times\left\{Y_e(\underline{r};\underline{p}_1\underline{p}_2) + \underline{r}\cdot\frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r};\underline{p}_1\underline{p}_2)\right\}\Omega_{\alpha}^{(2)}\left(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2 \middle| \underline{r}_{10}\,\underline{r}_{20}\,\underline{p}_{10}\,\underline{p}_{20}\right)\times \tag{2-20}$$

$$\times\left\{f_1(\underline{p}_{10})f_1(\underline{p}_{20}) + f_1(\underline{p}_{20})\left(\underline{r}_{10}-\underline{r}_1\right)\cdot\frac{\partial}{\partial \underline{r}_1} f_1(\underline{p}_{10}) \right. +$$

$$\left. + f_1(\underline{p}_{10})\left(\underline{r}_{20}-\underline{r}_1\right)\cdot\frac{\partial}{\partial \underline{r}_1} f_1(\underline{p}_{20})\right\}$$

where the local dependence on $\underline{r}_1$ has been suppressed in the notation. We shall see later that, for the purpose of evaluating the transport coefficients, the approximation of retaining only terms linear in the gradients is, in fact, exact.

After transforming to center-of-mass and relative motion coordinates, the integral operator $\Omega_{\alpha}^{(2)}$ may be substituted explicitly into equation (2-20) and the $\underline{R}_0$ and $\underline{\mathcal{P}}_0$ integrations performed trivially. The $\underline{r}_0$ and $\mathcal{P}$ integrations may be carried out exactly using the properties of Fourier integrals. The result, after some manipulation, may be written

The result, after some manipulation, may be written

$$\left\{\frac{\partial}{\partial t} + \frac{1}{m}\underline{p}_1 \cdot \frac{\partial}{\partial \underline{r}_1}\right\} f_1(\underline{p}_1) =$$

$$\frac{1}{m}\int d\underline{r}_2\, d\underline{p}_2\, d\underline{p}_0\, Y_e(\underline{r}\underline{p}_1\underline{p}_2)\left\{\underline{p}\,\underline{r} : \underline{\underline{\Delta}}_1 \frac{\partial F}{\partial \underline{r}} - F \underline{p}_0 \cdot \underline{\underline{\Delta}}_2 + \underline{\underline{\Delta}}_2 \underline{p} : \frac{\partial}{\partial \underline{r}} \underline{G}\right\}$$

$$+\frac{2}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \left\{Y_e(\underline{r}\underline{p}_1\underline{p}_2) + \underline{r} \cdot \frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r}\underline{p}_1\underline{p}_2)\right\} f_1(\tilde{\underline{p}}_1) f_1(\tilde{\underline{p}}_2)\, \underline{p} \cdot \frac{\partial F}{\partial \underline{r}}$$

$$+\int d\underline{r}\, d\underline{p}_0\, d\underline{p}_2 \left[\Theta_2 , \left\{Y_e(\underline{r}\underline{p}_1\underline{p}_2) + \underline{r} \cdot \frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r}\underline{p}_1\underline{p}_2)\right\}\right] \times$$

$$\times \left\{\frac{1}{2} F \underline{r} \cdot \underline{\underline{\Delta}}_1 + \frac{1}{2} \underline{G} \cdot \underline{\underline{\Delta}}_2 + F f_1(\tilde{\underline{p}}_1) f_1(\tilde{\underline{p}}_2)\right\} \tag{2-21}$$

where

$$\Delta_1 \equiv \frac{\partial}{\partial \mathbf{r}_1}\left\{ f_1(\tilde{\mathbf{p}}_1) f_1(\tilde{\mathbf{p}}_2) \right\} \qquad \Delta_2 \equiv f_1(\tilde{\mathbf{p}}_1)\frac{\partial}{\partial \mathbf{r}_1} f_1(\tilde{\mathbf{p}}_2) - f_1(\tilde{\mathbf{p}}_2)\frac{\partial}{\partial \mathbf{r}_1} f_1(\tilde{\mathbf{p}}_1)$$

$$F \equiv \left(\frac{2}{h}\right)^3 \int d\mathbf{s}\; e^{-\frac{2i}{\hbar}\mathbf{s}\cdot\mathbf{p}}\, \psi(\mathbf{r}+\mathbf{s};\mathbf{p}_0)\, \psi^*(\mathbf{r}-\mathbf{s};\mathbf{p}_0)$$

$$\mathbf{G} \equiv \frac{\hbar}{2i}\left(\frac{2}{h}\right)^3 \int d\mathbf{s}\; e^{-\frac{2i}{\hbar}\mathbf{s}\cdot\mathbf{p}} \left\{ \psi^*(\mathbf{r}-\mathbf{s};\mathbf{p}_0)\frac{\partial}{\partial \mathbf{p}_0}\psi(\mathbf{r}+\mathbf{s};\mathbf{p}_0) - \psi(\mathbf{r}+\mathbf{s};\mathbf{p}_0)\frac{\partial}{\partial \mathbf{p}_0}\psi^*(\mathbf{r}-\mathbf{s};\mathbf{p}_0) \right\} \tag{2-22}$$

$$\tilde{\mathbf{p}}_1 \equiv \frac{1}{2}\mathbf{P} - \mathbf{p}_0 \qquad\qquad \tilde{\mathbf{p}}_2 \equiv \frac{1}{2}\mathbf{P} + \mathbf{p}_0$$

$$[A,B] \equiv AB - BA$$

Equation (2-21) is then the desired quantum mechanical Boltzmann equation, modified to include collisional transfer and three-body effects in an approximate manner, and we shall refer to it as simply the Boltzmann equation. It may be shown that this form reduces to that of Imam-Rahajoe[16] when Y_e is taken to have a value of unity.

2.4 Linearization of the Boltzmann Equation

The transport coefficients are defined in terms of a linear approximation for the dependence of the momentum and energy fluxes on the system gradients and are valid only when the system is near equilibrium. Consequently, to develop expressions for the transport coefficients, it is only necessary to solve the Boltzmann equation for a singlet distribution function which is correct through first order in the gradients. For this reason, it is convenient to linearize the Boltzmann equation by a perturbation expansion due to Enskog[3].

The distribution function may be represented as a power series in a uniformity parameter ϵ ;

$$f_1(r_1 p_1) \equiv \sum_{i=0} \epsilon^i f_1^{(i)} \tag{2-23}$$

The uniformity parameter ϵ then serves as a measure of the deviation from equilibrium and its powers may be taken to represent the orders of the gradients of the macroscopic variables. In the final expressions, ϵ will be assigned a value of unity.

The quantity $F(\underline{r}; \underline{p}, \underline{p}_0)$ is a Wigner distribution function defined on the relative motion phase space of two particles. Consequently, $F(\underline{r}; \underline{p}, \underline{p}_0)$ is a time-independent solution to the Wigner equation for the relative motion of two particles:

$$\left\{ \frac{2}{m} \underline{p} \cdot \frac{\partial}{\partial \underline{r}} - \theta_2 \right\} F = 0 \tag{2-24}$$

Substituting the expansion (2-23) into the Boltzmann equation, retaining only terms of zero order in the gradients, and making use of equation (2-24), we obtain the equilibrium equation:

$$\int d\underline{r}\, dp_2\, dp_0\, \Theta_2\, Y_e(r p_1 p_2)\, F(r_i p_1 p_0)\, f_{1e}(\tilde{p}_1)\, f_{1e}(\tilde{p}_2) = 0 \qquad (2\text{-}25)$$

If linear terms in the perturbation are kept, the singlet distribution function may be written in terms of the equilibrium function as

$$f_1 \sim f_{1e} \left\{ 1 + \phi \right\} \qquad (2\text{-}26)$$

where the perturbation function ϕ is taken to be linear in the gradients. The streaming part of the Boltzmann equation is already linear in the gradients, thus linear in ϵ, and becomes simply

$$\left\{ \frac{\partial}{\partial t} + \frac{1}{m} p_1 \cdot \frac{\partial}{\partial \underline{r}_1} \right\} f_{1e}(p_1) \qquad (2\text{-}27)$$

Through terms linear in the gradients, the RHS of the Boltzmann equation is

$$\int d\underline{r}\, dp_2\, dp_0 \left[\Theta_2, \underline{r}\cdot\frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r}p_1p_2)\right] f_{1e}(\tilde{p}_1) f_{1e}(\tilde{p}_2)\, F$$

$$+\frac{1}{m}\int d\underline{r}\, dp_2\, dp_0\, Y_e(\underline{r}p_1p_2)\left\{ p\underline{r} : \underline{\underline{\Delta}}_{1e}\frac{\partial F}{\partial \underline{r}} - F p_0\cdot\underline{\underline{\Delta}}_{2e} + \underline{\underline{\Delta}}_{2e}\, p : \frac{\partial}{\partial \underline{r}}\, \underline{G}\right\}$$

$$+\int d\underline{r}\, dp_2\, dp_0 \left[\Theta_2, Y_e(\underline{r}p_1p_2)\right]\left\{\frac{1}{2} F \underline{r}\cdot\underline{\underline{\Delta}}_{1e} + \frac{1}{2}\underline{\underline{\Delta}}_{2e}\cdot \underline{G} + \right.$$

$$\left. + \left[1+\phi(\tilde{p}_1)+\phi(\tilde{p}_2)\right] f_{1e}(\tilde{p}_1) f_{1e}(\tilde{p}_1)\, F \right\} \qquad (2\text{-}28)$$

$$+\frac{2}{m}\int d\underline{r}\, dp_2\, dp_0 \left\{ p\cdot\frac{\partial F}{\partial \underline{r}}\right\}\left\{ f_{1e}(\tilde{p}_1) f_{1e}(\tilde{p}_2)\, \underline{r}\cdot\frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r}p_1p_2) + \right.$$

$$\left. + \left[1+\phi(\tilde{p}_1)+\phi(\tilde{p}_2)\right] Y_e(\underline{r}p_1p_2)\, f_{1e}(\tilde{p}_1) f_{1e}(\tilde{p}_2)\right\}$$

Here the vector functions $\underline{\underline{\Delta}}_{1e}$ and $\underline{\underline{\Delta}}_{2e}$ differ from the quantities defined in (2-22) only through the substitution of the equilibrium form of the singlet distribution functions.

After subtracting out the zero order equation and rearranging, the linearized form of the Boltzmann equation becomes

$$\left\{\frac{\partial}{\partial t}+\frac{1}{m}\underline{p}_1\cdot\frac{\partial}{\partial \underline{r}_1}\right\}f_{1e}$$

$$-\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, f_{1e}(\tilde{\underline{p}}_1)f_{1e}(\tilde{\underline{p}}_2)\,\Theta_2\left\{F\,\underline{r}\cdot\frac{\partial}{\partial \underline{r}_1}Y_e(\underline{r}\underline{p}_1\underline{p}_2)\right\}$$

$$-\frac{1}{2}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\left[\Theta_2, Y_e(\underline{r}\underline{p}_1\underline{p}_2)\right]\left\{F\,\underline{r}\cdot\underline{\underline{\Delta}}_{1e}+\underline{\underline{\Delta}}_{2e}:\underline{\underline{G}}\right\}$$

$$-\frac{1}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, Y_e(\underline{r}\underline{p}_1\underline{p}_2)\left\{\underline{p}\,\underline{r}:\underline{\underline{\Delta}}_{1e}\frac{dF}{d\underline{r}}-F\underline{p}_0\cdot\underline{\underline{\Delta}}_{2e}+\underline{\underline{\Delta}}_{2e}\underline{p}:\frac{\partial}{\partial \underline{r}}\underline{\underline{G}}\right\}$$

$$=\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\left\{\phi(\tilde{\underline{p}}_1)+\phi(\tilde{\underline{p}}_2)\right\}f_{1e}(\tilde{\underline{p}}_1)f_{1e}(\tilde{\underline{p}}_2)\,\Theta_2\,Y_e(\underline{r}\underline{p}_1\underline{p}_2)F$$

(2-29)

Since only those solutions which are time-independent functionals of the three macroscopic variables are of interest, we require that the defining equations for the number density n, stream velocity $\underline{u}$, and temperature T should hold for both the equilibrium and the perturbed distributions. This leads to the following auxiliary conditions on ϕ :

$$
\begin{aligned}
n\left[f_{1e}(1+\phi)\right] &= n\left[f_{1e}\right] \\
\underline{u}\left[f_{1e}(1+\phi)\right] &= \underline{u}\left[f_{1e}\right] \\
E\left[f_{1e}(1+\phi)\right] &= E\left[f_{1e}\right]
\end{aligned}
\qquad (2\text{-}30)
$$

The number density, stream velocity, and energy density E are defined explicitly in Chapter III (Eq. 3-40).

2.5 Equations of Change

According to the Enskog technique, we choose solutions to equation (2-29) for which the time development of f_1 arises only from a dependence upon the macroscopic variables n, $\underline{u}$, and T. In this section, the equations of change are employed to remove the explicit time dependence from the linearized Boltzmann equation. Since we ultimately seek only the first density corrections to the transport coefficients, it will be convenient to discard terms cubic and higher in the number density in the following development.

The three equations of change are independent of the choice of microscopic description of the system and may be written[4]:

<u>Equation of Continuity</u>

$$\frac{\partial n}{\partial t} + \frac{\partial}{\partial \underline{r}_1} \cdot (n\underline{u}) = 0 \tag{2-31}$$

<u>Equation of Motion</u>

$$\frac{\partial \underline{u}}{\partial t} + \underline{u} \cdot \frac{\partial}{\partial \underline{r}_1} \underline{u} + \frac{1}{nm} \frac{\partial}{\partial \underline{r}_1} \cdot \underline{\underline{P}} = 0$$

<u>Equation of Energy Balance</u>

$$\frac{\partial E}{\partial t} + \frac{\partial}{\partial \underline{r}_1} \cdot (E\underline{u}) + \underline{\underline{P}} : \frac{\partial}{\partial \underline{r}_1} \underline{u} + \frac{\partial}{\partial \underline{r}_1} \cdot \underline{q} = 0$$

where $\underline{\underline{P}}$ is the pressure tensor and $\underline{q}$ the heat flux vector.

At equilibrium,

$$\underline{\underline{P}}_e = P \underline{\underline{U}}$$

$$\underline{q}_e = 0 \tag{2-32}$$

where P is the hydrostatic pressure. Retaining terms up to quadratic in the number density, P may be written as the virial expansion:

$$P = nKT\left\{1 + nB\right\} \tag{2-33}$$

The equilibrium energy density may then be expressed in terms of the second virial coefficient as[4]:

$$E_e = \frac{3}{2}nKT - n^2KT^2\frac{dB}{dT} \tag{2-34}$$

Substitution of equations (2-32) into the equations of change then yields their equilibrium forms, the Euler equations:

$$\begin{aligned} &\frac{\partial n}{\partial t} + \frac{\partial}{\partial \underline{r}_1}\cdot(n\underline{u}) = 0 \\ &\frac{\partial \underline{u}}{\partial t} + \underline{u}\cdot\frac{\partial}{\partial \underline{r}_1}\underline{u} + \frac{1}{nm}\frac{\partial}{\partial \underline{r}_1}P = 0 \\ &\frac{\partial E_e}{\partial t} + \underline{u}\cdot\frac{\partial E_e}{\partial \underline{r}_1} + \left\{E_e + P\right\}\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} = 0 \end{aligned} \tag{2-35}$$

Combining equation (2-34) and the last of equations (2-35) then leads to an equation of change for the temperature:

$$\frac{dT}{dt} + \underline{u} \cdot \frac{dT}{d\underline{r}_1} +$$

$$+ \frac{2}{3} T \left\{ 1 + nB + \frac{7}{3} nT \frac{dB}{dT} + \frac{2}{3} nT^2 \frac{d^2B}{dT^2} \right\} \frac{\partial}{\partial \underline{r}_1} \cdot \underline{u} = 0$$

(2-36)

Be defining

$$\underline{P}_i \equiv \underline{p}_i - m\underline{u} \qquad (2\text{-}37)$$

and the substantial time derivative,

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \underline{u} \cdot \frac{\partial}{\partial \underline{r}_1} \qquad (2\text{-}38)$$

the streaming part of the Boltzmann equation may be rewritten as

$$\left\{ \frac{D}{Dt} + \frac{1}{m} \underline{P}_1 \cdot \frac{\partial}{\partial \underline{r}_1} \right\} f_{1e}(\underline{P}_1) \qquad (2\text{-}39)$$

Considering the functional dependence of f_{1e} on the macroscopic variables and simply writing out the total derivatives, (2-39) becomes

$$\left\{ \frac{\partial \ln f_{1e}}{\partial n} \left[\frac{n}{m} \underline{P}_1 \cdot \frac{\partial \ln n}{\partial \underline{r}_1} + \frac{Dn}{Dt} \right] + \right.$$

$$+ \frac{\partial \ln f_{1e}}{\partial T} \left[\frac{T}{m} \underline{P}_1 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} + \frac{DT}{Dt} \right] + \tag{2-40}$$

$$\left. + \frac{1}{m} \frac{\partial \ln f_{1e}}{\partial \underline{u}} \underline{P}_1 : \frac{\partial}{\partial \underline{r}_1} \underline{u} + \frac{\partial \ln f_{1e}}{\partial \underline{u}} \cdot \frac{D\underline{u}}{Dt} \right\} f_{1e}$$

It is now convenient to introduce the formal density expansion:

$$f_{1e} \equiv n \hat{f}_{1e} + n^2 \hat{\hat{f}}_{1e} + \ldots \tag{2-41}$$

for the local singlet equilibrium distribution function, where the lowest order term is the familiar Boltzmann form

$$\hat{f}_{1e} = \left(\frac{\lambda}{h} \right)^3 e^{-W_1^2} \tag{2-42}$$

and

$$\underline{W}_1 \equiv \frac{\underline{P}_1}{\sqrt{2mKT}} \qquad \lambda \equiv \frac{h}{\sqrt{2\pi mKT}} \tag{2-43}$$

An explicit expression for $\hat{\hat{f}}_{1e}$ will be adopted in the next section, but at this point it is only necessary to assume it to be a function of only the magnitude of $\underline{P}_1$.

With the Euler equations (2-35) and (2-36), the substantive derivatives may be removed from (2-40) and the streaming part of the Boltzmann equation finally written as a linear combination of the macroscopic gradients:

$$-\underline{K}''\cdot\frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{L}}'':\frac{\partial}{\partial \underline{r}_1}\underline{u} - M''\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} - \underline{N}''\cdot\frac{\partial \ln n}{\partial \underline{r}_1} \tag{2-44}$$

where

$$\underline{K}'' = n\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\left\{\left(\frac{5}{2}-W_1^2\right)\hat{f}_{1e} + n\left[\left(B+T\frac{dB}{dT}\right)\hat{f}_{1e} - \frac{\partial\hat{\hat{f}}_{1e}}{\partial W_1^2} - T\frac{\partial\hat{\hat{f}}_{1e}}{\partial T}\right]\right\}$$

$$\underline{\underline{L}}'' = -2n\underline{W}_1\underline{W}_1\left\{\hat{f}_{1e} - n\frac{\partial\hat{\hat{f}}_{1e}}{\partial W_1^2}\right\}$$

$$M'' = \frac{2}{3}nW_1^2\hat{f}_{1e} + \frac{2}{3}n^2\left\{3\hat{\hat{f}}_{1e} + T\frac{\partial\hat{\hat{f}}_{1e}}{\partial T} - \left(\frac{3}{2}-W_1^2\right)\left(B+\frac{7}{3}T\frac{dB}{dT}+\frac{2}{3}T^2\frac{d^2B}{dT^2}\right)\hat{f}_{1e}\right\} \tag{2-45}$$

$$\underline{N}'' = n^2\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\left\{2B\hat{f}_{1e} - \frac{\partial\hat{\hat{f}}_{1e}}{\partial W_1^2} - 2\hat{\hat{f}}_{1e}\right\}$$

and

$$\frac{\partial}{\partial W_1^2} \equiv \frac{\partial}{\partial \underline{W}_1}\cdot\frac{\partial}{\partial \underline{W}_1} \tag{2-46}$$

In order to similarly represent the collisional transfer and three-body portions of the Boltzmann equation as linear combinations of the macroscopic gradients and arrange the terms properly according to the density, a density expansion of Y_e is required. It is demonstrated in Appendix E that such an expansion may be written formally as

$$Y_e(\underline{r}\underline{p}_1\underline{p}_2) \equiv 1 + n\,\mathcal{Y}_e(\underline{r}\underline{p}_1\underline{p}_2) + \ldots \tag{2-47}$$

The vectors $\underline{\underline{\Delta}}_{1e}$ and $\underline{\underline{\Delta}}_{2e}$ are then evaluated by the same process of direct differentiation and substitution of the equations of change which was applied to the streaming part of the Boltzmann equation. The results are

$$\underline{\Delta}_{1e} = n^2 \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{2\,\frac{\partial \ln n}{\partial \underline{r}_1} + \frac{\underline{P}}{KT}\cdot\frac{\partial \underline{u}}{\partial \underline{r}_1} - \left[3 - \frac{P^2}{4mKT} - \frac{p_o^2}{mKT}\right]\frac{\partial \ln T}{\partial \underline{r}_1}\right\}$$

$$\underline{\Delta}_{2e} = \frac{n^2}{KT}\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\,\underline{p}_o\cdot\left\{\frac{1}{m}\underline{P}\,\frac{\partial \ln T}{\partial \underline{r}_1} + 2\,\frac{\partial}{\partial \underline{r}_1}\underline{u}\right\} \tag{2-48}$$

where

$$\underline{P} \equiv \underline{P}_1 + \underline{P}_2 \tag{2-49}$$

Substituting the results (2-41), (2-47), and (2-48), and using the fact that $[\Theta_2, 1]$ is a null operator, the collisional transfer terms of equation (2-29) may be expressed as the desired linear combination of the macroscopic gradients:

$$-\underline{K}'\cdot\frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{L}}':\frac{\partial}{\partial \underline{r}_1}\underline{u} - M'\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} - \underline{N}'\cdot\frac{\partial \ln n}{\partial \underline{r}_1} \tag{2-50}$$

where

$$\underline{K}' = \frac{-n^2}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\left[3 - \frac{P^2}{4mkT} - \frac{p_0^2}{mkT}\right]\underline{r}\,\underline{p}\cdot\frac{d\underline{F}}{d\underline{r}} + \right.$$

$$\left. + \frac{(\underline{p}_0\cdot\underline{P})}{mkT}\left[\underline{p}_0 F - \underline{p}\cdot\frac{d}{d\underline{r}}\underline{G}\right]\right\}$$

$$\underline{\underline{L}}' = \frac{n^2}{mkT}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\overset{\circ}{\underline{P}\,\underline{r}}\,\underline{p}\cdot\frac{d\underline{F}}{d\underline{r}} - 2\overset{\circ}{\underline{p}_0\underline{p}_0} + 2\overset{\circ}{\underline{p}_0\underline{p}}\cdot\frac{d}{d\underline{r}}\underline{G}\right\} \tag{2-51}$$

$$M' = \frac{2n^2}{3mkT}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\frac{1}{2}(\underline{P}\cdot\underline{r})\,\underline{p}\cdot\frac{d\underline{F}}{d\underline{r}} - p_0^2 F + \underline{p}_0\underline{p}:\frac{d}{d\underline{r}}\underline{G}\right\}$$

$$\underline{N}' = \frac{2n^2}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,\underline{r}\,\underline{p}\cdot\frac{d\underline{F}}{d\underline{r}}$$

The notation

$$\overset{\circ}{\underline{A}\,\underline{B}} \equiv \underline{A}\,\underline{B} - \frac{1}{3}\underline{A}\cdot\underline{B}\,\underline{\underline{U}} \tag{2-52}$$

has been introduced in equations (2-51) to indicate a traceless tensor.

These results for the collisional transfer terms are then identical to those obtained by Imam-Rahajoe[16]. This agreement may be seen to arise from the retention of only terms up to quadratic in the number density and the fact that in the low density limit Y_e is unity.

2.6 The Integral Equation

The Boltzmann equation has now been converted to an integral equation for the perturbation function ϕ. By combining the singly and doubly primed coefficients in equations (2-45) and (2-51), the integral equation may be written formally as

$$J = \Delta(\phi) \tag{2-53}$$

where the inhomogeneity J is

$$-\underline{K}\cdot\frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{L}}:\frac{\partial}{\partial \underline{r}_1}\underline{u} - M\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} - \underline{N}\cdot\frac{\partial \ln n}{\partial \underline{r}_1} \tag{2-54}$$

$$\underline{K} = \underline{K}' + \underline{K}'' \qquad \underline{\underline{L}} = \underline{\underline{L}}' + \underline{\underline{L}}''$$

$$M = M' + M'' \qquad \underline{N} = \underline{N}' + \underline{N}''$$

and $\Delta(\phi)$ is the integral operator on the RHS of equation (2-29):

$$\Delta(\phi) \equiv \int d\underset{\sim}{r}\, d\underset{\sim}{p}_2\, d\underset{\sim}{p}_0 \left\{ \phi(\tilde{\underset{\sim}{p}}_1) + \phi(\tilde{\underset{\sim}{p}}_2) \right\} f_{1e}(\tilde{\underset{\sim}{p}}_1)\, f_{1e}(\tilde{\underset{\sim}{p}}_2)\, \theta_2\, Y_e\, F \tag{2-55}$$

At this point, the integral equation (2-53) may be simplified by a demonstration that, for the system under consideration, the term in the inhomogeneity which is proportional to the density gradient vanishes identically through terms quadratic in the density. The non-vanishing result for this term obtained by Imam-Rahajoe may be shown to have arisen from his assumption of an incorrect form for the first density correction to the singlet equilibrium distribution function. This in turn is a result of his use of the molecular chaos assumption (Y=1) in developing the Boltzmann equation.

For a gas of particles which interact through a purely repulsive potential, all states lie in the continuum. It is shown in Appendix A that, from the results de Boer[23], the first density correction to the singlet equilibrium distribution function for such a gas may be written:

$$\hat{\hat{f}}_{1e}(\underset{\sim}{p}_1) = \left(\frac{2}{h}\right)^3 \int d\underset{\sim}{s}\; e^{\frac{2i}{\hbar}\underset{\sim}{s}\cdot\underset{\sim}{p}_1}\; e^{-\frac{4\pi s^2}{\lambda^2}} \times$$

$$\times \left\{ \int d\underset{\sim}{r} \left(e^{\frac{2\pi s^2}{\lambda^2}} g_0(\underset{\sim}{r}+\underset{\sim}{s};\underset{\sim}{r}-\underset{\sim}{s}) - g_0(\underset{\sim}{r};\underset{\sim}{r}) \right) \right\} \tag{2-56}$$

where

$$g_0(\underline{r};\underline{r}') \equiv 2^{3/2}\left(\frac{\lambda}{h}\right)^3 \int d\underline{p}\; \Psi^*(\underline{r}';\underline{p})\, \Psi(\underline{r};\underline{p})\, e^{-p^2/mKT} \tag{2-57}$$

The quantity $g_0(\underline{r};\underline{r})$ is the quantum mechanical radial distribution function, in the binary collision approximation, for a system which obeys Boltzmann statistics and cannot support bound states. The expression for $\hat{\hat{f}}_{1e}$ employed by Imam-Rahajoe corresponds to the first term of a Sonine polynomial expansion of (2-56). Expansion coefficients for the higher terms are non-zero, however.

In the proof that $\underline{N} = 0$, occasional use is made of the result of de Boer for the second virial coefficient in terms of the radial distribution function:

$$B = -\frac{1}{2}\int d\underline{r}\left\{ g_0(\underline{r};\underline{r}) - 1 \right\} \tag{2-58}$$

With the definition of $\underline{N}$ in equations (2-45), (2-51), and (2-54)

$$\begin{aligned} \underline{N} &= n^2\left(\frac{2KT}{m}\right)^{1/2} \underline{W}_1 \left\{ 2B\hat{f}_{1e} - \frac{\partial}{\partial W_1^2}\hat{f}_{1e} - 2\hat{\hat{f}}_{1e} \right\} \\ &+ \frac{2n^2}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \underline{r}\,\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} \end{aligned} \tag{2-59}$$

Using the result of lemma B-10, the second term on the RHS of equation (2-59) becomes

$$\frac{2n^2}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\underline{p}\left\{\delta(\underline{p}-\underline{p}_0)-F\right\} \tag{2-60}$$

After carrying out the trivial delta function integration and rearranging slightly, this may be written as

$$\frac{2n^2}{m}\left(\frac{\lambda}{h}\right)^6\int d\underline{r}\, d\underline{p}_2\, \underline{p}\, e^{-P^2/4mKT}\left\{e^{-p^2/mKT}\, - \right.$$

$$\left. -2^{-3/2}\left(\frac{\lambda}{h}\right)^3\int d\underline{s}\, e^{-\frac{2i}{\hbar}\underline{s}\cdot\underline{p}}\, g_0(\underline{r}+\underline{s};\underline{r}-\underline{s})\right\} \tag{2-61}$$

The $\underline{p}_2$ integration may be carried out directly in (2-61). Making use of the definition of $\hat{\hat{f}}_{1e}$, the result may be expressed as

$$n^2\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\left\{2\hat{\hat{f}}_{1e}+\frac{d}{dW_1^2}\hat{\hat{f}}_{1e}\right\}$$

$$+n^2\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\int d\underline{r}\left\{-\hat{f}_{1e}+\left(\frac{\lambda}{h}\right)^3 g_0(\underline{r};\underline{r})\left[2+\frac{d}{dW_1^2}\right]\times\right.$$

$$\left.\times\int d\underline{s}\; e^{\frac{i}{\hbar}(8mKT)^{1/2}\underline{W}_1\cdot\underline{s}}\quad e^{-4\pi s^2/\lambda^2}\right\} \tag{2-62}$$

Completing the $\underline{s}$ integration and the indicated differentiations then gives

$$n^2\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\left\{2\hat{\hat{f}}_{1e}+\frac{d}{dW_1^2}\hat{\hat{f}}_{1e}\right\}$$

$$n^2\left(\frac{2KT}{m}\right)^{1/2}\underline{W}_1\hat{f}_{1e}\int d\underline{r}\left\{g_0(\underline{r};\underline{r})-1\right\} \tag{2-63}$$

Finally, substitution of the result (2-63) into equation (2-59) and use of the defining equation (2-58) for the second virial coefficient completes the proof that $N = 0$.

CHAPTER III

SOLUTION OF THE INTEGRAL EQUATION

The perturbation function defined in the preceding chapter may be written as an expansion in powers of the number density. The Boltzmann equation is then separable on the basis of the density and may be solved independently for each order.

3.1 Density Separation

We begin by introducing a formal density expansion of the perturbation:

$$\phi(p_i) \equiv \frac{1}{n}\,\phi_0(p_i) + \phi_1(p_i) + \cdots \tag{3-1}$$

Then, using the density expansion of Y_e and the definition of the Δ operator in equation (2-55), $\Delta(\phi)$ may also be written as an expansion in powers of the density:

$$\begin{aligned}\Delta(\phi) = {} & n\Delta_0(\phi_0) + n^2\Delta_0(\phi_1) \\ & + n^2\int d\mathbf{r}\,d\mathbf{p}_2\,d\mathbf{p}_3\left\{\phi_0(\tilde{\mathbf{p}}_1) + \phi_0(\tilde{\mathbf{p}}_2)\right\}\Big\{\hat{f}_{1e}(\tilde{\mathbf{p}}_1)\hat{f}_{1e}(\tilde{\mathbf{p}}_2)\,\theta_2\,\mathcal{Y}_e F + \\ & + \left[\hat{f}_{1e}(\tilde{\mathbf{p}}_1)\hat{\hat{f}}_{1e}(\tilde{\tilde{\mathbf{p}}}_2) + \hat{f}_{1e}(\tilde{\mathbf{p}}_2)\hat{\hat{f}}_{1e}(\tilde{\tilde{\mathbf{p}}}_1)\right]\theta_2 F\Big\}\end{aligned} \tag{3-2}$$

where

$$\Delta_0(\phi_i) \equiv \int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \left\{ \phi_i(\tilde{\underline{p}}_1) + \phi_i(\tilde{\underline{p}}_2) \right\} \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \theta_2 F \tag{3-3}$$

The integral operator Δ_0 may be put into the form of the usual Boltzmann collision integral by substituting equation (2-24) into (3-3) and using the result of Hoffman, Mueller, and Curtiss[15]:

$$\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \left\{ \phi_i(\tilde{\underline{p}}_1) + \phi_i(\tilde{\underline{p}}_2) \right\} \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \underline{p}_0 \cdot \frac{dF}{d\underline{r}} =$$

(3-4)

$$\int d\hat{\underline{K}}\, d\underline{p}_2\, \hat{f}_{1e}(\underline{p}_1)\, \hat{f}_{1e}(\underline{p}_2) \left\{ \phi_i(\underline{p}_1') + \phi_i(\underline{p}_2') - \phi_i(\underline{p}_1) - \phi_i(\underline{p}_2) \right\} p\, \sigma(\theta)$$

where

$\hat{\underline{k}}$ = unit vector in the direction of the scattered particle

$\sigma(\theta)$ = differential cross-section (3-5)

$\underline{p}_1' = \frac{1}{2}\underline{P} - \hat{\underline{K}} \qquad \underline{p}_2' = \frac{1}{2}\underline{P} + \hat{\underline{K}}$

Then combining equations (2-45), (2-54), and (3-2), the lowest order Boltzmann equation, arising from terms linear in the number density, is

$$-\underset{\sim}{K}_0 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{L}}_0 : \frac{\partial}{\partial \underline{r}_1} \underline{u} - M_0 \frac{\partial}{\partial \underline{r}_1} \cdot \underline{u} = \Delta_0(\phi_0) \tag{3-6}$$

where

$$\underset{\sim}{K}_0 = \left(\frac{2KT}{m}\right)^{1/2} \left(\frac{5}{2} - W_1^2\right) \underline{W}_1 \hat{f}_{1e}$$

$$\underline{\underline{L}}_0 = -2 \overset{\circ}{\underline{W}_1 \underline{W}_1} \hat{f}_{1e}$$

$$M_0 = 0 \tag{3-7}$$

The inhomogeneity in equation (3-6) involves only terms from the streaming portion of the Boltzmann equation. With auxiliary conditions which will be discussed later, the first order equation is thus the ordinary Boltzmann equation for a simple gas. This problem has been solved by Chapman and Cowling[19] with an approximate matrix inversion technique and by Hirschfelder and Curtiss[24] with a variational method. Their solutions for the perturbation function ϕ_0 are identical and may be written in terms of the Sonine polynomials as

$$\underline{\phi}_0 = -\underline{A}_0 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{B}}_0 : \frac{\partial}{\partial \underline{r}_1} \underline{u}$$

$$\underline{A}_0 = \mathcal{A}_0(W_1^2)\underline{W}_1 \qquad \underline{\underline{B}}_0 = \mathcal{B}_0(W_1^2)\overset{\circ}{\underline{W}_1 \underline{W}_1} \tag{3-8}$$

where, to lowest order,

$$\mathcal{A}_0 = -\frac{15}{8}\left(\frac{KT}{2m}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1} S_{3/2}^{(1)}(W_1^2)$$

$$\mathcal{B}_0 = \frac{5}{4}\left(\Omega^{(2,2)}\right)^{-1} \tag{3-9}$$

An expression for the $\Omega^{(2,2)}$ integral for quantum systems is given in Appendix F.

The second order Boltzmann equation may now be written in terms of the known solution to the first order equation:

$$J_1 = \Delta_0(\phi_1) \tag{3-10}$$

where

$$J_1 = -\underline{K}_1 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{L}}_1 : \frac{\partial}{\partial \underline{r}_1} \underline{u} - M_1 \frac{\partial}{\partial \underline{r}_1} \cdot \underline{u} \tag{3-11}$$

$$\underline{K}_1 = \left(\frac{2KT}{m}\right)^{1/2} \underline{W}_1 \left\{ \left(B + T\frac{dB}{dT}\right)\hat{f}_{1e} - \frac{\partial \hat{\hat{f}}_{1e}}{\partial W_1^2} - T\frac{\partial \hat{\hat{f}}_{1e}}{\partial T} \right\}$$

$$- \frac{1}{m}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{ \left[3 - \frac{1}{mKT}\left(\frac{1}{4}P^2 + p_0^2\right)\right]\underline{r}\,\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} + \right.$$

$$\left. + \frac{1}{mKT}(\underline{p}_0\cdot\underline{P})\left(\underline{p}_0 F - \underline{p}\cdot\frac{\partial}{\partial \underline{r}}\underline{G}\right)\right\}$$

$$- \int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \left\{\underline{A}_0(\tilde{\underline{p}}_1) + \underline{A}_0(\tilde{\underline{p}}_2)\right\}\left\{ \left[\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2) + \hat{f}_{1e}(\tilde{\underline{p}}_2)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1)\right]\Theta_2 F + \right.$$

$$\left. + \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,\Theta_2\, \mathcal{Y}_e F \right\}$$

$$\underline{\underline{L}}_1 = 2\underline{W}_1^{\circ}\underline{W}_1 \frac{\partial \hat{\hat{f}}_{1e}}{\partial W_1^2} + \frac{1}{mKT}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{ \underline{P}\overset{\circ}{\underline{r}}\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} - 2\overset{\circ}{\underline{p}_0}\underline{p}_0 F + 2\underline{p}_0\overset{\circ}{\underline{p}}\cdot\frac{\partial}{\partial \underline{r}}\underline{G} \right\}$$

$$- \int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \left\{\underline{\underline{B}}_0(\tilde{\underline{p}}_1) + \underline{\underline{B}}_0(\tilde{\underline{p}}_2)\right\}\left\{ \left[\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2) + \hat{f}_{1e}(\tilde{\underline{p}}_2)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1)\right]\Theta_2 F + \right.$$

$$\left. + \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,\Theta_2\, \mathcal{Y}_e F \right\}$$

$$M_1 = 2\hat{\hat{f}}_{1e} + \frac{2}{3}T\frac{\partial \hat{\hat{f}}_{1e}}{\partial T} + \frac{2}{3}W_1^2\frac{\partial \hat{\hat{f}}_{1e}}{\partial W_1^2}$$

$$- \frac{2}{3}\left(\frac{3}{2} - W_1^2\right)\left(B + \frac{7}{3}T\frac{dB}{dT} + \frac{2}{3}T^2\frac{d^2B}{dT^2}\right)\hat{f}_{1e}$$

$$+ \frac{2}{3}(mKT)^{-1}\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{ \frac{1}{2}(\underline{r}\cdot\underline{P})\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} - p_0^2 F + \underline{p}_0\underline{p} : \frac{\partial}{\partial \underline{r}}\underline{G} \right\}$$

Here $\underline{\underline{L}}_1$ and M_1 have been adjusted to make $\underline{\underline{L}}_1$ traceless.

3.2 Solubility of the Second Order Equation

The second order Boltzmann equation is an inhomogenous integral equation. Accordingly, the condition for its solubility is that the inhomogeneity J_1 be orthogonal to the solutions of

$$\Delta_o^{+}(\phi_1) = 0 \tag{3-12}$$

where Δ_o^{+} is the adjoint of the Δ_o operator. The solutions to the homogenous adjoint equation are the five summational invariants: 1, $\underline{P}_1$, and P_1^2. Thus, to show that the second order equation is soluble, it is necessary to prove that

$$\int d\underline{P}_1 \, \underline{K}_1 \psi^{(i)} = \int d\underline{P}_1 \, \underline{\underline{L}}_1 \psi^{(i)} = \int d\underline{P}_1 \, M_1 \psi^{(i)} = 0 \tag{3-13}$$

$$i = 1, 2, 3$$

where

$$\psi^{(1)} \equiv 1 \qquad \psi^{(2)} \equiv \underline{P}_1 \qquad \psi^{(3)} \equiv P_1^2 \tag{3-14}$$

Since the tensors $\underline{K}_1$, $\underline{\underline{L}}_1$, and M_1 are functions of only $\underline{P}_1$, an integration over the angles of $\underline{P}_1$ in the orthogonality conditions must produce only isotropic tensors. There are no isotropic odd order tensors and the only second order isotropic tensor $\underline{U}$ is not traceless. The second order tensor $\underline{L}_1$ is traceless, however. Thus, the orthogonality conditions (3-13) reduce to

$$\int d\underline{P}_1 \underline{P}_1 \underline{K}_1 = \int d\underline{P}_1 M_1 = \int d\underline{P}_1 M_1 P_1^2 = 0 \tag{3-15}$$

The remainder of this section is devoted to proofs that the conditions (3-15) are satisfied.

3.2a Orthogonality condition on $\underline{\underline{K}}_1$

$$\int d\underline{P}_1 \underline{P}_1 \underline{K}_1 = 0 \tag{3-15'}$$

Proof:

With a straightforward integration of part of the first term and an integration by parts in the other, a change of variables in the second and third terms, and some rearrangement, the LHS becomes

$$\left\{KT\left(B+T\frac{dB}{dT}\right)+KT\int d\underset{\sim}{P}_1\,\hat{\hat{f}}_{1e}-\frac{1}{3m}T\frac{d}{dT}\int d\underset{\sim}{P}_1\,P_1^2\,\hat{\hat{f}}_{1e}\right\}\underset{\approx}{U}$$

$$-\frac{1}{m}\int d\underset{\sim}{r}\,d\underset{\sim}{p}_0\,d\underset{\sim}{P}\,d\underset{\sim}{p}\left(\tfrac{1}{2}\underset{\sim}{P}-\underset{\sim}{p}\right)\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{\left[3-\frac{1}{mKT}\left(\tfrac{1}{4}P^2+p_0^2\right)\right]\underset{\sim}{r}\underset{\sim}{p}\cdot\frac{dF}{d\underset{\sim}{r}}+\right.\tag{3-16}$$

$$\left.+\frac{1}{mKT}(\underset{\sim}{p}_0\cdot\underset{\sim}{P})\left[\underset{\sim}{p}_0F-\underset{\sim}{p}\cdot\frac{d}{d\underset{\sim}{r}}\underset{\sim}{G}\right]\right\}$$

$$-\int d\underset{\sim}{r}\,d\underset{\sim}{p}_0\,d\underset{\sim}{p}\,d\underset{\sim}{P}\left(\tfrac{1}{2}\underset{\sim}{P}-\underset{\sim}{p}\right)\left\{\underset{\sim}{A}_0(\tilde{p}_1)+\underset{\sim}{A}_0(\tilde{p}_2)\right\}\left\{\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\,\Theta_2\,\mathcal{Y}_e\,F+\right.$$

$$\left.+\left[\hat{f}_{1e}(\tilde{p}_1)\hat{\hat{f}}_{1e}(\tilde{p}_2)+\hat{f}_{1e}(\tilde{p}_2)\hat{\hat{f}}_{1e}(\tilde{p}_1)\right]\Theta_2 F\right\}$$

Substitution of lemmas B-1 and B-2 reduces the first term to

$$KT\left\{B+T\frac{dB}{dT}-\frac{1}{3}\epsilon_1-\frac{1}{3}T\frac{d\epsilon_1}{dT}\right\}\underset{\approx}{U}\tag{3-17}$$

where

$$\epsilon_i\equiv 2^{3/2}\left(\frac{\lambda}{h}\right)^3\int d\underset{\sim}{r}\,d\underset{\sim}{p}_0\,e^{-p_0^2/mKT}\times$$

$$\times\left\{\left(\frac{-\hbar^2}{mKT}\right)^i\psi^*\left(\frac{d}{d\underset{\sim}{r}}\cdot\frac{d}{d\underset{\sim}{r}}\right)^i\psi-2\left(i+\tfrac{1}{2}\right)!\,\psi\psi^*\right\}\tag{3-18}$$

The $\underline{P}$-integration may be performed directly in the second term of (3-16) to give

$$\frac{2^{3/2}}{m}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\; e^{-p_0^2/mKT} \left\{\frac{3}{2} - \frac{p_0^2}{mKT}\right\} \underline{r}\,\underline{p}\,\underline{p} \cdot \frac{d\underline{F}}{d\underline{r}} \tag{3-19}$$

$$-\frac{2^{3/2}}{m}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\; e^{-p_0^2/mKT} \left\{\underline{p}_0\underline{p}_0 F - \underline{p}_0\underline{p} \cdot \frac{d}{d\underline{r}}\,\underline{G}\right\}$$

The second integral in (3-19) vanishes on substitution of lemmas B-5 and B-11. With lemma (B-9) and the definition of the radial distribution function, the first integral yields

$$\frac{1}{6}\,\underline{\underline{U}}\;T\,\frac{\partial}{\partial T}\int d\underline{r}\; g_0(\underline{r};\underline{r})\; \underline{r}\cdot\frac{d\varphi}{d\underline{r}} \tag{3-20}$$

Then using an equivalent definition of the second virial coefficient, namely

$$B \equiv \frac{1}{3}\,\epsilon_1 - \frac{1}{6KT}\int d\underline{r}\; g_0(\underline{r};\underline{r})\; \underline{r}\cdot\frac{d\varphi}{d\underline{r}} \tag{3-21}$$

the first two terms in (3-16) add to zero.

Much of the proof that the final term vanishes is dependent upon symmetry relations satisfied by the functions and the operator in the integrand. Considering their definitions, we have the following:

$$\underline{A}_0(\tilde{p}_1) \xrightarrow[\underline{P}\to-\underline{P}]{} -\underline{A}_0(\tilde{p}_2) \xrightarrow[p_0\to-p_0]{} -\underline{A}_0(\tilde{p}_1)$$

$$\hat{f}_{1e}(\tilde{p}_1) \xrightarrow[\underline{P}\to-\underline{P}]{} \hat{f}_{1e}(\tilde{p}_2) \xrightarrow[p_0\to-p_0]{} \hat{f}_{1e}(\tilde{p}_1)$$

$$\hat{\hat{f}}_{1e}(\tilde{p}_1) \xrightarrow[\underline{P}\to-\underline{P}]{} \hat{\hat{f}}_{1e}(\tilde{p}_2) \xrightarrow[p_0\to-p_0]{} \hat{\hat{f}}_{1e}(\tilde{p}_1)$$

(3-22)

$$F(-\underline{r};-p,-p_0) = F(\underline{r};p,p_0)$$

$$\Theta_2(\underline{r};p) = \Theta_2(-\underline{r};-p)$$

Since $\mathcal{Y}_e$ must be unchanged by an inversion of the coordinate system or a particle interchange, it is also true that

$$\mathcal{Y}_e(\underline{r};\underline{p},\underline{P}) = \mathcal{Y}_e(-\underline{r};-\underline{p},-\underline{P}) = \mathcal{Y}_e(-\underline{r};-\underline{p},\underline{P}) \tag{3-23}$$

With equation (2-24), the final term in (3-16) may be written

$$-\frac{1}{m}\int d\underline{r}\,d\underline{p}_o\,d\underline{p}\,d\underline{P}\left\{\underline{A}_o(\tilde{\underline{p}}_1)+\underline{A}_o(\tilde{\underline{p}}_2)\right\}\underline{P}\underline{p}\cdot\frac{dF}{d\underline{r}}\left\{\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2)+\hat{f}_{1e}(\tilde{\underline{p}}_2)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1)\right\}$$

$$+\frac{2}{m}\int d\underline{r}\,d\underline{p}_o\,d\underline{p}\,d\underline{P}\left\{\underline{A}_o(\tilde{\underline{p}}_1)+\underline{A}_o(\tilde{\underline{p}}_2)\right\}\underline{p}\underline{p}\cdot\frac{dF}{d\underline{r}}\left\{\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2)+\hat{f}_{1e}(\tilde{\underline{p}}_2)\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1)\right\}$$

$$-\int d\underline{r}\,d\underline{p}_o\,d\underline{p}\,d\underline{P}\left(\tfrac{1}{2}\underline{P}-\underline{p}\right)\left\{\underline{A}_o(\tilde{\underline{p}}_1)+\underline{A}_o(\tilde{\underline{p}}_2)\right\}\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,\Theta_2\,\mathcal{Y}_e F \tag{3-24}$$

The first integral vanishes on completion of the $\underline{p}$ integration with lemma B-6. The second changes sign when the direction of the $\underline{P}$-integration is reversed and must, therefore, be zero. The same consideration reduces the last integral to

$$-\frac{1}{2}\int d\underline{P}\,d\underline{p}_o\,\underline{P}\left\{\underline{A}_o(\tilde{\underline{p}}_1)+\underline{A}_o(\tilde{\underline{p}}_2)\right\}\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,I(\underline{p}_o;\underline{P}) \tag{3-25}$$

where

$$I(p_0;\underline{P}) \equiv \int d\underline{r}\, d\underline{p}\ \Theta_2\, \mathcal{Y}_e(\underline{r};\underline{p},\underline{P})\, F(\underline{r};\underline{p},\underline{p}_0) \tag{3-26}$$

The proof of (3-15') is then reduced to showing that the function $I(p_0;\underline{P})$ is identically zero. Using an equivalent definition of the Θ_2 operator:

$$\Theta_2 \equiv \frac{1}{\hbar}\int d\underline{K}\, \alpha(\underline{K}) \sin(\underline{K}\cdot\underline{r}) \left\{ e^{\frac{\hbar}{2}\underline{K}\cdot\frac{\partial}{\partial \underline{p}}} - e^{-\frac{\hbar}{2}\underline{K}\cdot\frac{\partial}{\partial \underline{p}}} \right\}$$

(3-27)

$$\alpha(\underline{K}) \equiv (2\pi)^{-3} \int d\underline{r}'\, \cos(\underline{K}\cdot\underline{r}')\, \varphi(r')$$

and the Taylor series expansion for the exponentials, $I(p_0;\underline{P})$ becomes:

$$\frac{1}{\hbar}\int d\underline{r}\, d\underline{K}\, \alpha(\underline{K}) \sin(\underline{K}\cdot\underline{r}) \int dp\, \mathcal{Y}_e(\underline{r}; p + \tfrac{\hbar}{2}\underline{K}, p) F(\underline{r}; p + \tfrac{\hbar}{2}\underline{K}, p_0)$$

$$- \frac{1}{\hbar}\int d\underline{r}\, d\underline{K}\, \alpha(\underline{K}) \sin(\underline{K}\cdot\underline{r}) \int dp\, \mathcal{Y}_e(\underline{r}; p - \tfrac{\hbar}{2}\underline{K}, p) F(\underline{r}; p - \tfrac{\hbar}{2}\underline{K}, p_0) \qquad (3\text{-}28)$$

Finally, by shifting the origin of the p integration by $-\hbar\underline{K}$ in the first integral, it precisely cancels the second and the result follows.

3.2b First Orthogonality Condition on M_1

$$\int d\underline{P}_1\, M_1 = 0 \qquad (3\text{-}15'')$$

Proof:

Integrating the third term by parts, the LHS becomes

$$\left\{1+\frac{2}{3}T\frac{\partial}{\partial T}\right\}\int d\underset{\sim}{P}_1 \hat{\hat{f}}_{1e}$$

$$-\frac{2}{3}\pi^{-3/2}\left\{B+\frac{7}{3}T\frac{dB}{dT}+\frac{2}{3}T^2\frac{d^2B}{dT^2}\right\}\int d\underset{\sim}{W}_1\left(\frac{3}{2}-W_1^2\right)e^{-W_1^2} \tag{3-29}$$

$$+\frac{2}{3mKT}\int d\underset{\sim}{r}\, d\underset{\sim}{p}_0\, d\underset{\sim}{p}\, d\underset{\sim}{P}\, \hat{f}_{1e}(\tilde{\underset{\sim}{p}}_1)\hat{f}_{1e}(\tilde{\underset{\sim}{p}}_2)\left\{\frac{1}{2}(\underset{\sim}{r}\cdot\underset{\sim}{P})\underset{\sim}{p}\cdot\frac{\partial F}{\partial \underset{\sim}{r}}-p_0^2F+\underset{\sim}{p}_0\underset{\sim}{p}:\frac{\partial}{\partial \underset{\sim}{r}}\underset{\sim}{G}\right\}$$

The first integral in (3-29) is zero by lemma B-1. The second vanishes as a result of the orthogonality condition for Sonine polynomials. With lemma B-6, the third integral reduces to

$$-\frac{2}{3mKT}\int d\underset{\sim}{r}\, d\underset{\sim}{p}_0\, d\underset{\sim}{p}\, d\underset{\sim}{P}\, \hat{\hat{f}}_{1e}(\tilde{\underset{\sim}{p}}_1)\,\hat{\hat{f}}_{1e}(\tilde{\underset{\sim}{p}}_2)\left\{p_0^2F-\underset{\sim}{p}_0\underset{\sim}{p}:\frac{\partial}{\partial \underset{\sim}{r}}\underset{\sim}{G}\right\} \tag{3-30}$$

The $\underset{\sim}{p}$ integration can then be done with the aid of lemmas B-5 and B-11 and the result follows directly.

3.2c <u>Second Orthogonality Condition on M_1</u>

$$\int d\underset{\sim}{P}_1\, P_1^2\, M_1 = 0 \tag{3-15'''}$$

With an integration by parts in the third term, the LHS is

$$\left\{\frac{1}{3}+\frac{2}{3}T\frac{d}{dT}\right\}\int d\underline{P}_1\, P_1^2\, \hat{\hat{f}}_{1e}$$

$$-\frac{4}{3}\pi^{-3/2} mKT\left\{B+\frac{7}{3}T\frac{dB}{dT}+\frac{2}{3}T^2\frac{d^2B}{dT^2}\right\}\int d\underline{W}_1\, W_1^2\left(\frac{3}{2}-W_1^2\right)e^{-W_1^2} \qquad (3\text{-}31)$$

$$+\frac{2}{3mKT}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{\frac{1}{2}\underline{P}-\underline{p}\right\}^2 \times$$

$$\times\left\{\frac{1}{2}(\underline{r}\cdot\underline{P})\underline{p}\cdot\frac{dF}{d\underline{r}}-p_0^2F+\underline{p}_0\underline{p}:\frac{d}{d\underline{r}}\underline{G}\right\}$$

The first integral may be evaluated by use of lemma B-2. The second may be carried out directly. Then performing the $\underline{P}$ integration in the third, (3-31) becomes

$$mK\left\{\frac{1}{3}+\frac{2}{3}T\frac{\partial}{\partial T}\right\}\epsilon_1 T \;+2mKT\left\{B+\frac{7}{3}T\frac{dB}{dT}+\frac{2}{3}T^2\frac{d^2B}{dT^2}\right\}$$

$$-\frac{2^{5/2}}{3}\left(\frac{\lambda}{h}\right)^3\int d\underline{r}\,d\underline{p}_0\,d\underline{p}\; e^{-p_0^2/mKT}\;(\underline{r}\cdot\underline{p})\,\underline{p}\cdot\frac{\partial F}{\partial \underline{r}}$$

$$-2^{3/2}\left(\frac{\lambda}{h}\right)^3\int d\underline{r}\,d\underline{p}_0\,d\underline{p}\; e^{-p_0^2/mKT}\left(p_0^2 F-\underline{p}_0\underline{p}:\frac{\partial}{\partial \underline{r}}\underline{G}\right) \tag{3-32}$$

$$-\frac{2^{5/2}}{3mKT}\left(\frac{\lambda}{h}\right)^3\int d\underline{r}\,d\underline{p}_0\,d\underline{p}\; p^2\; e^{-p_0^2/mKT}\left(p_0^2 F-\underline{p}_0\underline{p}:\frac{\partial}{\partial \underline{r}}\underline{G}\right)$$

With lemma B-9 and the definition of the radial distribution function, the third term in (3-32) yields:

$$\frac{1}{3}m\int d\underline{r}\; g_0(\underline{r};\underline{r})\;\underline{r}\cdot\frac{d\varphi}{d\underline{r}} \tag{3-33}$$

The integral in the fourth term is identical to the one in (3-30) and has already been shown to be zero. The $\underline{p}$ integration can be carried out in the fifth term with lemmas B-7 and B-12 to give

$$\frac{\sqrt{2}}{3}\frac{\hbar^2}{KT}\left(\frac{\lambda}{h}\right)^3\int d\underline{r}\,d\underline{p}_0\, e^{-p_0^2/mKT}\, \underline{p}_0\,\frac{d\varphi}{d\underline{r}} :$$

$$:\left\{\psi^*\frac{\partial}{\partial\underline{r}}\frac{\partial}{\partial\underline{p}_0}\psi-\frac{\partial\psi^*}{\partial\underline{r}}\frac{\partial\psi}{\partial\underline{p}_0}-\frac{\partial\psi}{\partial\underline{r}}\frac{\partial\psi^*}{\partial\underline{p}_0}+\psi\frac{\partial}{\partial\underline{r}}\frac{\partial}{\partial\underline{p}_0}\psi^*\right\} \tag{3-34}$$

By using Green's theorem and the Schrodinger equation, this may be shown to reduce to

$$\frac{2^{5/2}}{3KT}\int d\underline{r}\,d\underline{p}_0\, e^{-p_0^2/mKT}\, p_0^2\,\varphi\,\psi\,\psi^* \tag{3-35}$$

With the definition (3-21) of the second virial coefficient and the definition (3-18) of the ϵ_1 integral, (3-35) becomes

$$-\frac{2}{3}mKT\left\{\frac{5}{2}\epsilon_1+T\frac{d\epsilon_1}{dT}+7T\frac{dB}{dT}+2T^2\frac{d^2B}{dT^2}\right\} \tag{3-36}$$

Combining the results of (3-32), (3-33), and (3-36), the LHS of equation (3-15''') is

$$2mKT\left\{B - \frac{1}{3}\epsilon_1 + \frac{1}{6KT}\int d\underline{r}\, g_0(\underline{r}_1;\underline{r})\, \underline{r} \cdot \frac{d\varphi}{d\underline{r}}\right\} \tag{3-37}$$

which is zero from the definition of the second virial coefficient in equation (3-21).

3.3 Formal Solution and Auxiliary Conditions

A special solution to the second order Boltzmann equation exists in the form of a linear combination of the macroscopic gradients. This solution can be made general by adding an arbitrary solution to the homogenous equation

$$\Delta_0(\phi_1) = 0 \tag{3-38}$$

The most general arbitrary solution of the homogenous equation is a linear combination of the five summational invariants. Consequently, a general solution to the second order Boltzmann equation may be written formally as:

$$\phi_1 = -\underline{A}_1 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} - \underline{\underline{B}}_1 : \frac{\partial}{\partial \underline{r}_1}\underline{u} - C_1 \frac{\partial}{\partial \underline{r}_1} \cdot \underline{u}$$

$$+ \delta + \underline{\gamma} \cdot \underline{P}_1 + \mathcal{H} P_1^2 \tag{3-39}$$

where $\underline{B}_1$ is a traceless tensor and δ, $\underline{\gamma}$, and $\mathcal{H}$ are five constants.

To uniquely fix the constants, we employ the three auxiliary conditions (2-30). These require that the definitions of the number density, stream velocity, and energy density hold for both the equilibrium and the perturbed distributions. The appropriate definitions are[16]

$$n(\underline{r}_1) \equiv \int d\underline{p}_1 \, f_1(\underline{r}_1; \underline{p}_1)$$

$$\underline{u}(\underline{r}_1) \equiv \frac{1}{nm} \int d\underline{p}_1 \, \underline{p}_1 \, f_1(\underline{r}_1; \underline{p}_1) \tag{3-40}$$

$$E(\underline{r}_1) \equiv \frac{1}{2m} \int d\underline{p}_1 \, P_1^2 \, f_1(\underline{r}_1; \underline{p}_1)$$

$$+ \frac{1}{2} \int d\underline{p}_1 \, d\underline{p}_2 \, d\underline{r}_2 \, \varphi(r) \, f_2(\underline{r}_1 \underline{r}_2; \underline{p}_1 \underline{p}_2)$$

In order to use the auxiliary condition on the energy density, the pair distribution function must first be expressed in terms of singlets through use of the definition (2-17). Before the definition may be used, however, it must be localized at $\underline{r}_1$. Retaining only terms at most linear in the gradients and remembering that Y has consistently been replaced by its equilibrium value, the result is

$$
\begin{aligned}
f_2(\underline{r};\underline{p},\underline{P}) \sim Y_e(\underline{r};\underline{p},\underline{P}) \int d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \Omega^{(2)}_{\alpha\beta}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}) \times \\
\times \Big\{ f_1(\underline{p}_{10}) f_1(\underline{p}_{20}) + f_1(\underline{p}_{10})(\underline{r}_{20}-\underline{r}_1)\cdot\frac{\partial}{\partial \underline{r}_1} f_1(\underline{p}_{20}) + \\
+ f_1(\underline{p}_{20})(\underline{r}_{10}-\underline{r}_1)\cdot\frac{\partial}{\partial \underline{r}_1} f_1(\underline{p}_{10}) \Big\} \\
+ \Big\{ \underline{r}\cdot\frac{\partial}{\partial \underline{r}_1} Y_e(\underline{r};\underline{p},\underline{P}) \Big\} \int d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \Omega^{(2)}_{\alpha\beta}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}) f_1(\underline{p}_{10}) f_1(\underline{p}_{20})
\end{aligned}
\tag{3-41}
$$

Since all functions are now evaluated at $\underline{r}_1$, this dependence has been suppressed in the notation.

The auxiliary conditions (2-30) may now be written out explicitly, again retaining only terms up to linear in the gradients:

$$\int d\underline{p}_1 f_{1e}(p_1)\,\phi(\underline{p}_1) = 0$$

$$\int d\underline{p}_1 f_{1e}(p_1)\,\underline{p}_1\,\phi(\underline{p}_1) = 0$$

$$\int d\underline{p}_1 P_1^2 f_{1e}(p_1)\,\phi(\underline{p}_1) = \tag{3-42}$$

$$-m\int d\underline{p}_1 d\underline{p}_2 d\underline{r}_2\, Y_e(\underline{r};\underline{p},\underline{P})\int d\underline{r}_{10} d\underline{r}_{20} d\underline{p}_{10} d\underline{p}_{20}\,\Omega_{eq}^{(2)}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20})\times$$

$$\times\Big\{f_{1e}(p_{10})f_{1e}(p_{20})\big[\phi(\underline{p}_{10})+\phi(\underline{p}_{20})\big] + f_{1e}(p_{10})\,(\underline{r}_{20}-\underline{r}_1)\cdot\frac{\partial}{\partial\underline{r}_1} f_{1e}(p_{20}) +$$

$$+ f_{1e}(p_{20})\,(\underline{r}_{10}-\underline{r}_1)\cdot\frac{\partial}{\partial\underline{r}_1} f_{1e}(p_{10})\Big\}\,\varphi(r)$$

$$-m\int d\underline{p}_1 d\underline{p}_2 d\underline{r}_2\,\varphi(r)\Big\{\underline{r}\cdot\frac{\partial Y_e}{\partial\underline{r}_1}\Big\}\int d\underline{r}_{10} d\underline{r}_{20} d\underline{p}_{10} d\underline{p}_{20}\,\Omega_{eq}^{(2)}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20})\times$$

$$\times f_{1e}(p_{10})\,f_{1e}(p_{20})$$

Carrying out the usual density expansions in (3-42) and retaining only terms of zero order in the density, we obtain

$$\int d\underline{p}_1 \hat{f}_{1e}(p_1)\, \phi_0(\underline{p}_1) = 0$$

$$\int d\underline{p}_1 \underline{p}_1 \hat{f}_{1e}(p_1)\, \phi_0(\underline{p}_1) = 0 \qquad (3\text{-}43)$$

$$\int d\underline{p}_1 P_1^2 \hat{f}_{1e}(p_1)\, \phi_0(\underline{p}_1) = 0$$

These are the three auxiliary conditions required in the solution of the first order Boltzmann equation for ϕ_0 .

Retaining only terms of first order in the density in equations (3-42) produces the auxiliary conditions on ϕ_1 for the solution of the second order Boltzmann equation. These conditions are expressed in terms of ϕ_0 , which is known from the solution to the first order equation, and are

$$\int d\underline{p}_1 \hat{f}_{1e}(\underline{p}_1)\, \phi_1(\underline{p}_1) = -\int d\underline{p}_1 \hat{\hat{f}}_{1e}(\underline{p}_1)\, \phi_0(\underline{p}_1)$$

(3-44)

$$\int d\underline{p}_1 \hat{f}_{1e}(\underline{p}_1)\, \underline{p}_1\, \phi_1(\underline{p}_1) = -\int d\underline{p}_1 \hat{\hat{f}}_{1e}(\underline{p}_1)\, \underline{p}_1\, \phi_0(\underline{p}_1)$$

$$\int d\underline{p}_1 P_1^2 \hat{f}_{1e}(\underline{p}_1)\, \phi_1(\underline{p}_1) = -\int d\underline{p}_1 P_1^2 \hat{\hat{f}}_{1e}(\underline{p}_1)\, \phi_0(\underline{p}_1)$$

$$-m \int d\underline{p}_1 d\underline{p}_2 d\underline{r}_2\, \varphi(r) \int d\underline{r}_{10} d\underline{r}_{20} d\underline{p}_{10} d\underline{p}_{20}\, \underline{\underline{\Omega}}_{c}^{(2)}(\underline{r}_1 \underline{r}_2 \underline{p}_1 \underline{p}_2 | \underline{r}_{10} \underline{r}_{20} \underline{p}_{10} \underline{p}_{20}) \times$$

$$\times \hat{f}_{1e}(\underline{p}_{10}) \hat{f}_{1e}(\underline{p}_{20}) \left\{ \phi_0(\underline{p}_{10}) + \phi_0(\underline{p}_{20}) \right\}$$

The general solution for the perturbation function ϕ_1 given in equation (3-39) involves three tensors $\underline{A}_1$, $\underline{B}_1$, and C_1, which are vector functions of only $\underline{W}_1$. Consequently, in analogy to the treatment of the first order equation, these tensors may be expressed as

$$\underline{A}_1 \equiv a_1(W_1^2)\,\underline{W}_1$$

$$\underline{\underline{B}}_1 \equiv \mathcal{B}_1(W_1^2)\,\overset{\circ}{\underline{W}_1\underline{W}_1} \qquad (3\text{-}45)$$

$$C_1 \equiv \mathcal{C}_1(W_1^2)$$

The five constants, δ , $\underline{\gamma}$, and $\mathcal{H}$, may then be taken to be zero provided that a_1 and $\mathcal{C}_1$ satisfy the following auxiliary conditions:

$$\int d\underline{W}_1\, \mathcal{C}_1(W_1^2)\,\hat{f}_{1e}(W_1) = 0$$

$$\int d\underline{W}_1\, a_1(W_1^2)\,\hat{f}_{1e}(W_1)\,W_1^2 = -\int d\underline{W}_1\, W_1^2\, a_0(W_1^2)\,\hat{\hat{f}}_{1e}(W_1) \qquad (3\text{-}46)$$

$$\int d\underline{W}_1\, W_1^2\, \mathcal{C}_1(W_1^2)\,\hat{f}_{1e}(W_1) = 0$$

These follow directly from equations (3-44) and (3-45) and a consideration of the tensor properties of the various integrals. Use has also been made of the result from the solution of the first order equation that $\mathcal{C}_0$ is zero. Because it is traceless, no further condition on $\underline{B}_1$ results. The function $\mathcal{A}_0$ is known from the approximate solution to the first order equation given in (3-9).

3.4 Solution of the Second Order Equation

With the results of the preceding section, the problem of solving the second order Boltzmann equation (3-10) is reduced to solving three inhomogeneous integral equations:

$$\begin{aligned} \underline{K}_1 &= \Delta_0(\underline{A}_1) \\ \underline{\underline{L}}_1 &= \Delta_0(\underline{\underline{B}}_1) \\ M_1 &= \Delta_0(C_1) \end{aligned} \tag{3-47}$$

subject to the conditions (3-46). These may be converted to three equivalent scalar equations:

$$\begin{aligned} \underline{W}_1 \cdot \underline{K}_1 &= \Delta_0(\underline{W}_1 \cdot \underline{A}_1) \\ \underline{W}_1 \overset{\circ}{\underline{W}}_1 : \underline{\underline{L}}_1 &= \Delta_0(\underline{W}_1 \overset{\circ}{\underline{W}}_1 : \underline{\underline{B}}_1) \\ M_1 &= \Delta_0(C_1) \end{aligned} \tag{3-48}$$

Following the usual treatment of the first order equation, we represent $\mathcal{A}_1$, $\mathcal{B}_1$, and $\mathcal{C}_1$ as a finite linear combinations of Sonine polynomials:

$$\mathcal{A}_1 = \sum_{j=0}^{\nu-1} \alpha_{ij} S_{3/2}^{(j)}(W_1^2)$$

$$\mathcal{B}_1 = \sum_{j=0}^{\nu-1} \beta_{ij} S_{5/2}^{(j)}(W_1^2) \tag{3-49}$$

$$\mathcal{C}_1 = \sum_{j=0}^{\nu-1} c_{ij} S_{1/2}^{(j)}(W_1^2)$$

It is then convenient to introduce the following notation:

$$K_1^{(i)} \equiv \int d\underline{p}_1 S_{3/2}^{(i)}(W_1^2)\, \underline{W}_1 \cdot \underline{K}_1$$

$$L_1^{(i)} \equiv \int d\underline{p}_1 S_{5/2}^{(i)}(W_1^2)\, \underline{W}_1 \overset{\circ}{\underline{W}_1} : \underline{\underline{L}}_1 \tag{3-50}$$

$$M_1^{(i)} \equiv \int d\underline{p}_1 S_{1/2}^{(i)}(W_1^2)\, M_1$$

and

$$\Delta_{ij} \equiv \int d\underline{p}_1 d\underline{p}_2 d\hat{\underline{k}}\, \sigma(\theta) \left|\frac{\underline{p}}{2m}\right| S_{3/2}^{(i)}(W_1^2)\, \hat{f}_{1e}(W_1)\, \hat{f}_{1e}(W_2)\, \underline{W}_1 \cdot$$

$$\cdot \left\{ \underline{W}_1' S_{3/2}^{(j)}(W_1'^2) + \underline{W}_2' S_{3/2}^{(j)}(W_2'^2) - \underline{W}_1 S_{3/2}^{(j)}(W_1^2) - \underline{W}_2 S_{3/2}^{(j)}(W_2^2) \right\}$$

$$\Delta_{ij}' \equiv \int d\underline{p}_1 d\underline{p}_2 d\hat{\underline{k}}\, \sigma(\theta) \left|\frac{\underline{p}}{2m}\right| S_{5/2}^{(i)}(W_1^2)\, \hat{f}_{1e}(W_1)\, \hat{f}_{1e}(W_2)\, \overset{\circ}{\underline{W}_1 \underline{W}_1} : \tag{3-51}$$

$$: \left\{ \overset{\circ}{\underline{W}_1' \underline{W}_1'} S_{5/2}^{(j)}(W_1'^2) + \overset{\circ}{\underline{W}_2' \underline{W}_2'} S_{5/2}^{(j)}(W_2'^2) - \overset{\circ}{\underline{W}_1 \underline{W}_1} S_{5/2}^{(j)}(W_1^2) - \overset{\circ}{\underline{W}_2 \underline{W}_2} S_{5/2}^{(j)}(W_2^2) \right\}$$

$$\Delta_{ij}'' \equiv \int d\underline{p}_1 d\underline{p}_2 d\hat{\underline{k}}\, \sigma(\theta) \left|\frac{\underline{p}}{2m}\right| S_{1/2}^{(i)}(W_1^2)\, \hat{f}_{1e}(W_1)\, \hat{f}_{1e}(W_2) \times$$

$$\times \left\{ S_{1/2}^{(j)}(W_1'^2) + S_{1/2}^{(j)}(W_2'^2) - S_{1/2}^{(j)}(W_1^2) - S_{1/2}^{(j)}(W_2^2) \right\}$$

With these, the three integral equations (3-48) may be written as three sets of algebraic equations:

$$K_1^{(i)} = \sum_{j=0}^{\nu-1} \alpha_{ij} \Delta_{ij}$$

$$L_1^{(i)} = \sum_{j=0}^{\nu-1} \beta_{ij} \Delta'_{ij} \qquad i = 0, 1, \ldots, \nu-1 \tag{3-52}$$

$$M_1^{(i)} = \sum_{j=0}^{\nu-1} c_{ij} \Delta''_{ij}$$

Since the five summational invariants 1, $\underline{P}_1$, and P_1^2 are eigenfunctions of the $\Delta_\circ$ operator with zero eigenvalues,

$$\Delta_{i0} = \Delta''_{i0} = \Delta''_{i1} = 0 \tag{3-53}$$

The matrices Δ_{ij} and Δ''_{ij} are therefore singular and cannot be inverted. A unique solution can still be secured, however, by requiring the auxiliary conditions in equations (3-46).

Upon substitution of the Sonine polynomial expansion in (3-49), the first auxiliary condition leads directly to the requirement

$$c_{10} = 0 \tag{3-54}$$

With the result from the solution of the first order equation for a_0 and lemmas B-2 and B-3, the second auxiliary condition reduces to

$$\alpha_{10} = \frac{5}{16}\left(\frac{KT}{2m}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1}\epsilon_2 \tag{3-55}$$

The third auxiliary condition then is

$$\sum_{j=0}^{\nu-1} c_{1j} \int dW_1\, W_1^4 e^{-W_1^2} S_{1/2}^{(j)}(W_1^2) = 0 \tag{3-56}$$

Using the identity

$$S_{1/2}^{(j)} = S_{3/2}^{(j)} - S_{3/2}^{(j-1)} \tag{3-57}$$

and the orthogonality and normalization relations of the Sonine polynomials, the integration may be performed to give

$$c_{10} = c_{11} \tag{3-58}$$

With equation (3-54), the third auxiliary condition is finally

$$C_{11} = 0 \tag{3-59}$$

The three auxiliary conditions on the expansion coefficients can now be used to replace the three sets of algebraic equations (3-52) with

$$K_1^{(i)} = \sum_{j=1}^{\nu-1} \alpha_{ij} \Delta_{ij} \qquad i = 1, 2, \ldots, \nu-1$$

(3-60)

$$L_1^{(i)} = \sum_{j=0}^{\nu-1} \beta_{ij} \Delta'_{ij} \qquad i = 0, 1, \ldots, \nu-1$$

$$M_1^{(i)} = \sum_{j=2}^{\nu-1} c_{ij} \Delta''_{ij} \qquad i = 2, 3, \ldots, \nu-1$$

The matrices represented by the Δ_{ij} , Δ'_{ij} , and Δ''_{ij} in (3-60) are now non-singular and may be inverted by the approximate matrix inversion technique discussed by Chapman and Cowling[19]. In the simplest approximation,

$$\mathcal{A}_1 \sim \frac{5}{16}\left(\frac{KT}{2m}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1}\epsilon_2 + \frac{K_1^{(1)}}{\Delta_{11}} S_{3/2}^{(1)}(W_1^2)$$

$$\mathcal{B}_1 \sim \frac{L_1^{(0)}}{\Delta'_{00}} \tag{3-61}$$

$$\mathcal{C}_1 \sim \frac{M_1^{(2)}}{\Delta''_{22}} S_{1/2}^{(2)}(W_1^2)$$

The problem of solving the second order Boltzmann equation is now reduced to the evaluation of the three matrix elements Δ_{11} , Δ'_{00} , and Δ''_{22} and the three inhomogeneities $K_1^{(1)}$, $L_1^{(0)}$, and $M_1^{(2)}$.

3.5 Evaluation of the Matrix Elements

The matrix elements may be expressed in terms of the well-known bracket integrals:

$$\Delta_{11} = -\frac{1}{2n^2}\left\{\underline{W}_1 S_{3/2}^{(1)}(W_1^2) ; \underline{W}_1 S_{3/2}^{(1)}(W_1^2)\right\} \tag{3-62}$$

$$\Delta'_{00} = -\frac{1}{2n^2}\left\{\underline{W}_1 \overset{\circ}{\underline{W}}_1 ; \underline{W}_1 \overset{\circ}{\underline{W}}_1\right\}$$

$$\Delta''_{22} = -\frac{1}{2n^2}\left\{S_{1/2}^{(2)}(W_1^2) ; S_{1/2}^{(2)}(W_1^2)\right\}$$

Results for the bracket integrals have been tabulated by Chapman and Cowling[19]. Substituting their results into (3-62) gives

$$\Delta_{11} = -4\,\Omega^{(2,2)}$$

$$\Delta'_{00} = -4\,\Omega^{(2,2)} \tag{3-63}$$

$$\Delta''_{22} = -2\,\Omega^{(2,2)}$$

The $\Omega^{(2,2)}$ integrals, as usual, refer to the quantum mechanical quantities.

3.6 Evaluation of the Inhomogeneities

From the results of section 3.4, it is clear that the following integrals of the inhomogeneities are necessary for the evaluation of the expansion coefficients:

$$K_1^{(1)} \equiv \int d\underline{p}_1 \left(\tfrac{5}{2} - W_1^2\right) \underline{W}_1 \cdot \underline{K}_1 \qquad (3\text{-}64)$$

$$L_1^{(0)} = \int d\underline{p}_1 \, \underline{W}_1 \mathring{\underline{W}}_1 : \underline{\underline{L}}_1$$

$$M_1^{(2)} = \int d\underline{p}_1 \left(\tfrac{15}{8} - \tfrac{5}{2} W_1^2 + \tfrac{1}{2} W_1^4\right) M_1$$

Each of the three integrals is now evaluated separately.

3.6a <u>Evaluation of $K_1^{(1)}$</u>

Because of its length, it is convenient to divide the calculation into four parts

$$K_1^{(1)} \equiv \sum_{i=1}^{4} K_1^{(1,i)} \qquad (3\text{-}65)$$

where

$$K_1^{(1,i)} \equiv \int d\underline{p}_1 \, \underline{W}_1 \cdot \underline{K}_{(1,i)} \left(\tfrac{5}{2} - W_1^2\right)$$

$$\underline{K}_{(1,1)} = \left(\frac{2KT}{m}\right)^{1/2} \left\{ \left(B + T\frac{dB}{dT}\right)\hat{\hat{f}}_{1e} - \frac{\partial \hat{\hat{f}}_{1e}}{\partial W_1^2} - T\frac{\partial \hat{\hat{f}}_{1e}}{\partial T} \right\} \underline{W}_1 \tag{3-66}$$

$$\underline{K}_{(1,2)} = -\frac{1}{m} \int d\underline{r} \, d\underline{p}_2 \, d\underline{p}_0 \, \hat{f}_{1e}(\tilde{p}_1) \hat{f}_{1e}(\tilde{p}_2) \left\{ \left[3 - \frac{1}{mKT}\left(\tfrac{1}{4}P^2 + p_0^2\right)\right] \underline{r}\underline{p} \cdot \frac{dF}{d\underline{r}} + \right.$$

$$\left. + \frac{1}{mKT}(\underline{p}_0 \cdot \underline{P}) \left[\underline{p}_0 F - \underline{p} \cdot \frac{d}{d\underline{r}} \underline{G}\right] \right\}$$

$$\underline{K}_{(1,3)} = -\int d\underline{r} \, d\underline{p}_0 \, d\underline{p}_2 \left\{ \underline{A}_0(\tilde{p}_1) + \underline{A}_0(\tilde{p}_2) \right\} \left\{ \hat{f}_{1e}(\tilde{p}_1) \hat{\hat{f}}_{1e}(\tilde{p}_2) + \hat{f}_{1e}(\tilde{p}_2) \hat{\hat{f}}_{1e}(\tilde{p}_1) \right\} \Theta_2 F$$

$$\underline{K}_{(1,4)} = -\int d\underline{r} \, d\underline{p}_0 \, d\underline{p}_2 \left\{ \underline{A}_0(\tilde{p}_1) + \underline{A}_0(\tilde{p}_2) \right\} \hat{f}_{1e}(\tilde{p}_1) \hat{f}_{1e}(\tilde{p}_2) \, \Theta_2 \, \mathcal{Y}_e \, F$$

Each term is then considered individually.

i. $K_1^{(1,1)}$

By straightforward integration and the use of lemmas B-2 and B-3,

$$K_1^{(1,1)} = \left(\frac{KT}{2m}\right)^{1/2} \left\{ \epsilon_2 + \frac{1}{2} T \frac{d\epsilon_2}{dT} \right\} \tag{3-67}$$

ii. $K_1^{(1,2)}$

Imam-Rahajoe[16] has evaluated integrals of this type. The computation is based upon integral properties of the functions $F(\underline{r}; \underline{p}, \underline{p}_0)$ and $\underline{G}(\underline{r}; \underline{p}, \underline{p}_0)$ and the assumed short range character of the intermolecular potential. In our notation, the result is

$$K_1^{(1,2)} = \left(\frac{KT}{2m}\right)^{1/2} \left\{ \frac{15}{2} B - \frac{5}{2} Q_2 + \frac{5}{4} T \frac{d\epsilon_1}{dT} - \epsilon_2 - \frac{1}{2} T \frac{d\epsilon_2}{dT} \right\} \tag{3-68}$$

where

$$Q_2 \equiv \frac{m\hbar^2}{5}(2mkT)^{-2}(2)^{3/2}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, e^{-p_0^2/mkT}\, \underline{\underline{X}} : \underline{\underline{H}}$$

$$\underline{\underline{H}} \equiv \psi^* \frac{\partial}{\partial \underline{r}} \frac{\partial}{\partial \underline{p}_0} \psi - \frac{\partial \psi^*}{\partial \underline{r}} \frac{\partial \psi}{\partial \underline{p}_0} - \frac{\partial \psi}{\partial \underline{r}} \frac{\partial \psi^*}{\partial \underline{p}_0} + \psi \frac{\partial}{\partial \underline{r}} \frac{\partial}{\partial \underline{p}_0} \psi^* \tag{3-69}$$

$$\underline{\underline{X}} \equiv \underline{p}_0 \frac{d\varphi}{d\underline{r}} + \underline{p}_0 \cdot \frac{d\varphi}{d\underline{r}} \underline{\underline{U}} + \frac{d\varphi}{d\underline{r}} \underline{p}_0$$

<u>iii.</u> $K_1^{(1,3)}$

We first change to center-of-mass and relative motion coordinates and remove terms which have integrands that are odd in $\underline{P}$. Then, with lemma B-6,

$$\frac{2}{m}(2mKT)^{-3/2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P} \left\{ \hat{f}_{1e}(\tilde{p}_1)\hat{\hat{f}}_{1e}(\tilde{p}_2) + \hat{f}_{1e}(\tilde{p}_2)\hat{\hat{f}}_{1e}(\tilde{p}_1) \right\} \underline{p}\underline{p}\underline{p} \vdots$$

$$\vdots \left\{ \underline{A}_0(\tilde{p}_1) + \underline{A}_0(\tilde{p}_2) \right\} \underline{P}\, \frac{\partial F}{\partial \underline{r}} \tag{3-70}$$

$$+\frac{1}{m}(2mKT)^{-3/2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P} \left\{ \hat{f}_{1e}(\tilde{p}_1)f_{1e}(\tilde{p}_2) + \hat{f}_{1e}(\tilde{p}_2)f_{1e}(\tilde{p}_1) \right\} \times$$

$$\times p^2 \left\{ \underline{A}_0(\tilde{p}_1) + \underline{A}_0(\tilde{p}_2) \right\} \underline{p} : \frac{\partial F}{\partial \underline{r}}\, \underline{P}$$

The second term vanishes by lemma B-8. With the asymptotic form of $F(\underline{r};\underline{p},\underline{p}_0)$ from Hoffman, Mueller, and Curtiss[15],

$$F \rightarrow \delta(\underline{p}-\underline{p}_0) + \frac{1}{r^2}\left\{ \delta(\underline{p}-p_0\hat{\underline{K}})\,\sigma(\theta_0) - \delta(\hat{\underline{p}}_0-\hat{\underline{K}})\,\delta(\underline{p}-\underline{p}_0)\sum \right\} + \mathcal{O}(r^{-4}) \tag{3-71}$$

where

$$\sum \equiv \int d\hat{\underline{K}}\; \sigma(\theta)$$

$$\cos\theta_0 \equiv \hat{\underline{p}}_0 \cdot \hat{\underline{K}} \qquad \cos\theta \equiv \hat{\underline{p}} \cdot \hat{\underline{K}} \tag{3-72}$$

the $\underline{r}$-integration in the first term yields

$$\int d\underline{r}\, \frac{d\underline{F}}{d\underline{r}} = \hat{p}\,\sigma\left(\cos^{-1}\hat{p}_0\cdot\hat{p}\right)\delta(p-p_0) - \hat{p}_0\,\delta(p-p_0)\sum \tag{3-73}$$

The p_0 -integration can then be done trivially and, with some rearrangement involving the symmetry properties (3-22) of $\underline{A}_0(p_i)$, the first term in (3-70) becomes

$$\frac{4}{m}(2mKT)^{-3/2}\int d\hat{\underline{K}}\,dp\,d\underline{P}\,p\,\sigma(\theta)\left\{\hat{f}_{1e}(p_1)\hat{\hat{f}}_{1e}(p_2)+\hat{f}_{1e}(p_2)\hat{\hat{f}}_{1e}(p_1)\right\}\times$$
$$\times\,\underline{A}_0(p_1)\,\underline{P}:\left\{p^2\hat{\underline{K}}\hat{\underline{K}}-\underline{p}\underline{p}\right\} \tag{3-74}$$

Using the explicit result for $\underline{A}_0(p_1)$ from the solution to the first order Boltzmann equation and again removing terms which are odd in $\underline{P}$, (3-74) reduces to

$$-\frac{15}{8}mK^2T^2\left(\frac{KT}{2m}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1}\int d\hat{\underline{K}}\,d\gamma\,\gamma\,\sigma(\theta)\left\{\gamma^2\hat{\underline{K}}\hat{\underline{K}}-\underline{\gamma}\underline{\gamma}\right\}:$$
$$:\left\{-\underline{\underline{D}}_1+\left[5-\gamma^2-2\underline{\gamma}\underline{\gamma}\cdot\right]\underline{\underline{D}}_2\right\} \tag{3-75}$$

where we have introduced

$$\underline{\underline{D}}_1 \equiv \frac{1}{8}(mkT)^{-2}\int d\underline{P}\, P^2 \underline{P}\underline{P}\, \hat{f}_{1e}(p_1)\hat{\hat{f}}_{1e}(p_2)$$

$$\underline{\underline{D}}_2 \equiv \frac{1}{2}(mkT)^{-1}\int d\underline{P}\, \underline{P}\underline{P}\, \hat{f}_{1e}(p_1)\hat{\hat{f}}_{1e}(p_2) \qquad (3\text{-}76)$$

$$\underline{\gamma} \equiv \frac{p}{\sqrt{mkT}}$$

When the explicit forms for $\hat{f}_{1e}$ and $\hat{\hat{f}}_{1e}$ are substituted, the integrals $\underline{\underline{D}}_1$ and $\underline{\underline{D}}_2$ can be evaluated by a straightforward, though lengthy, application of the properties of Fourier integrals. The results are:

$$\underline{\underline{D}}_1 = 7\left\{2\Gamma + 5\Gamma^{(1)} + 4\Gamma^{(2)} + \Gamma^{(3)}\right\}\underline{\gamma}\underline{\gamma}$$

$$+5\left\{2\Gamma + 2\Gamma^{(1)} + \tfrac{1}{2}\Gamma^{(2)}\right\}\underline{\underline{U}}$$

$$+\left\{2\Gamma + 5\Gamma^{(1)} + 4\Gamma^{(2)} + \Gamma^{(3)}\right\}\gamma^2\underline{\underline{U}} \tag{3-77}$$

$$+2\left\{\Gamma + 4\Gamma^{(1)} + 6\Gamma^{(2)} + 4\Gamma^{(3)} + \Gamma^{(4)}\right\}\gamma^2\underline{\gamma}\underline{\gamma}$$

$$\underline{\underline{D}}_2 = 2\left\{\Gamma + 2\Gamma^{(1)} + \Gamma^{(2)}\right\}\underline{\gamma}\underline{\gamma} + \left\{2\Gamma + \Gamma^{(1)}\right\}\underline{\underline{U}}$$

where

$$\Gamma(\gamma^2) \equiv \left(\frac{4}{h}\right)^3 \int d\underline{s}\; e^{-\frac{4(2\pi)^{1/2}}{\lambda} i\,\underline{\gamma}\cdot\underline{s}}\; e^{-\frac{8\pi s^2}{\lambda^2}} \times$$

$$\times \int d\underline{r}\left\{e^{\frac{2\pi s^2}{\lambda^2}} g_0(\underline{r}+\underline{s};\underline{r}-\underline{s}) - g_0(\underline{r};\underline{r})\right\} \tag{3-78}$$

$$\Gamma^{(i)} \equiv \left(\frac{\partial}{\partial\underline{\gamma}}\cdot\frac{\partial}{\partial\underline{\gamma}}\right)^i \Gamma$$

By substituting equations (3-77) and performing the tensor operations, (3-75) becomes:

$$\frac{15}{8}(KT)^2\left(\frac{mKT}{2}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1}\int d\hat{\underline{K}}\, d\underline{\gamma}\, \sigma(\theta)\left\{(\hat{\underline{\gamma}}\cdot\hat{\underline{K}})^2 - 1\right\} \times$$

$$\times\left\{\gamma^5\left[8\Gamma + 17\Gamma^{(1)} + 18\Gamma^{(2)} + 7\Gamma^{(3)}\right] + \right. \tag{3-79}$$

$$\left. + 2\gamma^7\left[4\Gamma + 10\Gamma^{(1)} + 9\Gamma^{(2)} + 4\Gamma^{(3)} + \Gamma^{(4)}\right]\right\}$$

The three trivial angle integrations may then be carried out to yield

$$-\frac{15}{2}\pi(KT)^2\left(\frac{mKT}{2}\right)^{1/2}\left(\Omega^{(2,2)}\right)^{-1}\int_0^\infty d\gamma\, Q^{(2)}(\gamma) \times$$

$$\times\left\{\gamma^7\left[8\Gamma + 17\Gamma^{(1)} + 18\Gamma^{(2)} + 7\Gamma^{(3)}\right] + \right. \tag{3-80}$$

$$\left. + 2\gamma^9\left[4\Gamma + 10\Gamma^{(1)} + 9\Gamma^{(2)} + 4\Gamma^{(3)} + \Gamma^{(4)}\right]\right\}$$

where the definition of the ℓ^{th} moment of the cross-section

$$Q^{(\ell)}(\gamma) \equiv 2\pi \int_0^{\pi} d\chi \, \sin\chi \left\{ 1 - \cos^{\ell}\chi \right\} \sigma(\chi;\gamma) \tag{3-81}$$

and the change of variables

$$\cos\chi \equiv \hat{\underset{\sim}{\gamma}} \cdot \hat{\underset{\sim}{K}} \tag{3-82}$$

have been introduced.

Finally

$$K_1^{(1,3)} = \frac{15}{2}\left(\frac{KT}{2m}\right)^{1/2} \mathcal{R}_1 \tag{3-83}$$

$$\mathcal{R}_1 \equiv 8R^{(0,2)} + 17R^{(1,2)} + 18R^{(2,2)} + 7R^{(3,2)} + 8R^{(0,3)}$$

$$+ 20R^{(1,3)} + 18R^{(2,3)} + 8R^{(3,3)} + 2R^{(4,3)}$$

where

$$R^{(\mu,\nu)} \equiv -\frac{1}{2}(KT)\left(\frac{h}{\lambda}\right)^2 \left(\Omega^{(2,2)}\right)^{-1} \int_0^{\infty} d\gamma \, Q^{(2)}(\gamma) \, \gamma^{2\nu+3} \, T^{(\mu)} \tag{3-84}$$

The $R^{(\mu,\nu)}$ integrals may be regarded as a generalization of the usual $\Omega^{(2,\nu)}$ integrals (reduced by $\Omega^{(2,2)}$) in which the $e^{-\gamma^2}$ has been replaced by the function $T(\gamma)$. The factor $e^{-\gamma^2}$ is of the form $\hat{f}_{1e}(\gamma)$, while $T(\gamma)$ is related to $\hat{\hat{f}}_{1e}$. The result (3-83) agrees with that of Imam-Rahajoe if only the first term is retained of an expansion of $T(\gamma)$ in the Sonine polynomials, $S_{1/2}^{(i)}(\gamma^2)$, and proper account is taken of the fact that the density separation was made much later in his development.

iv. $K_1^{(1,4)}$

Changing to center-of-mass and relative motion coordinates and removing terms which have integrands that are odd in $\underline{P}$ with relations (3-22), this may be written:

$$
\begin{aligned}
&-\frac{5}{4}(2mkT)^{-1/2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\, \underline{P}\cdot\{\underline{A}_0(\tilde{p}_1)+\underline{A}_0(\tilde{p}_2)\}\,\Theta_2\,\mathcal{Y}_e F \\
&+(2mkT)^{-3/2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\}^2\left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\}\cdot \\
&\cdot\{\underline{A}_0(\tilde{p}_1)+\underline{A}_0(\tilde{p}_2)\}\,\Theta_2\,\mathcal{Y}_e F
\end{aligned}
\tag{3-85}
$$

Then substituting a Taylor series representation for the Θ_2 operator,

$$\Theta_2 \sim -\frac{2}{\hbar}\left\{\frac{\hbar}{2}\frac{d\varphi}{d\underline{r}}\cdot\frac{\partial}{\partial \underline{p}} - \frac{1}{6}\left(\frac{\hbar}{2}\right)^3 \frac{d\varphi}{d\underline{r}}\frac{d\varphi}{d\underline{r}}\frac{d\varphi}{d\underline{r}} \vdots \frac{\partial}{\partial \underline{p}}\frac{\partial}{\partial \underline{p}}\frac{\partial}{\partial \underline{p}} + \cdots\right\} \tag{3-86}$$

and integrating by parts on $\underline{p}$, the first term vanishes. With the same considerations, the second term becomes finally

$$K_1^{(1,4)} = \frac{15}{2}\left(\frac{KT}{2m}\right)^{1/2} \mathcal{K}(\mathcal{Y}_e) \tag{3-87}$$

where

$$\mathcal{K}(\mathcal{Y}_e) \equiv \frac{2}{15}(mK^2T^2)^{-1}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \mathcal{Y}_e\, F \,\times$$

$$\times\, \underline{A}_0(\tilde{\underline{p}}_1)\cdot\left\{\underline{P}\left(\underline{p}\cdot\frac{d\varphi}{d\underline{r}}\right) + \frac{d\varphi}{d\underline{r}}(\underline{p}\cdot\underline{P}) + \underline{p}\left(\underline{P}\cdot\frac{d\varphi}{d\underline{r}}\right)\right\} \tag{3-88}$$

Further reduction of this term now requires an explicit analytic form for $\mathcal{Y}_e$.

Combining all contributions,

$$K_1^{(1)} = \frac{15}{2}\left(\frac{KT}{2m}\right)^{1/2}\left\{B + \mathcal{R}_1 + \mathcal{K}(\mathcal{Y}_e) + \frac{1}{6}T\frac{d\epsilon_1}{dT} - \frac{1}{3}Q_2\right\} \tag{3-89}$$

where the quantities $\mathcal{R}_1$ and $\mathcal{K}(\mathcal{Y}_e)$ are given by (3-83) and (3-88), respectively.

3.6b <u>Evaluation of $L_1^{(0)}$</u>

Again it is convenient to divide the calculation into four parts:

$$L_1^{(0)} = \sum_{i=1}^{4} L_1^{(0,i)} \tag{3-90}$$

$$L_1^{(0,i)} \equiv \int dp_1\, \underline{W}_1 \overset{\circ}{\underline{W}} : \underline{\underline{L}}_{(1,i)}$$

where

$$\underline{\underline{L}}_{(1,1)} \equiv 2\,\underline{W}_1 \overset{\circ}{\underline{W}}_1 \frac{\partial \hat{\hat{f}}_{1e}}{\partial W_1^2}$$

$$\underline{\underline{L}}_{(1,2)} \equiv (mKT)^{-1} \int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2) \Big\{ \overset{\circ}{\underline{P}}_{\underline{r}}\, \underline{p} \cdot \frac{\partial F}{\partial \underline{r}} - 2\overset{\circ}{\underline{p}_0}\underline{p}_0 F + 2\underline{p}_0 \overset{\circ}{\underline{p}} \cdot \frac{\partial}{\partial \underline{r}} \underline{G} \Big\} \qquad (3\text{-}91)$$

$$\underline{\underline{L}}_{(1,3)} \equiv -\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0 \Big\{ \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2) + \hat{f}_{1e}(\tilde{\underline{p}}_2) \hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1) \Big\} \times \Big\{ \underline{\underline{B}}_0(\tilde{\underline{p}}_1) + \underline{\underline{B}}_0(\tilde{\underline{p}}_2) \Big\} \theta_2 F$$

$$\underline{\underline{L}}_{(1,4)} \equiv -\int d\underline{r}\, d\underline{p}_2\, d\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2) \Big\{ \underline{\underline{B}}_0(\tilde{\underline{p}}_1) + \underline{\underline{B}}_0(\tilde{\underline{p}}_2) \Big\} \theta_2 \mathcal{Y}_e F$$

Each term may then be considered separately.

<u>i.</u> $L_1^{(0,1)}$

With an integration by parts and the use of lemma B-2, this yields the contribution

$$L_1^{(0,1)} = -\frac{5}{3}\epsilon_1 \tag{3-92}$$

ii. $L_1^{(0,2)}$

Imam-Rahajoe[16] has evaluated terms of this form. The calculation involves directly the integral properties of $F(\underline{r};\not{p},\not{p}_0)$ and $\underline{G}(\underline{r};\not{p},\not{p}_0)$ and the definitions (2-58) and (3-21) of the second virial coefficient. In our notation,

$$L_1^{(0,2)} = 5\left\{\frac{1}{2}Q_2 - B + \frac{7}{6}T\frac{dB}{dT} + \frac{1}{3}T^2\frac{d^2B}{dT^2} + \right.$$

$$\left. + \frac{3}{4}\epsilon_1 + \frac{1}{6}T\frac{d\epsilon_1}{dT}\right\} \tag{3-93}$$

iii. $L_1^{(0,3)}$

After changing to center-of-mass and relative motion coordinates and removing terms from the integrand which are odd in $\underline{P}$, the $\underline{r}$ and $\not{p}_0$ integrations may be done with relation (3-73) to yield:

$$2(m^2KT)^{-1}\int d\underline{p}\, d\underline{P}\, d\hat{\underline{K}}\; p\,\sigma(\theta)\left\{\hat{f}_{1e}(p_1)\hat{\hat{f}}_{1e}(p_2)+\hat{\hat{f}}_{1e}(p_2)\hat{f}_{1e}(p_1)\right\}\times$$

$$\times\left\{\underline{p}\underline{p}-p^2\hat{\underline{K}}\hat{\underline{K}}\right\}:\underline{\underline{B}}_0(p_1) \tag{3-94}$$

Substituting the explicit result for $\underline{\underline{B}}_o$ from the solution to the first order equation and again removing terms odd in $\underline{P}$,

$$\frac{5}{4}m(KT)^2\left(\Omega^{(2,2)}\right)^{-1}\int d\underline{\gamma}\, d\hat{\underline{K}}\;\gamma\,\sigma(\theta)\left\{\underline{\gamma}\underline{\gamma}-\gamma^2\hat{\underline{K}}\hat{\underline{K}}\right\}: \tag{3-95}$$

$$:\left\{\underline{\underline{D}}_2+\underline{\gamma}\underline{\gamma}\,D_3\right\}$$

where

$$D_3\equiv 2\int d\underline{P}\;\hat{f}_{1e}(p_1)\hat{\hat{f}}_{1e}(p_2) \tag{3-96}$$

As in the treatment of $\underline{\underline{D}}_1$ and $\underline{\underline{D}}_2$, the D_3 integral may then be written in terms of the $T(\gamma^2)$ integrals:

$$D_3 = 2T' \tag{3-97}$$

With the results of equations (3-77) and (3-97), the tensor operation and the three trivial angle integrations can be carried out to give

$$5KT\left(\frac{h}{\lambda}\right)^2 \left(\Omega^{(2,2)}\right)^{-1} \int d\gamma\, \gamma^7 Q^{(2)}(\gamma) \left\{2T' + 2T'^{(1)} + T'^{(2)}\right\} \tag{3-98}$$

The result is then

$$L_1^{(0,2)} = -5\mathcal{R}_2 \tag{3-99}$$

where

$$\mathcal{R}_2 \equiv 4R^{(0,2)} + 4R^{(1,2)} + 2R^{(2,2)} \tag{3-100}$$

and the $R^{(\mu,\nu)}$ integrals have been defined in equation (3-84).

iv. $L_1^{(0,4)}$

Changing to center-of-mass and relative motion coordinates, terms in the integrand which are odd in $\underline{P}$ may be removed to give:

$$-(8mkT)^{-1}\int d\underline{r}\,d\underline{p}\,d\underline{P}\,d\underline{p}_o\,\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\,\overset{\circ}{\underline{P}\underline{P}}:\{\underline{\underline{B}}_o(\tilde{p}_1)+\underline{\underline{B}}_o(\tilde{p}_2)\}\,\theta_2\,\mathcal{Y}_e F$$

(3-101)

$$-(2mkT)^{-1}\int d\underline{r}\,d\underline{p}\,d\underline{P}\,d\underline{p}_o\,\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\,\overset{\circ}{\underline{p}\underline{p}}:\{\underline{\underline{B}}_o(\tilde{p}_1)+\underline{\underline{B}}_o(\tilde{p}_2)\}\,\theta_2\,\mathcal{Y}_e F$$

The first term vanishes on substitution of the Taylor series for θ_2 and integration by parts. Similar treatment of the second term then gives the result:

$$L_1^{(0,4)} = -5\,\mathcal{L}(\mathcal{Y}_e) \qquad (3\text{-}102)$$

where

$$\mathcal{L}(\mathcal{Y}_e) \equiv (5mkT)^{-1}\int d\underline{r}\,d\underline{p}\,d\underline{P}\,d\underline{p}_o\,\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\,\mathcal{Y}_e F\;\underline{\underline{B}}_o(\tilde{p}_1):$$

$$:\left\{\overset{\circ}{\frac{d\varphi}{d\underline{r}}\,\underline{p}}+\overset{\circ}{\underline{p}\,\frac{d\varphi}{d\underline{r}}}\right\} \qquad (3\text{-}103)$$

To further reduce the term $\mathcal{L}(\mathcal{Y}_e)$, an explicit expression for $\mathcal{Y}_e$ is required.

Finally, combining all contributions,

$$L_1^{(0)} = 5\left\{\frac{1}{2}Q_2 - B + \frac{7}{6}T\frac{dB}{dT} + \frac{1}{3}T^2\frac{d^2B}{dT^2} + \right.$$

$$\left. + \frac{5}{12}\epsilon_1 + \frac{1}{6}T\frac{d\epsilon_1}{dT} - \mathcal{R}_2 - \mathcal{L}(\mathcal{Y}_e)\right\} \tag{3-104}$$

3.6c <u>Evaluation of $M_1^{(2)}$</u>

We divide the calculation into three parts:

$$M_1^{(2)} \equiv \sum_{i=1}^{3} M_1^{(2,i)} \tag{3-105}$$

$$M_1^{(2,i)} \equiv \int d\not{p}_1\, M_{(1,i)}\left\{\frac{15}{8} - \frac{5}{2}W_1^2 + \frac{1}{2}W_1^4\right\}$$

where

$$M_{(1,1)} = 2\hat{\hat{f}}_{1e} + \frac{2}{3}T\frac{d\hat{\hat{f}}_{1e}}{dT} + \frac{2}{3}W_1^2\frac{\partial\hat{\hat{f}}_{1e}}{\partial W_1^2}$$

$$M_{(1,2)} = -\frac{2}{3}\left\{\frac{3}{2} - W_1^2\right\}\left\{B + \frac{7}{3}T\frac{dB}{dT} + \frac{2}{3}T^2\frac{d^2B}{dT^2}\right\}\hat{f}_{1e} \qquad \text{(3-106)}$$

$$M_{(1,3)} = \frac{2}{3}(mKT)^{-1}\int d\underset{\sim}{r}\, d\underset{\sim}{p}_2\, d\underset{\sim}{p}_0\, \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{\frac{1}{2}(\underset{\sim}{r}\cdot\underset{\sim}{P})\underset{\sim}{p}\cdot\frac{\partial F}{\partial\underset{\sim}{r}} - \right.$$

$$\left. - p_0^2 F + \underset{\sim}{p}_0\underset{\sim}{p} : \frac{\partial}{\partial\underset{\sim}{r}}\underset{\sim}{G}\right\}$$

The three contributions may now be evaluated individually.

i. $M_1^{(2,1)}$

After an integration by parts, the use of lemmas B-1, B-2, and B-3 leads directly to

$$M_1^{(2,1)} = -\frac{1}{8}\left\{5\epsilon_1 - \epsilon_2\right\} - \frac{1}{12}T\left\{5\frac{d\epsilon_1}{dT} - \frac{d\epsilon_2}{dT}\right\} \qquad \text{(3-107)}$$

ii. $M_1^{(2,2)}$

By the orthogonality condition of the Sonine polynomials, this term gives no contribution.

$$M_1^{(2,2)} = 0 \tag{3-108}$$

iii. $M_1^{(2,3)}$

Imam-Rahajoe[16] has evaluated integrals of this form. In our notation,

$$M_1^{(2,3)} = -\frac{1}{12}\left\{10T\frac{dB}{dT} + 11T^2\frac{d^2B}{dT^2} + 2T^3\frac{d^3B}{dT^3}\right\}$$
$$+\frac{1}{8}\left\{5\epsilon_1 - \epsilon_2\right\} + \frac{1}{12}T\left\{5\frac{d\epsilon_1}{dT} - \frac{d\epsilon_2}{dT}\right\} \tag{3-109}$$

Finally, combining all three terms,

$$M_1^{(2)} = -\frac{1}{12}\left\{10T\frac{dB}{dT} + 11T^2\frac{d^2B}{dT^2} + 2T^3\frac{d^3B}{dT^3}\right\} \tag{3-110}$$

This completes the formal solution of the second order Boltzmann equation. With this solution for the perturbation function ϕ, the approximate non-equilibrium singlet distribution function has now been obtained.

CHAPTER IV

THE TRANSPORT PHENOMENA

The non-equilibrium state of a single component gas is specified by the density, stream velocity, and temperature as functions of position. The time development of the three macroscopic variables is governed by the equations of change (2-31), which involve explicitly the momentum and energy fluxes. Physically, this transport of momentum and energy takes place in two distinct ways: a purely kinetic mechanism due to the motion of individual molecules, and a collisional transfer mechanism arising from the transfer of momentum and energy from one molecule to another by interaction through the intermolecular potential. For a system not too far displaced from equilibrium, the fluxes are linearly related to the macroscopic gradients. The proportionality constants are then the transport coefficients.

4.1 The Energy Flux Vector

In the near equilibrium approximation, the energy flux vector is given by

$$q \equiv -\lambda \frac{\partial T}{\partial \underline{r}_1} \tag{4-1}$$

where λ is the coefficient of thermal conductivity. The energy flux vector and the coefficient of thermal conductivity may be conveniently written as the sum of three contributions[16]:

$$q(\underline{r}_1|f_1) \equiv q_{I} + q_{II} + q_{III}$$

$$\lambda \equiv \lambda_{I} + \lambda_{II} + \lambda_{III} \qquad (4\text{-}2)$$

$$q_{I} \equiv -\lambda_{I} \frac{\partial T}{\partial \underline{r}_1} = (2m^2)^{-1} \int d\underline{p}_1\, p_1^2\, \underline{p}_1\, f_1(\underline{p}_1)$$

$$q_{II} \equiv -\lambda_{II} \frac{\partial T}{\partial \underline{r}_1} = -(4m)^{-1} \int d\underline{p}_1 d\underline{p}_2 d\underline{r}\, \frac{d\varphi}{dr}\, \frac{\underline{r}\,\underline{r}}{r} \cdot (\underline{p}_1 + \underline{p}_2)\, \times$$

$$\times \int_0^1 d\mu\, f_2(\underline{r}_1 + \underline{r}\{\mu - 1\};\, \underline{r}_1 + \mu \underline{r};\, \underline{p}_1 \underline{p}_2 | f_1)$$

$$q_{III} \equiv -\lambda_{III} \frac{\partial T}{\partial \underline{r}_1} = (2m)^{-1} \int d\underline{p}_1 d\underline{p}_2 d\underline{r}\, \underline{p}_1\, \varphi\, f_2(\underline{r}_1 \underline{r}_2;\, \underline{p}_1 \underline{p}_2 | f_1)$$

where explicit note has been taken that the energy flux vector is to be localized at $\underline{r}_1$ and is taken to be a functional of singlet distribution functions.

In the classical development, it is possible to classify the various contributions to the heat flux vector as being of either a kinetic or a potential origin. In the quantum case, however, such a classification --- while providing useful terminology --- is not strictly correct. This situation results directly from the non-commutation of the coordinate and momentum operators.

In the preceding chapter, an approximate non-equilibrium singlet distribution function of the form

$$f_1 \sim f_{1e} \{1 + \phi\} \tag{2-26'}$$

was obtained. This expansion may now be used to evaluate the energy flux vector. To be consistent with the restrictions on our solution for f_1, equations (4-2) must be written in terms of functions localized at $\underline{r}_1$. As before, this is done by making appropriate Taylor series expansions and retaining only terms at most linear in the gradients. Careful consideration of equations (4-2) and our expansion for f_1 shows that the energy flux vector is determined only through terms of first order in the number density. Hence, terms quadratic and higher in n must be consistently discarded. The three contributions to the thermal conductivity are now considered separately. Finally, the results are written as a virial expansion and compared with those of Imam-Rahajoe[16].

4.1a Evaluation of λ_I

With equation (2-26), the first contribution to the energy flux vector may be expressed in terms of the perturbation function ϕ as:

$$\underline{q}_I = \frac{1}{2m^2}\int d\underline{p}_1 P_1^2 \underline{P}_1 f_{1e}(\underline{p}_1) + \frac{1}{2m^2}\int d\underline{p}_1 P_1^2 \underline{P}_1 f_{1e}(\underline{p}_1)\,\phi(\underline{p}_1) \tag{4-3}$$

The first term is clearly odd in $\underline{P}_1$ and vanishes. Performing the usual density expansion in the second term and retaining terms up to first order in the density,

$$\underline{q}_I = \frac{1}{2m^2}\int d\underline{p}_1 P_1^2 \underline{P}_1 \hat{f}_{1e}\,\phi_0 + \frac{n}{2m^2}\int d\underline{p}_1 P_1^2 \underline{P}_1 \left\{ \hat{\hat{f}}_{1e}\,\phi_1 + \hat{\hat{f}}_{1e}\,\phi_0 \right\} \tag{4-4}$$

With the results of equations (3-8), (3-9), (3-39), and (3-45) and use of the properties of tensors, it may be seen that only the part of the perturbation involving the temperature gradient is non-vanishing:

$$q_{\mathrm{I}} = -(2m^2)^{-1}(2mKT)^{-1/2}\Big\{\int d\underline{p}_1\, \underline{P}_1 \underline{P}_1 P_1^2 \hat{f}_{1e}\, a_0 \; +$$

$$+ n\int d\underline{p}_1\, \underline{P}_1 \underline{P}_1 P_1^2 \big\{\hat{f}_{1e}\, a_1 + \hat{\hat{f}}_{1e}\, a_0\big\}\Big\} \cdot \frac{\partial \ln T}{\partial \underline{r}_1} \tag{4-5}$$

Since $\hat{f}_{1e}$, $\hat{\hat{f}}_{1e}$, a_0 , and a_1 are all functions of only the magnitude of $\underline{P}_1$, the first contribution to the thermal conductivity is

$$\lambda_{\mathrm{I}} = \frac{2}{3}K^2 T (2mKT)^{-5/2}\Big\{\int d\underline{p}_1\, P_1^4 \hat{f}_{1e}\, a_0 \; + \tag{4-6}$$

$$+ n\int d\underline{p}_1\, P_1^4 \hat{f}_{1e}\, a_1 + n\int d\underline{p}_1\, P_1^4 \hat{\hat{f}}_{1e}\, a_0\Big\}$$

Substituting the result for a_0 from the solution to the first order Boltzmann equation given in equation (3-9), the $\underline{p}_1$ -integration in the first term may be performed to give the contribution:

$$\lambda_0 \equiv \frac{75}{32} \frac{K^2 T}{m} \left(\Omega^{(2,2)} \right)^{-1} \tag{4-7}$$

This is the usual low density result for the thermal conductivity. Similarly, with the results (3-61), (3-63), and (3-89) for a_1 , the second term in (4-6) leads to

$$n\lambda_0 \left\{ B + \frac{1}{6} \epsilon_2 + \frac{1}{6} T \frac{d\epsilon_1}{dT} - \frac{1}{3} Q_2 + R_1 + \mathcal{X}(\mathcal{Y}_e) \right\} \tag{4-8}$$

The final term may then be written

$$\frac{1}{6} n\lambda_0 \left\{ \frac{1}{5} (mKT)^{-3} \int d\mathbf{p}_1 P_1^6 \hat{\hat{f}}_{1e} - (mKT)^{-2} \int d\mathbf{p}_1 P_1^4 \hat{\hat{f}}_{1e} \right\} \tag{4-9}$$

With lemmas B-3 and B-4, the $\mathbf{p}_1$ -integration can be carried out to give

$$\frac{1}{6} n\lambda_0 \left\{ \frac{1}{4}\epsilon_1 + \frac{11}{10}\epsilon_2 + \frac{1}{5}\epsilon_3 \right\} \tag{4-10}$$

Summing the three terms finally yields

$$\lambda_I = \lambda_0 + n\lambda_0 \left\{ B - \frac{1}{3}Q_2 + \mathcal{R}_1 + \mathcal{K}(\mathcal{Y}_e) + \right.$$
$$\left. + \frac{1}{6}\left(\frac{1}{4}\epsilon_1 + \frac{21}{10}\epsilon_2 + \frac{1}{5}\epsilon_3 + T\frac{d\epsilon_1}{dT} \right) \right\} \tag{4-11}$$

4.1b <u>Evaluation of λ_{III}</u>

The definition in (2-17) of the quantity $Y(\underline{r}_1 \underline{r}_2; \underline{p}_1 \underline{p}_2)$ may be used to express g_{II} in terms of singlet distribution functions:

$$g_{II} = -\frac{1}{4m}\int_0^1 du \int d\underline{p}_1\, d\underline{p}_2\, d\underline{r}\, d\underline{p}_{10}\, d\underline{p}_{20}\, d\underline{r}_{10}\, d\underline{r}_{20}\, Y(\underline{r}_1 + \{u-1\}\underline{r}; \underline{r}_1 + u\underline{r}; \underline{p}_1 \underline{p}_2) \times$$
$$\times \frac{1}{r}\frac{d\varphi}{dr}\underline{r}\,\underline{r}\cdot(\underline{P}_1 + \underline{P}_2)\,\Omega_{4C}^{(2)}(\underline{r}_1 + \{u-1\}\underline{r}; \underline{r}_1 + u\underline{r}; \underline{p}_1 \underline{p}_2 | \underline{r}_{10}\, \underline{r}_{20}\, \underline{p}_{10}\, \underline{p}_{20}) \times$$
$$\times f_1(\underline{r}_{10}\underline{p}_{10}) f_1(\underline{r}_{20}\underline{p}_{20}) \tag{4-12}$$

The RHS must now be expressed in terms of functions evaluated at $\underline{r}_1$, by means of Taylor series expansions. We have consistently retained only terms up to first order in the gradients and have replaced Υ by its equilibrium value. With these considerations, the localization and density expansion of equation (4-12) gives

$$q_{II} = -\frac{n}{4m}\int_0^1 d\mu \int d\underline{p}_1\, d\underline{p}_2\, d\underline{r}\, d\underline{p}_{10}\, d\underline{p}_{20}\, d\underline{r}_{10}\, d\underline{r}_{20}\, \frac{1}{r}\frac{d\varphi}{dr}\, \underline{r}\,\underline{r}\cdot(\underline{P}_1+\underline{P}_2)\, \times$$

$$\times\, \Omega_{\alpha}^{(2)}\left(\underline{r}_1 + \{\mu-1\}\underline{r};\, \underline{r}_1+\mu\underline{r};\, \underline{p}_1\underline{p}_2 \middle|\, \underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}\right) \times \qquad (4\text{-}13)$$

$$\times\, \hat{f}_{1e}(\underline{p}_{10})\, \hat{f}_{1e}(\underline{p}_{20}) \left\{ \phi_0(\underline{p}_{10}) + \phi_0(\underline{p}_{20}) \right\}$$

where the form (2-26) has been employed to express the non-equilibrium singlet distribution functions in terms of the equilibrium functions.

Changing to center-of-mass and relative motion coordinates and substituting the explicit expression (2-14) for the $\Omega_{\alpha}^{(2)}$ operator, the $\underline{r}_0$, $\underline{R}_0$, $\underline{\xi}_0$, $\underline{p}$, μ, and $\underline{\sigma}$ integrations may be carried out trivially to yield

$$q_{II} = -\frac{n}{4m}\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, \frac{1}{r}\frac{d\varphi}{dr}\, \underline{r}\,\underline{r}\cdot\underline{P}\, \Psi(\underline{r};\underline{p}_0)\, \Psi^*(\underline{r};\underline{p}_0)\, \times$$

$$\times\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2) \left\{ \phi_0(\tilde{\underline{p}}_1) + \phi_0(\tilde{\underline{p}}_2) \right\} \qquad (4\text{-}14)$$

Use of the symmetry and tensor properties of the integrand is then sufficient to show that only the temperature gradient part of the perturbation is non-vanishing. Then with the definition (4-2) and the result (3-9) for a_0,

$$\lambda_{II} = \frac{1}{15} n\lambda_0 (mK^2T^2)^{-1} \int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, \frac{1}{r}\frac{d\varphi}{dr}\, \underline{r}\,\underline{r} : \underline{P}\, \tilde{\underline{p}}_1 \times$$

$$\times \psi(\underline{r};\underline{p}_0)\, \psi^*(\underline{r};\underline{p}_0)\, \hat{f}_{1e}(\tilde{p}_1)\, \hat{f}_{1e}(\tilde{p}_2)\, S^{(1)}_{3/2}\left(\frac{\tilde{P}^2}{2mKT}\right) \tag{4-15}$$

The $\underline{P}$ integration may then be carried out directly. After some rearrangement, the result is

$$\lambda_{II} = \frac{2^{3/2} n\lambda_0}{18\,KT}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, r\frac{d\varphi}{dr}\, \psi(\underline{r};\underline{p}_0)\, \psi^*(\underline{r};\underline{p}_0)\, S^{(1)}_{1/2}\left(\frac{p_0^2}{mKT}\right) e^{-\frac{p_0^2}{mKT}}$$

$$-\frac{2}{3} n\lambda_0 \sigma_{12} \tag{4-16}$$

where we have introduced

$$\sigma_{12} \equiv \frac{2^{3/2}}{15 m K^2 T}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, r \frac{d\psi}{dr}\, p_0^2\, \Psi\Psi^* P_2(\cos\phi)\, e^{-p_0^2/mKT}$$

$$\cos\phi \equiv \hat{\underline{r}} \cdot \hat{\underline{p}}_0 \tag{4-17}$$

and P_2 is the second Legendre polynomial. The first term in (4-16) may then be written in terms of the quantum mechanical radial distribution function:

$$-\frac{n\lambda_0}{18K}\frac{d}{dT}\int d\underline{r}\; r\frac{d\psi}{dr}\, g_0(\underline{r};\underline{r}) \tag{4-18}$$

Finally, with the definition (3-21) of the second virial coefficient,

$$\lambda_{II} = \frac{1}{3} n\lambda_0 \Big\{ B + T\frac{dB}{dT} - 2\sigma_{12} \tag{4-19}$$

$$- \frac{1}{3} T \frac{d\epsilon_1}{dT} - \frac{1}{3}\epsilon_1 \Big\}$$

4.1c Evaluation of λ_{III}

As in the treatment of q_{II}, equations (2-17) and (2-26) must first be used to represent f_2 in terms of equilibrium singlet distribution functions and the perturbation ϕ. Then, localizing at $\underline{r}_1$ with Taylor series expansions, performing the density expansion, and retaining only terms up to first order in the density and the gradients:

$$q_{III} = \frac{n}{m}\int d\underline{p}_1\, d\underline{p}_2\, d\underline{r}\, d\underline{p}_{10}\, d\underline{p}_{20}\, d\underline{r}_{10}\, d\underline{r}_{20}\, \underline{P}_1\, \varphi\, \Omega^{(2)}_{\infty}(\underline{r}_1\underline{r}_2\underline{p}_1\underline{p}_2|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}) \times \tag{4-20}$$

$$\times \hat{f}_{1e}(\underline{p}_{10})\hat{f}_{1e}(\underline{p}_{20})\left\{\phi_0(\underline{p}_{10}) + \phi_0(\underline{p}_{20})\right\}$$

Changing to center-of-mass and relative motion coordinates and substituting the explicit form of the $\Omega^{(2)}_{\infty}$ operator, the trivial $\underline{\gamma}_0$, $\underline{\sigma}$, $\underline{R}_0$, and $\underline{r}_0$ integrations may be carried out to give

$$q_{III} = -\frac{n}{2m}\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, d\underline{p}\, \underline{p}\, \varphi\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\phi_0(\tilde{\underline{p}}_1) + \phi_0(\tilde{\underline{p}}_2)\right\} F$$

$$+\frac{n}{4m}\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, d\underline{p}\, \underline{P}\, \varphi\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\phi_0(\tilde{\underline{p}}_1) + \phi_0(\tilde{\underline{p}}_2)\right\} F \tag{4-21}$$

where the definition (2-22) of $F(\underline{r};\underline{p},\underline{p}_o)$ has been used. With the symmetry relations (3-22), the first integrand may be shown to change sign when the directions of the $\underline{p}$, $\underline{p}_o$, and $\underline{r}$ integrations are reversed; hence, the integral must vanish. Performing the $\underline{p}$ integration in the second term with lemma B-5,

$$q_{III} = \frac{n}{4m}\int d\underline{r}\, d\underline{P}\, d\underline{p}_o\, \underline{P}\, \varphi\, \Psi^*(\underline{r};\underline{p}_o)\, \Psi(\underline{r};\underline{p}_o)\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \times \times \left\{ \phi_o(\tilde{\underline{p}}_1) + \phi_o(\tilde{\underline{p}}_2) \right\} \tag{4-22}$$

With the solution (3-9) for ϕ_o, it again follows from the tensor properties that only the term in the temperature gradient is non-vanishing. Then, with the definition (4-2), the third contribution to the thermal conductivity is

$$\lambda_{III} = \frac{-n\lambda_o}{15\, m K^2 T^2}\int d\underline{r}\, d\underline{p}_o\, d\underline{P}\, \varphi\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, S^{(1)}_{3/2}\left(\frac{\tilde{p}_1^2}{2mKT}\right) \times \times \left\{ \tfrac{1}{2}P^2 - \underline{p}_o \cdot \underline{P} \right\} \Psi(\underline{r};\underline{p}_o)\, \Psi^*(\underline{r};\underline{p}_o) \tag{4-23}$$

The $\underline{P}$ integration may be carried out directly. After some rearrangement, the result may be written in terms of the quantum mechanical radial distribution function:

$$\lambda_{III} = \frac{n\lambda_0}{6K} \frac{d}{dT} \int d\underline{r}\, \varphi\, g_0(\underline{r};\underline{r}) \tag{4-24}$$

By substituting the Schrodinger equation and introducing the definitions of ϵ_1 and the second virial coefficient,

$$\lambda_{III} = -\frac{1}{6} n\lambda_0 \left\{ 4T\frac{dB}{dT} + 2T^2\frac{d^2B}{dT^2} + \epsilon_1 + T\frac{d\epsilon_1}{dT} \right\} \tag{4-25}$$

4.1d Virial Expansion of the Thermal Conductivity

It is convenient to write the thermal conductivity as a density expansion of the form:

$$\lambda = \lambda_0 \left\{ 1 + nB_\lambda + \dots \right\} \tag{4-26}$$

where λ_0 is the usual low density limit given in equation (4-7). From the results of the preceding sections,

$$B_\lambda = \frac{1}{3}\left\{ 4B - T\frac{dB}{dT} - T^2\frac{d^2B}{dT^2} - Q_2 - 2\sigma_{12} \right.$$

$$\left. - \frac{17}{24}\epsilon_1 + \frac{21}{20}\epsilon_2 + \frac{1}{10}\epsilon_3 - \frac{1}{3}T\frac{d\epsilon_1}{dT} \right\} \qquad (4\text{-}27)$$

$$+ \mathcal{R}_1 \quad + \mathcal{K}(\mathcal{Y}_e)$$

B_λ is then independent of the density and is referred to as the second thermal conductivity virial coefficient.

A comparison with the results of Imam-Rahajoe[16] for B_λ can now be made. B and its derivatives occur identically in both treatments. Aside from slight differences in definitions, the same is true for both the Q_2 and σ_{12} terms. Terms involving the ϵ_i integrals do not agree, however. This may be shown to result directly from Imam-Rahajoe's use of a form for $\hat{\hat{f}}_{1e}$ which corresponds to only the first term of an expansion of de Boer's expression (2-56) in Sonine polynomials of order one-half.

The three-body term $\mathcal{R}_1$ agrees with the corresponding quantity in the work of Imam-Rahajoe only if the approximation discussed in section (3.6a-iii) is used. This, again is a consequence of the different forms assumed for $\hat{\hat{f}}_{1e}$. The second three-body term,

$\mathcal{K}(\mathcal{Y}_e)$, does not occur in Imam-Rahajoe's treatment due to his use of molecular chaos in the development of an expression for the pair distribution function.

4.2 The Pressure Tensor

For a gas which is not too far displaced from equilibrium, the pressure tensor may be written:

$$\underline{\underline{P}} = P\,\underline{\underline{U}} - 2\eta\,\underline{\underline{S}} - \mathcal{H}\,\underline{\underline{U}}\left(\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u}\right) \tag{4-28}$$

where P , η , and $\mathcal{H}$ are the hydrostatic pressure, coefficient of shear viscosity, and coefficient of bulk viscosity, respectively. $\underline{S}$ is the rate of shear tensor and is defined by

$$\underline{\underline{S}} = \frac{1}{2}\left\{\frac{\partial}{\partial \underline{r}_1}\underline{u} + \left(\frac{\partial}{\partial \underline{r}_1}\underline{u}\right)^{+}\right\} - \frac{1}{3}\left(\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u}\right)\underline{\underline{U}} \tag{4-29}$$

A formulation of the pressure tensor which is appropriate for the quantum development may be conveniently expressed as the sum of two contributions[16]:

$$\underline{\underline{P}}(\underline{r}_1|f_1) \equiv \underline{\underline{P}}_{\mathrm{I}} + \underline{\underline{P}}_{\mathrm{II}}$$

$$\underline{\underline{P}}_{\mathrm{I}} = \frac{1}{m}\int d\underline{p}_1\, \underline{p}_1\underline{p}_1\, f_1(\underline{p}_1)$$

(4-30)

$$\underline{\underline{P}}_{\mathrm{II}} = -\frac{1}{2}\int_0^1 d\mu \int d\underline{r}\, d\underline{p}_1\, d\underline{p}_2\, \frac{1}{r}\frac{d\varphi}{dr}\, \underline{r}\,\underline{r}\; \times$$

$$\times f_2\left(\underline{r}_1 + \underline{r}\{\mu - 1\};\, \underline{r}_1 + \mu\underline{r};\, \underline{p}_1\underline{p}_2 \middle| f_1\right)$$

where it has been explicitly indicated that the pressure tensor must be localized at $\underline{r}_1$ and is taken to be a functional of singlet distribution functions. Paralleling the treatment of the heat flux vector, we also define

$$\underline{\underline{P}}_{\mathrm{I}} \equiv P_{\mathrm{I}}\,\underline{\underline{U}} - 2\eta_{\mathrm{I}}\,\underline{\underline{S}} - \mathcal{H}_{\mathrm{I}}\,\underline{\underline{U}}\left(\frac{\partial}{\partial \underline{r}_1}\cdot \underline{u}\right)$$

(4-31)

$$\underline{\underline{P}}_{\mathrm{II}} \equiv P_{\mathrm{II}}\,\underline{\underline{U}} - 2\eta_{\mathrm{II}}\,\underline{\underline{S}} - \mathcal{H}_{\mathrm{II}}\,\underline{\underline{U}}\left(\frac{\partial}{\partial \underline{r}_1}\cdot \underline{u}\right)$$

then

$$\underline{\underline{P}} = \underline{\underline{P}}_{I} + \underline{\underline{P}}_{II}$$

$$\eta = \eta_{I} + \eta_{II} \qquad (4\text{-}32)$$

$$\mathcal{H} = \mathcal{H}_{I} + \mathcal{H}_{II}$$

The solution of the first and second order Boltzmann equations allows the hydrostatic pressure and the coefficient of bulk viscosity to be evaluated through terms second order in the number density. The coefficient of shear viscosity is determined only to order n, however. Consequently, it is convenient to separate the contributions of $\underline{\underline{P}}_{I}$ and $\underline{\underline{P}}_{II}$ to $\underline{\underline{P}}$, η, or $\mathcal{H}$ prior to performing the density separation.

It is necessary then to write the perturbation function as

$$\phi \equiv -\mathcal{A}\, \underline{W}_1 \cdot \frac{\partial \ln T}{\partial \underline{r}_1} - \mathcal{B}\, \overset{\circ}{\underline{W}_1 \underline{W}_1} : \frac{\partial}{\partial \underline{r}_1} \underline{u} - \mathcal{C} \frac{\partial}{\partial \underline{r}_1} \cdot \underline{u} \qquad (4\text{-}33)$$

where $\mathcal{A}$, $\mathcal{B}$, and $\mathcal{C}$ are functions of the magnitude of $\underline{P}_1$ and have density expansions given by:

$$\mathcal{A} \sim \frac{1}{n}\mathcal{A}_0 + \mathcal{A}_1 + \ldots$$

$$\mathcal{B} \sim \frac{1}{n}\mathcal{B}_0 + \mathcal{B}_1 + \ldots \tag{4-34}$$

$$\mathcal{C} \sim \mathcal{C}_1 + n\mathcal{C}_2 + \ldots$$

The coefficients $\mathcal{A}_0$, $\mathcal{A}_1$, $\mathcal{B}_0$, $\mathcal{B}_1$, and $\mathcal{C}_1$ are known from the solutions to the first and second order Boltzmann equations.

The two contributions to the pressure tensor are now evaluated separately. Finally, $\mathbb{P}$, η , and $\mathcal{H}$ are expressed as virial expansions and compared with the results of Imam-Rahajoe[16].

4.2a <u>Evaluation of $\mathbb{P}_{\mathrm{I}}$, η_{I} , and $\mathcal{H}_{\mathrm{I}}$</u>

With the definition of (2-26), the first contribution to the pressure tensor may be expressed in terms of the equilibrium singlet distribution function:

$$\underline{\underline{\mathbb{P}}}_{\mathrm{I}} = \frac{1}{m}\int d\underline{p}_1 \, \underline{p}_1 \underline{p}_1 f_{1e} \phi + \frac{1}{m}\int d\underline{p}_1 \, \underline{p}_1 \underline{p}_1 f_{1e} \tag{4-35}$$

Using relation (4-33) for the perturbation function and the fact that f_{1e} and $\mathcal{A}$ are functions only of the magnitude of $\underline{P}_1$, the terms in the temperature gradient must vanish to give

$$\underline{\underline{P}}_I = \frac{1}{3m}\int d\underline{p}_1\, P_1^2 f_{1e}\, \underline{\underline{U}} - \frac{1}{3m}\underline{\underline{U}}\left(\frac{\partial}{\partial \underline{r}_1}\cdot\underline{u}\right)\int d\underline{p}_1\, P_1^2 f_{1e}\, \mathcal{C}$$

$$-\left(2m^2KT\right)^{-1}\int d\underline{p}_1\, f_{1e}\, \mathcal{B}\, \underline{P}_1\underline{P}_1\overset{\circ}{\underline{P}_1\underline{P}_1} : \frac{\partial}{\partial \underline{r}_1}\underline{u} \tag{4-36}$$

The integral

$$\int d\underline{p}_1\, f_{1e}\, \mathcal{B}\, \underline{P}_1\underline{P}_1\overset{\circ}{\underline{P}_1\underline{P}_1} \tag{4-37}$$

is a fourth order tensor and must be isotropic since $\mathcal{B}$ and f_{1e} are functions only of the magnitude of $\underline{P}_1$. Every fourth order isotropic tensor is a linear combination of the tensors $\underline{\underline{\underline{\underline{\mathbb{U}}}}}$, $\underline{\underline{\underline{\underline{\mathbb{W}}}}}$, and $\underline{\underline{U}}\,\underline{\underline{U}}$, defined by

$$\mathbb{U}_{ijkl} \equiv \delta_{il}\,\delta_{jk}$$

$$\mathbb{W}_{ijkl} \equiv \delta_{ik}\,\delta_{jl} \qquad (4\text{-}38)$$

$$\left(\underline{\underline{U}}\;\underline{\underline{U}}\right)_{ijkl} \equiv \delta_{ij}\,\delta_{kl}$$

Hence, the integral (4-37) may be expressed as a linear combination of orthonormal fourth order tensors in the following way:

$$\int dp_1 f_{1e} B \underline{P}_1 \underline{P}_1 \underline{P}_1 \mathring{\underline{P}}_1 = \mathcal{J}_1 \left\{ \frac{1}{2\sqrt{5}} \left(\underline{\underline{\underline{\underline{\mathbb{U}}}}} + \underline{\underline{\underline{\underline{\mathbb{W}}}}} \right) - \frac{1}{3\sqrt{5}} \underline{\underline{U}}\;\underline{\underline{U}} \right\}$$

$$+ \mathcal{J}_2 \left\{ \frac{1}{3} \underline{\underline{U}}\;\underline{\underline{U}} \right\} \qquad (4\text{-}39)$$

$$+ \mathcal{J}_3 \left\{ \frac{1}{2\sqrt{3}} \underline{\underline{\underline{\underline{\mathbb{U}}}}} - \frac{1}{2\sqrt{3}} \underline{\underline{\underline{\underline{\mathbb{W}}}}} \right\}$$

The problem of evaluating the integral is then reduced to determining the three expansion coefficients $\mathcal{J}_1$, $\mathcal{J}_2$, and $\mathcal{J}_3$.

From the orthonormality of the three tensors chosen, it follows that

$$\mathcal{T}_1 = \frac{1}{\sqrt{5}}\left\{\frac{1}{2}\left(\underline{\underline{\underline{\underline{U}}}} + \underline{\underline{\underline{\underline{W}}}}\right) - \frac{1}{3}\underline{\underline{U}}\,\underline{\underline{U}}\right\} \vdots\vdots \int d\underline{p}_1\, f_{1e}\, B\, \underline{p}_1\underline{p}_1\underline{p}_1\mathring{\underline{p}}_1$$

$$\mathcal{T}_2 = \frac{1}{3}\underline{\underline{U}}\,\underline{\underline{U}} \vdots\vdots \int d\underline{p}_1\, f_{1e}\, B\, \underline{p}_1\underline{p}_1\underline{p}_1\mathring{\underline{p}}_1 \qquad (4\text{-}40)$$

$$\mathcal{T}_3 = \frac{1}{2\sqrt{3}}\left\{\underline{\underline{\underline{\underline{U}}}} - \underline{\underline{\underline{\underline{W}}}}\right\} \vdots\vdots \int d\underline{p}_1\, f_{1e}\, B\, \underline{p}_1\underline{p}_1\underline{p}_1\mathring{\underline{p}}_1$$

Performing the indicated tensor operations,

$$\mathcal{T}_1 = \frac{2}{3\sqrt{5}} \int d\underline{p}_1\, f_{1e}\, B\, p_1^4 \qquad (4\text{-}41)$$

$$\mathcal{T}_2 = \mathcal{T}_3 = 0$$

Then, noting that

$$\left\{\frac{1}{2}\left(\underline{\underline{\underline{\underline{U}}}} + \underline{\underline{\underline{\underline{W}}}}\right) - \frac{1}{3}\underline{\underline{U}}\,\underline{\underline{U}}\right\} : \frac{d}{d\underline{r}_1}\underline{u} = \underline{\underline{S}} \tag{4-42}$$

equation (4-36) becomes

$$\begin{aligned} \underline{\underline{P}}_I = {} & \left\{\frac{1}{3m}\int d\underline{p}_1\, P_1^2 f_{1e}\right\}\underline{\underline{U}} \\ & - 2\left\{(30\, m^2 kT)^{-1}\int d\underline{p}_1\, f_{1e}\, \mathcal{B}\, P_1^4\right\}\underline{\underline{S}} \\ & - \left\{\frac{1}{3m}\int d\underline{p}_1\, P_1^2 f_{1e}\, \mathcal{C}\right\}\underline{\underline{U}}\,\frac{d}{d\underline{r}_1}\cdot\underline{u} \end{aligned} \tag{4-43}$$

Finally, with the definition (4-31),

$$\begin{aligned} P_I &= \frac{1}{3m}\int d\underline{p}_1\, P_1^2 f_{1e} \\ \eta_I &= (30\, m^2 kT)^{-1}\int d\underline{p}_1\, f_{1e}\, \mathcal{B}\, P_1^4 \\ \mathcal{H}_I &= \frac{1}{3m}\int d\underline{p}_1\, f_{1e}\, \mathcal{C}\, P_1^2 \end{aligned} \tag{4-44}$$

$\mathbb{P}_I$, η_I , and $\mathcal{H}_I$ are now considered individually.

i. $\mathbb{P}_I$

Performing the density expansion and retaining terms up to quadratic in the number density,

$$\mathbb{P}_I = \frac{n}{3m}\int dp_1 \hat{f}_{1e} P_1^2 + \frac{n^2}{3m}\int dp_1 \hat{\hat{f}}_{1e} P_1^2 \tag{4-45}$$

The first integral may be carried out directly and the second with lemma B-2 to give

$$\mathbb{P}_I = nKT\left\{1 + \tfrac{1}{3}n\epsilon_1\right\} \tag{4-46}$$

ii. η_I

Retaining terms up to first order in the number density,

$$\eta_I = (30m^2KT)^{-1}\left\{\int dp_1 \hat{f}_{1e} B_0 P_1^4 + n\int dp_1 \hat{\hat{f}}_{1e} B_0 P_1^4 + n\int dp_1 \hat{f}_{1e} B_1 P_1^4\right\} \tag{4-47}$$

Using the results for $\mathcal{B}_0$ and $\mathcal{B}_1$ from the solutions to the first and second order Boltzmann equations, the integrals in (4-47) can be carried out with the aid of lemma B-3 to give

$$\eta_I = \eta_0 + n\eta_0 \left\{ B - \frac{7}{6} T \frac{dB}{dT} - \frac{1}{3} T^2 \frac{d^2B}{dT^2} - \frac{1}{2} Q_2 \right.$$

$$- \frac{1}{12}\epsilon_1 - \frac{1}{6} T \frac{d\epsilon_1}{dT} + \frac{1}{15}\epsilon_2 \tag{4-48}$$

$$\left. + \mathcal{R}_2 + \mathcal{L}(\mathcal{Y}_e) \right\}$$

where

$$\eta_0 \equiv \frac{5}{8} KT \left(\Omega^{(2,2)} \right)^{-1} \tag{4-49}$$

is the usual low density expression for the coefficient of shear viscosity.

iii. $\mathcal{H}_I$

Performing the density expansion and discarding terms cubic and higher in the number density,

$$\mathcal{H}_I = \frac{n}{3m}\int d\mathbf{p}_1 \hat{f}_{1e} \mathcal{C}_1 P_1^2 + \frac{n^2}{3m}\int d\mathbf{p}_1 \hat{\hat{f}}_{1e} \mathcal{C}_1 P_1^2$$

$$+ \frac{n^2}{3m}\int d\mathbf{p}_1 \hat{f}_{1e} \mathcal{C}_2 P_1^2 \tag{4-50}$$

With the solution (3-61) for $\mathcal{C}_1$ and the orthogonality condition for the Sonine polynomials, this immediately reduces to

$$\mathcal{H}_I = \frac{n^2}{3m}\int d\mathbf{p}_1 P_1^2 \left\{ \hat{f}_{1e} \mathcal{C}_2 + \hat{\hat{f}}_{1e} \mathcal{C}_1 \right\} \tag{4-51}$$

A complete evaluation of $\mathcal{C}_2$ would require the solution of the third order Boltzmann equation. However, the particular integral (4-51) is uniquely determined by the auxiliary conditions for the third order Boltzmann equation. Substituting relations (4-33) and (4-34) for the perturbation into the third of the auxiliary conditions (3-42), retaining only terms second order in the density, and making use of the tensor properties,

$$\int d\underline{p}_1 P_1^2 \left\{ \hat{f}_{1e} C_2 + \hat{\hat{f}}_{1e} C_1 \right\} = -m \int d\underline{p}_1 d\underline{p}_2 d\underline{r}\, d\underline{p}_{10}\, d\underline{p}_{20}\, d\underline{r}_{10}\, d\underline{r}_{20}\, \varphi(r) \times$$

$$\times\, \Omega_{\infty}^{(2)}(\underline{r}_1 \underline{r}_2 \underline{p}_1 \underline{p}_2 | \underline{r}_{10} \underline{r}_{20} \underline{p}_{10} \underline{p}_{20})\, \hat{f}_{1e}(\underline{p}_{10})\, \hat{f}_{1e}(\underline{p}_{20}) \times$$

$$\times \left\{ C_1(\underline{p}_{10}) + C_1(\underline{p}_{20}) + \frac{1}{3KT}\left[\underline{r}_0 \cdot \underline{p}_0 + \underline{R}_0 \cdot \underline{P} - \underline{r}_1 \cdot \underline{P} \right] \right\}$$

(4-52)

Changing to relative motion and center-of-mass coordinates and substituting the explicit expression (2-14) for the $\Omega_{\infty}^{(2)}$ operator into (4-52), the trivial $\underline{\sigma}$, $\underline{r}_0$, $\underline{R}_0$, and $\underline{\rho}_0$ integrations may be carried out. After removing terms which are odd in $\underline{P}$ from the integrand, the RHS of the auxiliary condition (4-52) becomes

$$-m \int d\underline{r}\, d\underline{p}\, d\underline{P}\, d\underline{p}_0\, \varphi(r)\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2) \left\{ C_1(\tilde{\underline{p}}_1) + C_1(\tilde{\underline{p}}_2) \right\} F(\underline{r}; \underline{p}, \underline{p}_0)$$

$$+ \frac{m\hbar i}{6KT} \int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, \varphi(r)\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \underline{p}_0 \cdot \left\{ \psi^* \frac{\partial \psi}{\partial \underline{p}_0} - \psi \frac{\partial \psi^*}{\partial \underline{p}_0} \right\} \quad (4\text{-}53)$$

With the expression (3-61) for $\mathcal{C}_1$, the $\underline{P}$ integration can be carried out directly in both terms. Then, using the definition of the quantum mechanical radial distribution function, equation (4-52) may be written:

$$\int dp_1 P_1^2 \left\{ \hat{f}_{1e} \mathcal{C}_2 + \hat{\hat{f}}_{1e} \mathcal{C}_1 \right\} = 3 m Q_1 - \frac{1}{4} \frac{M_1^{(2)}}{\Delta_{22}^{11}} m T^2 \frac{d^2}{dT^2} \int d\underline{r}\, \varphi\, g_0(\underline{r};\underline{r}) \tag{4-54}$$

where

$$Q_1 \equiv \frac{\sqrt{2}\, i\hbar}{9KT} \left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, dp_0\, \varphi\, e^{-p_0^2/mKT} p_0 \left\{ \psi^* \frac{d\psi}{dp_0} - \psi \frac{d\psi^*}{dp_0} \right\} \tag{4-55}$$

Combining equations (4-51) and (4-54),

$$\mathcal{H}_I = n^2 Q_1 - \frac{1}{12} n^2 \frac{M_1^{(2)}}{\Delta_{22}^{11}} T^2 \frac{d^2}{dT^2} \int d\underline{r}\, \varphi\, g_0(\underline{r};\underline{r}) \tag{4-56}$$

The integral in (4-56) may be carried out by the same techniques involved in the evaluation of (4-24). Finally, substituting the results of (3-63) and (3-110),

$$\mathcal{H}_{I} = n^2 Q_1 +$$

$$+ \frac{n^2 KT}{144}\left(\Omega^{(2,2)}\right)^{-1}\left\{10T\frac{dB}{dT} + 11T^2\frac{d^2B}{dT^2} + 2T^3\frac{d^3B}{dT^3}\right\}\times$$

$$\times\left\{2T\frac{dB}{dT} + 4T^2\frac{d^2B}{dT^2} + T^3\frac{d^3B}{dT^3} + T\frac{d\epsilon_1}{dT} + \frac{1}{2}T^2\frac{d^2\epsilon_1}{dT^2}\right\}$$

(4-57)

It may be noted that, in the treatment of a classical gas, the auxiliary condition on the energy completely determines the kinetic contribution to the bulk viscosity, specifically zero. In the quantum case, this auxiliary condition is sufficient to completely evaluate $\mathcal{H}_{I}$, the quantum analogue to the kinetic portion of the classical bulk viscosity. The first of the auxiliary conditions (3-42), related to the number density, provides an additional condition on $\mathcal{C}$ which is superfluous to the evaluation of $\mathcal{H}_{I}$.

4.2b Evaluation of $\underline{\underline{P}}_{II}$, η_{II}, and $\mathcal{H}_{II}$

The definition (2-17) of $Y(\underline{r}_1\underline{r}_2;\underline{p}_1\underline{p}_2)$ may be used to first express $\underline{\underline{P}}_{II}$ in terms of singlet distribution functions:

$$\underline{\underline{P}}_{II} = -\frac{1}{2}\int_0^1 d\mu \int d\underline{r}\, d\underline{p}_1 d\underline{p}_2\, d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \frac{1}{r}\frac{d\psi}{dr}\,\underline{r}\,\underline{r}\, Y_e(\underline{r};\underline{p}_1\underline{p}_2)\times$$

$$\times\,\Omega_{\infty}^{(2)}\left(\underline{r}_1+\{\mu-1\}\underline{r};\underline{r}_1+\mu\underline{r};\underline{p}_1\underline{p}_2\middle|\underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}\right) f_1(\underline{r}_{10}\underline{p}_{10}) f_1(\underline{r}_{20}\underline{p}_{20}) \tag{4-58}$$

where we have again replaced $Y(\underline{r};\underline{p}_1\underline{p}_2)$ by its equilibrium value. The RHS must be written in terms of functions evaluated at $\underline{r}_1$ by means of Taylor series expansions. The definition (2-26) can then be used to express the non-equilibrium singlet distribution functions in terms of their equilibrium values. As usual, only terms linear or less in the gradients are to be retained:

$$\underline{\underline{P}}_{II} = -\frac{1}{2}\int_0^1 d\mu \int d\underline{r}\, d\underline{p}_1\, d\underline{p}_2\, d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, Y_e \frac{1}{r}\frac{d\varphi}{dr}\,\underline{r}\,\underline{r} \; \times$$

$$\times\, \Omega_{\alpha}^{(2)}\left(\underline{r}_1 + \{\mu - 1\}\underline{r};\, \underline{r}_1 + \mu\underline{r};\, \underline{p}_1\underline{p}_2 \middle| \underline{r}_{10}\underline{r}_{20}\underline{p}_{10}\underline{p}_{20}\right) \times$$

$$\times\Big\{f_{1e}(\underline{p}_{10}) f_{1e}(\underline{p}_{20})\left[1 + \phi(\underline{p}_{10}) + \phi(\underline{p}_{20})\right] + \tag{4-59}$$

$$+ f_{1e}(\underline{p}_{20})(\underline{r}_{10} - \underline{r}_1)\cdot\frac{\partial}{\partial \underline{r}_1} f_{1e}(\underline{p}_{10}) + f_{1e}(\underline{p}_{10})(\underline{r}_{20} - \underline{r}_1)\cdot\frac{\partial}{\partial \underline{r}_1} f_{1e}(\underline{p}_{20})\Big\}$$

After changing to center-of-mass and relative motion coordinates and substituting explicitly for the $\Omega_{\alpha}^{(2)}$ operator, the μ , $\underline{\sigma}$, $\underline{\xi}_0$, $\underline{r}_0$, and $\underline{R}_0$ integrations may be carried out trivially to give

$$\underline{\underline{P}}_{II} = -\frac{1}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\varphi}{dr}\, Y_e(\underline{r};\underline{p}\underline{P})\,\underline{r}\,\underline{r} \; \times$$

$$\times\Big\{F f_{1e}(\tilde{\underline{p}}_1) f_{1e}(\tilde{\underline{p}}_2)\left[1 + \phi(\tilde{\underline{p}}_1) + \phi(\tilde{\underline{p}}_2)\right] + \tag{4-60}$$

$$+\frac{1}{2} F\,\underline{r}\cdot\left[f_{1e}(\tilde{\underline{p}}_1)\frac{\partial}{\partial \underline{r}_1} f_{1e}(\tilde{\underline{p}}_2) + f_{1e}(\tilde{\underline{p}}_2)\frac{\partial}{\partial \underline{r}_1} f_{1e}(\tilde{\underline{p}}_1)\right] +$$

$$+\frac{1}{2}\,\underline{G}\cdot\left[f_{1e}(\tilde{\underline{p}}_1)\frac{\partial}{\partial \underline{r}_1} f_{1e}(\tilde{\underline{p}}_2) - f_{1e}(\tilde{\underline{p}}_2)\frac{\partial}{\partial \underline{r}_1} f_{1e}(\tilde{\underline{p}}_1)\right]\Big\}$$

At this point, the treatment may be simplified by recognizing that, since no terms higher than quadratic in the number density were retained in $\underline{\underline{P}}_{I}$, a density expansion of $\underline{\underline{P}}_{II}$ may be truncated at the same order of the density. After performing the density expansion, substituting equations (4-33) and (4-34) for the perturbation, and making use of the tensor properties and the symmetries developed in equations (3-22), the second contribution to the pressure tensor becomes:

$$
\begin{aligned}
\underline{\underline{P}}_{II} = &-\frac{n^2}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, \underline{r}\,\underline{r}\, F\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2) \\
&+\frac{n}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, \underline{r}\,\underline{r}\, F\, f_{1e}(\tilde{\underline{p}}_1)\, f_{1e}(\tilde{\underline{p}}_2)\left\{\underline{\underline{B}}_0(\tilde{\underline{p}}_1)+\underline{\underline{B}}_0(\tilde{\underline{p}}_2)\right\} : \frac{\partial}{\partial \underline{r}_1}\underline{u} \\
&+\frac{n^2}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, \underline{r}\,\underline{r}\, F\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\mathcal{C}_1(\tilde{\underline{p}}_1)+\mathcal{C}_1(\tilde{\underline{p}}_2)\right\} \frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} \\
&-\frac{n^2}{6KT}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, \underline{r}\,\underline{r}\, \underline{G}\cdot\underline{p}_0\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \frac{\partial}{\partial \underline{r}_1}\cdot\underline{u} \\
&+\frac{n^2}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, \underline{r}\,\underline{r}\, F\left\{\hat{f}_{1e}(\tilde{\underline{p}}_1)\,\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_2)+\hat{f}_{1e}(\tilde{\underline{p}}_2)\,\hat{\hat{f}}_{1e}(\tilde{\underline{p}}_1)\right\}\times \\
&\qquad\qquad \times\left\{\underline{\underline{B}}_0(\tilde{\underline{p}}_1)+\underline{\underline{B}}_0(\tilde{\underline{p}}_2)\right\} : \frac{\partial}{\partial \underline{r}_1}\underline{u} \\
&+\frac{n^2}{2}\int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, \frac{1}{r}\frac{d\psi}{dr}\, F\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \underline{r}\,\underline{r}\,\times \\
&\qquad \times\left\{\gamma_e\left[\underline{\underline{B}}_0(\tilde{\underline{p}}_1)+\underline{\underline{B}}_0(\tilde{\underline{p}}_2)\right]+\left[\underline{\underline{B}}_1(\tilde{\underline{p}}_1)+\underline{\underline{B}}_1(\tilde{\underline{p}}_2)\right]\right\} : \frac{\partial}{\partial \underline{r}_1}\underline{u}
\end{aligned}
\tag{4-61}
$$

Finally, using equation (4-31) and remembering that $\underline{\underline{P}}_{I}$ and $\mathcal{H}_{I}$ were evaluated to second order in the number density and η_{I} to first order, $\underline{\underline{P}}_{II}$, η_{II} , and $\mathcal{H}_{II}$ may be identified by the same techniques employed in the treatment of $\underline{\underline{P}}_{I}$. The results are

$$\underline{\underline{P}}_{II} = -\frac{1}{6} n^2 \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, r \frac{d\varphi}{dr} F \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2)$$

$$\eta_{II} = -\frac{n}{20} \left\{ \frac{1}{2} \left(\underline{\underline{\underline{\underline{U}}}} + \underline{\underline{\underline{\underline{U}}}} \right) - \frac{1}{3} \underline{\underline{U}}\, \underline{\underline{U}} \right\} \vdots \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P} \frac{1}{r} \frac{d\varphi}{dr} F \times$$

$$\times \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \underline{r}\,\underline{r} \left\{ \underline{\underline{B}}_0(\tilde{\underline{p}}_1) + \underline{\underline{B}}_0(\tilde{\underline{p}}_2) \right\}$$

$$\mathcal{H}_{II} = -\frac{n^2}{6} \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, r \frac{d\varphi}{dr} F \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2) \left\{ \mathcal{C}_1(\tilde{\underline{p}}_1) + \mathcal{C}_1(\tilde{\underline{p}}_2) \right\}$$

(4-62)

$$+ \frac{n^2}{18KT} \int d\underline{r}\, d\underline{p}_0\, d\underline{p}\, d\underline{P}\, r \frac{d\varphi}{dr} \underline{G} \cdot \underline{p}_0 \hat{f}_{1e}(\tilde{\underline{p}}_1) \hat{f}_{1e}(\tilde{\underline{p}}_2)$$

$\underline{\underline{P}}_{II}$, η_{II} , and $\mathcal{H}_{II}$ are now evaluated separately.

i. P_{II}

The $\underline{P}$ integration in the expansion (4-62) for P_{II} may be carried out directly. The $\not{p}$ integration can then be performed with the aid of lemma B-5 and the result written in terms of the radial distribution function as

$$P_{II} = -\frac{1}{6} n^2 \int d\underline{r}\; r \frac{d\varphi}{dr}\, g_0(\underline{r};\underline{r}) \tag{4-63}$$

With the definition (3-21) of the second virial coefficient,

$$P_{II} = n^2 KT \left\{ B - \frac{1}{3}\epsilon_1 \right\} \tag{4-64}$$

ii. η_{II}

The $\not{p}$ integration can be performed with the aid of lemma B-5 to yield:

$$\eta_{II} = -\frac{1}{10}\eta_0 (mK^2T^2)^{-1} \left\{ \frac{1}{2}\left(\underline{\underline{\underline{\underline{W}}}} + \underline{\underline{\underline{\underline{W}}}} \right) - \frac{1}{3}\underline{\underline{U}}\,\underline{\underline{U}} \right\} \vdots \vdots$$

(4-65)

$$\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, \frac{1}{r}\frac{d\varphi}{dr}\, \psi\, \psi^* \, \hat{f}_{1e}(\tilde{p}_1)\, \hat{f}_{1e}(\tilde{p}_2)\, \underline{r}\,\underline{r}\, \tilde{\underline{p}}_1 \mathring{\tilde{\underline{p}}}_1$$

The $\underline{P}$ integration may then be done directly. After performing the tensor operation, the result is

$$\eta_{II} = -n\,\eta_0\,\sigma_{12} \tag{4-66}$$

where σ_{12} has been defined in equation (4-17).

iii. $\mathcal{H}_{II}$

The $\underline{p}$ integration in the first term can be done with Lemma B-5; the $\underline{p}$ integration in the second follows directly from the definition (2-22) of the function $\underline{G}$ and the properties of Fourier integrals. With this, the second contribution to the bulk viscosity becomes

$$-\frac{n^2}{6}\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, r\frac{d\varphi}{dr}\psi\psi^* \hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\left\{\mathcal{C}_1(\tilde{p}_1)+\mathcal{C}_1(\tilde{p}_2)\right\}$$

(4-67)

$$-\frac{n^2 i\hbar}{36KT}\int d\underline{r}\, d\underline{p}_0\, d\underline{P}\, r\frac{d\varphi}{dr}\hat{f}_{1e}(\tilde{p}_1)\hat{f}_{1e}(\tilde{p}_2)\underline{p}_0\cdot\left\{\psi^*\frac{\partial}{\partial \underline{p}_0}\psi-\psi\frac{\partial}{\partial \underline{p}_0}\psi^*\right\}$$

Substituting the result (3-61) for $\mathcal{C}_1$, the $\underline{P}$ integration may be carried out in both terms. The result may then be written as

$$\mathcal{H}_{II}=-\frac{n^2}{24}\frac{M_1^{(2)}}{\Delta_{22}^{''}}T^2\frac{d^2}{dT^2}\int d\underline{r}\, r\frac{d\varphi}{dr}g_0(\underline{r};r)\ +n^2\sigma_{30} \qquad (4\text{-}68)$$

where we have introduced

$$\sigma_{30}\equiv\frac{-\sqrt{2}\, i\hbar}{18KT}\left(\frac{\lambda}{h}\right)^3\int d\underline{r}\, d\underline{p}_0\, r\frac{d\varphi}{dr}e^{-\frac{p_0^2}{mKT}}\underline{p}_0\cdot\left\{\psi^*\frac{\partial\psi}{\partial \underline{p}_0}-\psi\frac{\partial\psi^*}{\partial \underline{p}_0}\right\}$$

(4-69)

Finally, with results (3-63) and (3-110) and the definition (3-21) of the second virial coefficient,

$$\mathcal{H}_{II} = n^2 \sigma_{30} + \frac{n^2 KT}{144}\left(\Omega^{(2,2)}\right)^{-1}\left\{10T\frac{dB}{dT} + 11T^2\frac{d^2B}{dT^2} + 2T^3\frac{d^3B}{dT^3}\right\}\times$$

$$\times\left\{3T\frac{dB}{dT} + \frac{3}{2}T^2\frac{d^2B}{dT^2} - T\frac{d\epsilon_1}{dT} - \frac{1}{2}T^2\frac{d^2\epsilon_1}{dT^2}\right\} \qquad (4\text{-}70)$$

4.2c Virial Expansion of P, η, and $\mathcal{H}$

Combining equations (4-32), (4-46), and (4-64), we have the usual virial expansion for the hydrostatic pressure

$$P = nKT\left\{1 + nB\right\} \qquad (4\text{-}71)$$

where B is defined by equation (3-21). Analogous virial expansions may be written for the coefficients of shear and bulk viscosity:

$$\eta \equiv \eta_0\left\{1 + nB_\eta + \dots\right\}$$

$$\mathcal{H} \equiv n^2 C_{\mathcal{H}} + \dots \qquad (4\text{-}72)$$

With the results of the preceding sections,

$$B_\eta = B - \frac{7}{6}T\frac{dB}{dT} - \frac{1}{3}T^2\frac{d^2B}{dT^2} - \frac{1}{2}Q_2 - \sigma_{12}$$

$$-\frac{1}{12}\epsilon_1 - \frac{1}{6}T\frac{d\epsilon_1}{dT} + \frac{1}{15}\epsilon_2 + \mathcal{R}_2 + \mathcal{L}(\mathcal{Y}_e) \tag{4-73}$$

and

$$C_\mathcal{H} = Q_1 + \sigma_{30} + \frac{1}{72}KT\left(\Omega^{(2,2)}\right)^{-1} \times$$

$$\times\left\{5T\frac{dB}{dT} + \frac{11}{2}T^2\frac{d^2B}{dT^2} + T^3\frac{d^3B}{dT^3}\right\}^2 \tag{4-74}$$

These expressions for B_η and $C_\mathcal{H}$ may now be compared with the results of Imam-Rahajoe[16]. In the case of B_η, the integral Q_2 and the second virial coefficient and its temperature derivatives occur identically in both treatments. The two expressions for B_η differ in regard to the σ_{12} integral by a factor of five, although this is not apparent due to slight differences in definitions adopted in the two treatments. This disagreement appears to have resulted from an incorrect normalization of the fourth order tensor $\{3(\underline{\underline{\underline{\underline{\mathbb{W}}}}} - \underline{\underline{\underline{\underline{\mathbb{W}}}}}) - 2\underline{\underline{U}}\,\underline{\underline{U}}\}$ in Imam-Rahajoe's evaluation of $\underline{\underline{P}}_{\mathrm{II}}$. Terms involving the $\mathcal{E}_i$ integrals do not agree because of the different forms for $\hat{\hat{f}}_{1e}$ used in the two treatments. As noted previously, this is ultimately related to the use of molecular chaos in Imam-Rahajoe's development. The three-body term $\mathcal{R}_2$ agrees with the corresponding quantity in the work of Imam-Rahajoe only if the approximation discussed in section 3.6a-iii is used. This also is a consequence of the different forms assumed for $\hat{\hat{f}}_{1e}$. The absence of the other three-body term, $\mathcal{L}(\mathcal{Y}_e)$, in the results of Imam-Rahajoe is directly attributable to his use of the molecular chaos assumption.

In the case of $C_{\mathcal{H}}$, aside from slight differences in definitions, the integrals Q_1 and σ_{30} appear identically in both treatments. The $\mathcal{E}_1$ and $\mathcal{E}_2$ integrals and several of their temperature derivatives occur in the results of Imam-Rahajoe, while both are absent entirely from our expression (4-74). This difference stems in part from the different forms assumed for $\hat{\hat{f}}_{1e}$ in the two developments and partly from a slight numerical error in Imam-Rahajoe's treatment. Correcting the numerical error and using the form (2-56) for $\hat{\hat{f}}_{1e}$ then leads to a fortuitous cancellation of the $\mathcal{E}_i$ integrals in $C_{\mathcal{H}}$. In general, there are no three-body contributions to $C_{\mathcal{H}}$.

CHAPTER V

THE RIGID SPHERE MODEL

The formal theory developed in the preceding chapters is applicable only to gases composed of molecules which interact through a purely repulsive potential. A mathematically convenient example of such an intermolecular potential is the rigid sphere:

$$\begin{aligned} \varphi(r) &= \infty \qquad r < \sigma \\ &= 0 \qquad r > \sigma \end{aligned} \tag{5-1}$$

Although the rigid sphere model is not physically realistic, its simplicity has led many authors to use it, particularly in classical treatments, as a testing ground for transport theories.

5.1 Quantum Two-body Contributions

In the preceding chapter, the transport coefficients were divided into kinetic contributions: λ_{I} , η_{I} , and $\mathcal{H}_{I}$, and potential or "collisional transfer" contributions: λ_{II} , λ_{III} , η_{II} , and $\mathcal{H}_{II}$. It is now convenient to divide the contributions to the first transport virial coefficients into two parts on a different basis. We let the first group consist of those terms which involve only two-body dynamics and the second group be terms which involve some three-body dynamics. Accordingly,

$$B_\lambda \equiv B_\lambda^{(2)} + B_\lambda^{(3)}$$

$$B_\eta \equiv B_\eta^{(2)} + B_\eta^{(3)} \tag{5-2}$$

$$C_{\mathcal{H}} \equiv C_{\mathcal{H}}^{(2)} + C_{\mathcal{H}}^{(3)}$$

where

$$B_\lambda^{(2)} = \frac{1}{3}\Big\{4B - T\frac{dB}{dT} - T^2\frac{d^2B}{dT^2} - Q_2 - 2\sigma_{12}$$

$$-\frac{17}{24}\epsilon_1 + \frac{21}{20}\epsilon_2 + \frac{1}{10}\epsilon_3 - \frac{1}{3}T\frac{d\epsilon_1}{dT}\Big\}$$

$$B_\lambda^{(3)} = \mathcal{R}_1 + \mathcal{K}(\mathcal{Y}_e)$$

$$B_\eta^{(2)} = B - \frac{7}{6}T\frac{dB}{dT} - \frac{1}{3}T^2\frac{d^2B}{dT^2} - \frac{1}{2}Q_2 - \sigma_{12} \tag{5-3}$$

$$-\frac{1}{12}\epsilon_1 - \frac{1}{6}T\frac{d\epsilon_1}{dT} + \frac{1}{15}\epsilon_2$$

$$B_{\eta}^{(3)} = \mathcal{R}_2 + \mathcal{L}(\mathcal{Y}_e)$$

$$C_{\mathcal{H}}^{(2)} = \frac{KT}{72}\left(\Omega^{(2,2)}\right)^{-1}\left\{5T\frac{dB}{dT} + \frac{11}{2}T^2\frac{d^2B}{dT^2} + T^3\frac{d^3B}{dT^3}\right\}^2$$

$$+ Q_1 + \sigma_{30}$$

$$C_{\mathcal{H}}^{(3)} = 0$$

For the special case of a quantum gas of rigid spheres, the expressions for $B_{\lambda}^{(2)}$, $B_{\eta}^{(2)}$, and $C_{\mathcal{H}}^{(2)}$ simplify considerably. Each of the six-fold integrals involved may be reduced to a single integral and a sum over the angular momentum quantum number.

The method of reduction is based upon the partial wave expression:

$$\psi(\underline{r};p_0) \equiv \frac{\hbar}{r p_0} \sum_{\ell} \alpha_{\ell}(p_0) P_{\ell}(\cos\phi) R_{\ell}(r;p_0) \qquad (5\text{-}4)$$

where

$$\alpha_\ell \equiv i^\ell (2\ell+1) e^{i\eta_\ell} \tag{5-5}$$

$$\cos\phi \equiv \hat{\underline{r}} \cdot \hat{\underline{p}}_0$$

The η_ℓ are the usual phase shifts and the R_ℓ are those solutions to the radial Schrodinger equation

$$\left\{ \frac{d^2}{dr^2} + \frac{1}{\hbar^2} p_0^2 - \frac{1}{r^2}\ell(\ell+1) - \frac{m\varphi}{\hbar^2} \right\} R_\ell = 0 \tag{5-6}$$

with the asymptotic form:

$$R_\ell \underset{r\to\infty}{\longrightarrow} \sin\left\{ \frac{r p_0}{\hbar} - \frac{\ell\pi}{2} + \eta_\ell \right\} \tag{5-7}$$

The wave function represented by equation (5-4) is then a solution to the relative motion Schrodinger equation (2-16) for any spherically symmetric potential and has the appropriate asymptotic form. Each of the seven two-body integrals is now considered individually for the special case of rigid spheres. In the following sections, a bar will be written over symbols to indicate that they refer to the rigid sphere quantities.

5.1a Evaluation of $\bar{\epsilon}_1$

By substituting the Schrodinger equation and rearranging, the definition (3-18) of ϵ_1 may be rewritten as

$$\epsilon_1 = -2T\frac{dB}{dT} - \frac{2^{3/2}}{KT}\left(\frac{\lambda}{h}\right)^3 \int d\underline{r}\, d\underline{p}_0\, \varphi\, \psi\, \psi^* e^{-p_0^2/mKT} \tag{5-8}$$

Performing the partial wave expansion and the trivial angle integrations, the second term in (5-8) becomes

$$-\frac{8\sqrt{2}\,h^2}{KT}\left(\frac{\lambda}{h}\right)^3 \sum_{\ell}(2\ell+1)\int_0^\infty dp_0\, e^{-p_0^2/mKT}\int_0^\infty dr\, \varphi\, R_\ell^2 \tag{5-9}$$

With the aid of lemma C-3, the r-integral in (5-9) may be shown to vanish for the rigid sphere potential. Then

$$\bar{\epsilon}_1 = -2T\frac{d\bar{B}}{dT} \tag{5-10}$$

where $\bar{B}$ refers to the quantum mechanical second virial coefficient for a gas of rigid spheres.

5.1b Evaluation of $\bar{\epsilon}_2$

With the relation

$$\int d\underline{r}\, \psi^* \left[\frac{\partial}{\partial \underline{r}} \cdot \frac{\partial}{\partial \underline{r}}, \mathcal{H}\right] \psi = 0 \tag{5-11}$$

and the Schrodinger equation, the definition (3-18) of ϵ_2 may be written as

$$\epsilon_2 = 4T\frac{dB}{dT} + 2T^2\frac{d^2B}{dT^2} + 5\epsilon_1 + 2T\frac{d\epsilon_1}{dT} + (KT)^{-2}\int d\underline{r}\, \varphi^2 g_0(\underline{r};\underline{r}) \tag{5-12}$$

Substituting the definition of $g_0(\underline{r};\underline{r})$, performing the partial wave expansion, and carrying out the angle integrations, the last term in (5-12) becomes

$$\frac{16}{m}\left(\frac{\pi KT}{m}\right)^{1/2}\int_0^\infty dp_0\, e^{-p_0^2/mKT}\sum_l (2l+1)\int_0^\infty dr\, \varphi^2 R_l^2 \qquad (5\text{-}13)$$

Again, for the rigid sphere potential, the r-integral vanishes by lemma C-3 and

$$\bar{\epsilon}_2 = -10T\frac{d\bar{B}}{dT} - 2T^2\frac{d^2\bar{B}}{dT^2} \qquad (5\text{-}14)$$

where the result of equation (5-10) has been used for $\bar{\epsilon}_1$

5.1c <u>Evaluation of $\bar{\epsilon}_3$</u>

By techniques entirely analogous to those used in the treatment of $\bar{\epsilon}_1$ and $\bar{\epsilon}_2$, although somewhat lengthier, it may be shown that

$$\bar{\epsilon}_3 = -\frac{105}{2} T \frac{d\bar{B}}{dT} - 21 T^2 \frac{d^2\bar{B}}{dT^2} - 2T^3 \frac{d^3\bar{B}}{dT^3}$$

$$+ (KT)^{-3} \int_{r.s.} d\underline{r}\, \varphi^3 g_0(\underline{r};\underline{r}) - (KT)^{-2} \left\{ \frac{9}{2} + 3T\frac{d}{dT} \right\} \int_{r.s.} d\underline{r}\, \varphi^2 g_0(\underline{r};\underline{r}) \tag{5-15}$$

$$+ 3(KT)^{-1} \left\{ \frac{15}{4} + 5T\frac{d}{dT} + T^2 \frac{d^2}{dT^2} \right\} \int_{r.s.} d\underline{r}\, \varphi\, g_0(\underline{r};\underline{r})$$

After substituting the definition of $g_0(\underline{r};\underline{r})$ and using the partial wave expansion, the r-integrals again vanish by lemma C-3 to give

$$\bar{\epsilon}_3 = -\frac{105}{2} T \frac{d\bar{B}}{dT} - 21 T^2 \frac{d^2\bar{B}}{dT^2} - 2T^3 \frac{d^3\bar{B}}{dT^3} \tag{5-16}$$

5.1d Evaluation of $\bar{Q}_1$

With the partial wave expansion, the trivial angle integrations may be carried out in the definition (4-55) of Q_1 to give

$$\bar{Q}_1 = -\frac{2}{9} m h^3 (\pi m K T)^{-5/2} \sum_\ell (2\ell+1) \times$$

$$\times \int_0^\infty dp_0\, p_0 \left(\frac{d\bar{\eta}_\ell}{dp_0}\right) e^{-p_0^2/mKT} \int_{\substack{0\\ \text{r.s.}}}^\infty dr\, \varphi R_\ell^2 \qquad (5\text{-}17)$$

Then, with lemma C-3,

$$\bar{Q}_1 = 0 \qquad (5\text{-}18)$$

5.1e Evaluation of $\overline{\sigma_{30}}$

Introduction of the partial wave expansion into the definition (4-69) of σ_{30} allows the angle integrations to be carried out with the result:

$$\overline{\sigma}_{30} = \frac{h^3}{9KT}(\pi m K T)^{-3/2} \sum_{\ell}(2\ell+1) \times$$

$$\times \int_0^\infty dp_0\, p_0 \left(\frac{d\bar{\eta}_\ell}{dp_0}\right) e^{-p_0^2/mKT} \int_{0 \atop r.s.}^\infty dr\, r\, R_\ell^2 \frac{d\varphi}{dr} \tag{5-19}$$

With the result of lemma C-1, this reduces to

$$\overline{\sigma}_{30} = \frac{8\sqrt{\pi}\,\hbar^4}{9}(mKT)^{-5/2} \sum_{\ell}(2\ell+1)\int_0^\infty dp_0\, p_0^3 \left(\frac{d\bar{\eta}_\ell}{dp_0}\right)^2 e^{-p_0^2/mKT} \tag{5-20}$$

for the case of the rigid sphere potential.

5.1f <u>Evaluation of $\overline{\sigma}_{12}$</u>

After substituting the partial wave expansion into the definition (4-17) of $\overline{\sigma}_{12}$, the angle integrations may be carried out to give

$$\sigma_{12} = \frac{16\sqrt{\pi}\,\hbar^2}{15\,KT}(mKT)^{-5/2}\int_0^\infty dp_0\, p_0^2\, e^{-p_0^2/mKT} \times$$

$$\times \sum_{\ell,j}\begin{pmatrix}\ell & j & 2\\ 0 & 0 & 0\end{pmatrix}^2 \alpha_\ell^* \alpha_j \int_0^\infty dr\, R_\ell R_j \frac{d\varphi}{dr} \tag{5-21}$$

where we have introduced the Wigner 3-j symbol:

$$\begin{pmatrix}\ell & j & K\\ 0 & 0 & 0\end{pmatrix} \equiv (-1)^P \sqrt{\Delta(\ell j K)}\ \frac{P!}{(P-\ell)!\,(P-j)!\,(P-K)!}$$

$$2P \equiv \ell + j + K \tag{5-22}$$

$$\Delta(\ell j K) \equiv \frac{(\ell+j-K)!\,(\ell+K-j)!\,(j+K-\ell)!}{(\ell+j+K+1)!}$$

The r-integration in (5-21) may be carried out with lemma C-1. After some rearrangement,

$$\bar{\sigma}_{12} = \frac{16\sqrt{\pi}\,\hbar^3}{15}(mkT)^{-\frac{7}{2}} \sum_{\ell}(2\ell+1)\int_0^\infty dp_0\, p_0^4\, e^{-p_0^2/mkT} \times$$

$$\times\left\{-2(2\ell+5)\begin{pmatrix}\ell & \ell+2 & 2\\ 0 & 0 & 0\end{pmatrix}^2\left(\frac{d\bar{\eta}_\ell}{dp_0}\cdot\frac{d\bar{\eta}_{\ell+2}}{dp_0}\right)^{1/2}\cos\left(\bar{\eta}_{\ell+2}-\bar{\eta}_\ell\right) + \right. \tag{5-23}$$

$$\left. + (2\ell+1)\begin{pmatrix}\ell & \ell & 2\\ 0 & 0 & 0\end{pmatrix}^2\left(\frac{d\bar{\eta}_\ell}{dp_0}\right)\right\}$$

where the triangle rule for the 3-j symbols has been used to reduce the double sum to a single sum.

5.1g <u>Evaluation of $\bar{Q}_2$</u>

By substituting the partial wave expansion into the definition (3-69) of Q_2, the trivial angle integrations may be performed. Then, using lemma C-4,

$$Q_2 = \frac{mh^4}{40}(\pi mkT)^{-\frac{7}{2}} \int_0^{\infty} dr \, \frac{1}{r}\frac{d\varphi}{dr} \int_0^{\infty} dp_0 \, e^{-p_0^2/mkT} \int_0^{\pi} d\phi \, \sin\phi \, \times$$

$$\times \sum_{\ell,j} \Big\{ 2\alpha_\ell \alpha_j^* R_\ell R_j P_\ell' P_j' \cos^3\phi + 2\left[P_\ell P_j' - P_\ell' P_j\right]\cos\phi \, \times$$

$$\times (\cos^2\phi - 1)\left[\alpha_j^*\left(\frac{d\alpha_\ell}{dp_0}\right)p_0 R_\ell R_j + \alpha_\ell \alpha_j^* p_0 R_j \frac{dR_\ell}{dp_0}\right] + \tag{5-24}$$

$$+ \alpha_\ell \alpha_j^* R_\ell R_j \left[P_j P_\ell'' - P_\ell' P_j'\right](1 - 2\cos^2\phi)(1 - \cos^2\phi)$$

$$+ \text{complex conjugates} \Big\}$$

where P_ℓ' and P_ℓ'' are the first and second derivatives of the $\ell^{\underline{th}}$ Legendre polynomial with respect to the argument. The ϕ integration can be carried out with the aid of lemmas D-1 and D-2 and the r-integrations with lemmas C-1 and C-2. The result is

$$\bar{Q}_2 = \frac{h^5}{10\pi\sigma^2}(\pi m K T)^{-\frac{7}{2}} \sum_{\ell}(\ell+1)(\ell+2)\int_0^\infty dp_0\, p_0^2\, e^{-p_0^2/mKT} \times$$

$$\times\left(\frac{d\bar{\eta}_\ell}{dp_0}\cdot\frac{d\bar{\eta}_{\ell+2}}{dp_0}\right)^{1/2}\left\{p_0\left[\frac{d\bar{\eta}_\ell}{dp_0}+\frac{d\bar{\eta}_{\ell+2}}{dp_0}\right]\sin\left(\bar{\eta}_{\ell+2}-\bar{\eta}_\ell\right) + \right.$$

$$+\left[\frac{d}{dp_0}\ln\left(\frac{d\bar{\eta}_{\ell+2}}{dp_0}\Big/\frac{d\bar{\eta}_\ell}{dp_0}\right)\right]p_0\cos\left(\bar{\eta}_{\ell+2}-\bar{\eta}_\ell\right) -$$

$$\left. -(2\ell+3)\cos\left(\bar{\eta}_{\ell+2}-\bar{\eta}_\ell\right)\right\} \tag{5-25}$$

This completes the analytic reduction of the two-body contributions: $\bar{B}_\lambda^{(2)}$, $\bar{B}_\eta^{(2)}$, and $C_{\mathcal{H}}^{(2)}$. The results may now be conveniently summarized in the form:

$$\bar{B}_\lambda^{(2)} = \frac{4}{3}\bar{B} + \frac{2}{3}\bar{Q}_3 - \frac{44}{9}T\frac{d\bar{B}}{dT} - \frac{68}{45}T^2\frac{d^2\bar{B}}{dT^2} - \frac{1}{15}T^3\frac{d^3\bar{B}}{dT^3}$$

$$\bar{B}_\eta^{(2)} = \bar{B} + \bar{Q}_3 - \frac{4}{3}T\frac{d\bar{B}}{dT} - \frac{2}{15}T^2\frac{d^2\bar{B}}{dT^2}$$

$$\bar{C}_{\mathcal{H}}^{(2)} = \frac{KT}{72}\left(\bar{\Omega}^{(2,2)}\right)^{-1}\left\{5T\frac{d\bar{B}}{dT} + \frac{11}{2}T^2\frac{d^2\bar{B}}{dT^2} + T^3\frac{d^3\bar{B}}{dT^3}\right\}^2$$

$$+\ \bar{\sigma}_{30} \tag{5-26}$$

where

$$\bar{Q}_3 \equiv -\overline{\sigma_{12}} - \frac{1}{2}\bar{Q}_2$$

$$\equiv \frac{8}{5}\sqrt{\pi}\,\sigma^{-3}\beta^{7}\sum_{\ell}(\ell+1)(\ell+2)\int_0^{\infty}dz\; z^2 e^{-\beta^2 z^2}\left(\dot{\eta}_\ell\,\dot{\eta}_{\ell+2}\right)^{1/2}\times$$

$$\times\left\{\left[2z^2(2\ell+3)^{-1}+(2\ell+3)-z\left(\frac{\ddot{\eta}_{\ell+2}}{\dot{\eta}_{\ell+2}}-\frac{\ddot{\eta}_\ell}{\dot{\eta}_\ell}\right)\right]\times\right.$$

$$\times\cos(\eta_{\ell+2}-\eta_\ell) - \left[\dot{\eta}_\ell+\dot{\eta}_{\ell+2}\right]z\sin(\eta_{\ell+2}-\eta_\ell) - \tag{5-27}$$

$$\left.-\frac{2}{3}\frac{(2\ell+3)}{(2\ell+1)(2\ell+5)}z^2\dot{\eta}_{\ell+1}\left(\dot{\eta}_\ell\,\dot{\eta}_{\ell+2}\right)^{-1/2}\right\}$$

$$\overline{\sigma_{30}} \equiv \frac{8}{9}\sqrt{\pi m k T}\,\sigma^{-4}\beta^{6}\sum_{\ell}(2\ell+1)\int_0^{\infty}dz\; z^3\left(\dot{\eta}_\ell\right)^2 e^{-\beta^2 z^2}$$

and we have introduced

$$\beta \equiv \frac{\hbar}{\sigma\sqrt{mKT}} \qquad z \equiv \frac{p_0\sigma}{\hbar} \tag{5-28}$$

$$\dot{\bar{\eta}}_\ell \equiv \frac{d\bar{\eta}_\ell}{dz}$$

For a quantum gas of rigid spheres, the problem of computing the two-body contribution to the first transport virial coefficients is then reduced to a numerical evaluation of $\bar{Q}_3$, $\overline{\sigma_{30}}$, and $\bar{B}$ and its first three temperature derivatives. Such a numerical treatment is considered in section 5.3.

5.2 Classical Two-body Contributions

The transport properties of a moderately dense classical gas of rigid spheres were first treated by Enskog[7]. By taking into consideration that the frequency of collisions in a gas of rigid spheres differs by a factor of y from that in a gas of point particles, Enskog obtained the results:

$$\lambda = \lambda_0 \left\{ \frac{1}{\mathcal{Y}} + \frac{4}{5}\pi n \sigma^3 + O(n^2) \right\}$$

$$\eta = \eta_0 \left\{ \frac{1}{\mathcal{Y}} + \frac{8}{15}\pi n \sigma^3 + O(n^2) \right\} \tag{5-29}$$

$$\mathcal{H} = \frac{4}{9} n^2 \sigma^4 \mathcal{Y} \sqrt{\pi m K T}$$

The factor $\mathcal{Y}$ introduces a "three-body" effect by correcting for the fact that, in a moderately dense gas, the molecules are close enough to shield one another from collisions with a third molecule. The quantity $\mathcal{Y}$ is density dependent, with a low density limit of unity. In a density expansion of the reciprocal of $\mathcal{Y}$, the term linear in the density corresponds classically to our "three-body" terms $\mathcal{K}(\mathcal{Y}_e)$ and $\mathcal{L}(\mathcal{Y}_e)$. Based on the results of Enskog, the appropriate classical rigid sphere limit for the "two-body" terms is then

$$\left(\bar{B}_{\lambda}^{(2)}\right)_{cl} = \frac{4}{5}\pi\sigma^{3}$$

$$\left(\bar{B}_{\eta}^{(2)}\right)_{cl} = \frac{8}{15}\pi\sigma^{3} \tag{5-30}$$

$$\left(\bar{C}_{\mathcal{H}}^{(2)}\right)_{cl} = \frac{4}{9}\sigma^{4}\sqrt{\pi m K T}$$

To compare the classical limits of equations (5-26) with the results of Enskog, it is first necessary to obtain classical expressions for the quantities $\bar{B}$, $\bar{Q}_3$, and $\bar{\sigma}_{30}$. The second virial coefficient for a classical gas of rigid spheres is well-known and is given by

$$\bar{B}_{cl} = \frac{2}{3}\pi\sigma^{3} \tag{5-31}$$

The classical limits of $\bar{Q}_3$ and $\bar{\sigma}_{30}$ may be obtained in the usual way; namely, by employing the Euler-MacLaurin approximation to convert the sum over ℓ to an integration over the impact parameter b:

$$\sum_{\ell} \longrightarrow \frac{z}{\sigma}\int db \qquad \ell \longrightarrow \frac{bz}{\sigma} \tag{5-32}$$

To zero order in $\hbar$, it may be shown from the results of Mueller[25] that

$$\dot{\bar{\eta}}_{\ell} \longrightarrow -\left(1-\frac{b^2}{\sigma^2}\right)^{1/2}$$

$$\cos\left(\bar{\eta}_{\ell+2}-\bar{\eta}_{\ell}\right) \longrightarrow 2\frac{b^2}{\sigma^2}-1$$

$$\sin\left(\bar{\eta}_{\ell+2}-\bar{\eta}_{\ell}\right) \longrightarrow 2\frac{b}{\sigma}\left(1-\frac{b^2}{\sigma^2}\right)^{1/2} \tag{5-33}$$

$$\left\{\frac{\ddot{\bar{\eta}}_{\ell+2}}{\dot{\bar{\eta}}_{\ell+2}}-\frac{\ddot{\bar{\eta}}_{\ell}}{\dot{\bar{\eta}}_{\ell}}\right\} \longrightarrow 0$$

Using (5-32) and (5-33) and introducing the dimensionless variables

$$\omega \equiv \beta z \qquad x \equiv \frac{b}{\sigma} \tag{5-34}$$

the classical limit of $\bar{Q}_3$ becomes

$$\bar{Q}_3^{cl} = \frac{32\sqrt{\pi}}{15}\,\sigma^{3}\left\{\int_0^\infty d\omega\,\omega^6 e^{-\omega^2}\right\}\int_0^1 dx\,(x-3x^3)(1-x^2)^{1/2}$$

$$= -\frac{2}{15}\,\pi\sigma^3 \tag{5-35}$$

Similarly,

$$\bar{\sigma}_{30}^{cl} = \frac{16}{9}\sqrt{\pi m k T}\,\sigma^{4}\left\{\int_0^\infty d\omega\,\omega^5 e^{-\omega^2}\right\}\int_0^1 dx\,(x-x^3)$$

$$= \frac{4}{9}\sqrt{\pi m k T}\,\sigma^4 \tag{5-36}$$

Substitution of equations (5-31), (5-35), and (5-36) into our expressions (5-26) for the two-body contributions to the first transport virial coefficients then gives agreement with the classical results of Enskog.

5.3 Numerical Treatment

It is desirable, in the course of a numerical treatment of the results of the preceding section, to compare numerical results with those of Herman[18] who, using a correlation function method, computed the potential contributions to $B_\lambda^{(2)}$ and $B_\eta^{(2)}$ for a gas of hard sphere bosons. The expressions arrived at by Herman for these potential contributions are in error by a factor of two in the case of both $\bar{\bar{B}}_\lambda^{(2)}$ and $\bar{\bar{B}}_\eta^{(2)}$. This becomes evident upon a more careful comparison of his classical limits with the earlier classical results of Enskog and taking into account the fact that, in the classical case, precisely half of both $\bar{\bar{B}}_\lambda^{(2)}$ and $\bar{\bar{B}}_\eta^{(2)}$ is of a potential origin. This error, however, does not seriously affect a comparison of the quantum corrections to these terms. In this section, we shall first consider the full $\bar{\bar{B}}_\lambda^{(2)}$ and $\bar{\bar{B}}_\eta^{(2)}$, then compute their potential portions, $\bar{\bar{B}}_{\lambda;\varphi}^{(2)}$ and $\bar{\bar{B}}_{\eta;\varphi}^{(2)}$, and finally compare the latter results with those of Herman.

Throughout the preceding development, Maxwell-Boltzmann statistics have been consistently assumed. To render a comparison with the results of Herman feasible, it is first necessary to construct analogues to our expressions which are valid for Bose-Einstein statistics. In the following, we shall consider only spinless particles. For a gas of particles of non-zero spin, it would be necessary to introduce the usual mixing of states.

The correct procedure here may be seen from the partial wave expansion (5-4) which formed the basis of the development of the expressions (5-27) for $\bar{Q}_3$ and $\overline{\sigma_{30}}$. For Bose-Einstein statistics, the proper method is to multiply the wave function by $\sqrt{2}$ and allow the sum to range only over all even integers and zero. Similarly, for Fermi-Dirac statistics, the wave functions must again be multiplied by $\sqrt{2}$, but only odd integer values of ℓ are included in the sum.

It follows, therefore, that for a gas of bosons, the expressions for $\bar{Q}_3$ and $\overline{\sigma_{30}}$ must be multiplied by a factor of two and only even integers and zero retained in the sums over the angular momentum quantum number. Likewise, for a gas of fermions, the results for $\bar{Q}_3$ and $\overline{\sigma_{30}}$ must be multiplied by a factor of two, but only odd integer values of ℓ are to be kept in the sums.

For numerical purposes, it is also convenient to make all quantities in (5-26) and (5-27) dimensionless by dividing by their respective classical limits. Then

$$\bar{B}_\lambda^{(2)*} = \frac{1}{9}\left\{10\bar{B}^* - \frac{110}{3}T\frac{d\bar{B}^*}{dT} - \frac{34}{3}T^2\frac{d^2\bar{B}^*}{dT^2} - \frac{1}{2}T^3\frac{d^3\bar{B}^*}{dT^3} - \bar{Q}_3^*\right\}$$

$$\bar{B}_\eta^{(2)*} = \frac{5}{4}\bar{B}^* - \frac{1}{4}\bar{Q}_3^* - \frac{5}{3}T\frac{d\bar{B}^*}{dT} - \frac{1}{6}T^2\frac{d^2\bar{B}^*}{dT^2}$$

$$\bar{C}_{\mathcal{H}}^{(2)*} = \frac{\pi}{4}\left(\overline{\Omega}^{(2,2)*}\right)^{-1}\left\{5T\frac{d\bar{B}^*}{dT} + \frac{11}{2}T^2\frac{d^2\bar{B}^*}{dT^2} + T^3\frac{d^3\bar{B}^*}{dT^3}\right\}^2 \qquad (5\text{-}37)$$

$$+ \overline{\sigma_{30}}^*$$

where

$$\bar{B}^{*}_{\substack{B.E.\\F.D.}} = \mp \frac{3}{4}\sqrt{\pi}\,\beta^{3} - \frac{12}{\sqrt{\pi}} \sum_{\substack{\ell\\ \text{even}\\ \text{odd}}} (2\ell+1) \int_{0}^{\infty} dz\, \dot{\bar{\eta}}_{\ell}\, e^{-\beta^{2} z^{2}}$$

$$\bar{\sigma}^{*}_{30;\substack{B.E.\\F.D.}} = 4 \sum_{\substack{\ell\\ \text{even}\\ \text{odd}}} (2\ell+1) \int_{0}^{\infty} dz\, z^{3} \left(\dot{\bar{\eta}}_{\ell}\right)^{2} e^{-\beta^{2} z^{2}}$$

$$\bar{Q}^{*}_{3;\substack{B.E.\\F.D.}} = -\frac{24}{\sqrt{\pi}}\beta^{7} \sum_{\substack{\ell\\ \text{even}\\ \text{odd}}} (\ell+1)(\ell+2) \int_{0}^{\infty} dz\, z^{2}\, e^{-\beta^{2} z^{2}} \times \tag{5-38}$$

$$\times \left(\dot{\bar{\eta}}_{\ell}\,\dot{\bar{\eta}}_{\ell+2}\right)^{1/2} \Bigg\{ -\left[\dot{\bar{\eta}}_{\ell} + \dot{\bar{\eta}}_{\ell+2}\right] z \sin\left(\bar{\eta}_{\ell+2} - \bar{\eta}_{\ell}\right) -$$

$$- \frac{2}{3} z^{2}\, \dot{\bar{\eta}}_{\ell+1} \left(\dot{\bar{\eta}}_{\ell}\,\dot{\bar{\eta}}_{\ell+2}\right)^{-1/2} \left[\frac{(2\ell+3)}{(2\ell+1)(2\ell+5)}\right] +$$

$$+ \left[2z^{2}(2\ell+3)^{-1} + (2\ell+3) - z\left(\frac{\ddot{\bar{\eta}}_{\ell+2}}{\dot{\bar{\eta}}_{\ell+2}} - \frac{\ddot{\bar{\eta}}_{\ell}}{\dot{\bar{\eta}}_{\ell}}\right)\right] \cos\left(\bar{\eta}_{\ell+2} - \bar{\eta}_{\ell}\right) \Bigg\}$$

It is clear from the preceding chapter that $\bar{B}^{(2)}_{\lambda;\varphi}$ contains only terms arising from λ_{II} and λ_{III}; similarly, $\bar{B}^{(2)}_{\eta;\varphi}$ involves only those from η_{II}. Then, with the results of the last chapter, it is a simple matter to show that

$$\bar{B}^{(2)*}_{\lambda;\varphi} = \frac{5}{9}\bar{B}^{*} + \frac{35}{27}T\frac{d\bar{B}^{*}}{dT} + \frac{10}{27}T^{2}\frac{d^{2}\bar{B}^{*}}{dT^{2}} + \frac{4}{9}\bar{\sigma}_{12}^{*}$$

(5-39)

$$\bar{B}^{(2)*}_{\eta;\varphi} = \bar{\sigma}_{12}^{*}$$

where

$$\bar{B}^{(2)*}_{\lambda;\varphi} \equiv \frac{\bar{B}^{(2)}_{\lambda;\varphi}}{\left(\bar{B}^{(2)}_{\lambda;\varphi}\right)^{cl}} = \frac{\bar{B}^{(2)}_{\lambda;\varphi}}{\frac{2}{5}\pi\sigma^{3}}$$

$$\bar{B}^{(2)*}_{\eta;\varphi} \equiv \frac{\bar{B}^{(2)}_{\eta;\varphi}}{\left(\bar{B}^{(2)}_{\eta;\varphi}\right)^{cl}} = \frac{\bar{B}^{(2)}_{\eta;\varphi}}{\frac{4}{15}\pi\sigma^{3}}$$

$$\bar{\sigma}^{(2)}_{12;\,\substack{B.E.\\F.D.}} \equiv -\frac{8}{\sqrt{\pi}}\beta^{7}\sum_{\substack{\ell\\ \text{even}\\ \text{odd}}}\int_{0}^{\infty}dz\, z^{4}e^{-\beta^{2}z^{2}} \times \qquad \text{(5-40)}$$

$$\times\left\{-2(2\ell+1)(2\ell+5)\begin{pmatrix}\ell & \ell+2 & 2\\ 0 & 0 & 0\end{pmatrix}^{2}\left(\dot{\bar{\eta}}_{\ell}\dot{\bar{\eta}}_{\ell+2}\right)^{1/2}\cos\left(\bar{\eta}_{\ell+2}-\bar{\eta}_{\ell}\right) + \right.$$

$$\left. + (2\ell+1)^{2}\begin{pmatrix}\ell & \ell & 2\\ 0 & 0 & 0\end{pmatrix}^{2}\dot{\bar{\eta}}_{\ell}\right\}$$

The analytic form of the rigid sphere phase shifts is well-known and may be written simply in terms of Bessel functions of order half an odd integer:

$$\tan \bar{\eta}_\ell = (-1)^{\ell+1} \frac{J_{\ell+1/2}(z)}{J_{-\ell-1/2}(z)} \tag{5-41}$$

With this, the evaluation of $\bar{B}_\lambda^{(2)*}$, $\bar{B}_\eta^{(2)*}$, $\bar{C}_\mathcal{H}^{(2)*}$, $\bar{B}_{\lambda;\varphi}^{(2)*}$, and $\bar{B}_{\eta;\varphi}^{(2)*}$ then involves only straightforward numerical integrations of the quantities: $\bar{\Omega}^{(2,2)*}$, $\bar{Q}_3^*$, $\bar{\sigma}_{30}^*$, $\bar{\sigma}_{12}^*$, and $\bar{B}^*$ and its first three temperature derivatives.

In this study, calculations were made with the aid of a Univac 1108 computer, using Simpson's rule for the numerical integrations. The results, over a range of β values, for $\bar{B}^*$, $\bar{B}_\lambda^{(2)*}$, $\bar{B}_\eta^{(2)*}$, and $\bar{C}_\mathcal{H}^{(2)*}$ are given in Tables I, II, III, and IV, respectively. Tables V and VI consist of $\bar{B}_{\lambda;\varphi;B.E.}^{(2)*}$ and $\bar{B}_{\eta;\varphi;B.E.}^{(2)*}$ compared with the corresponding quantities, Λ and η_2, of Herman. Figure 1 compares $\bar{B}^*$, $\bar{B}_\lambda^{(2)*}$, and $\bar{B}_\eta^{(2)*}$ for the case of Boltzmann statistics. Separate data listings for $\bar{Q}_3^*$, $\bar{\sigma}_{30}^*$, $\bar{\Omega}^{(2,2)*}$, and the first three temperature derivatives of $\bar{B}^*$ are included in Appendix F. The results are conservatively estimated to be accurate to the number of significant figures presented.

TABLE I

β	$\bar{B}^*_{BOLTZ.}$	$\bar{B}^*_{B.E.}$	$\bar{B}^*_{F.D.}$
7.00	+ 151.394	− 161.913	+ 464.701
6.00	+ 112.359	− 71.0697	+ 295.787
5.00	+ 79.3026	− 16.0709	+ 174.676
4.00	+ 52.2074	+ 11.0703	+ 93.3445
3.00	+ 31.0313	+ 18.3603	+ 43.7023
2.00	+ 15.6684	+ 13.8692	+ 17.4675
1.00	+ 5.84976	+ 5.83900	+ 5.86053
0.90	+ 5.15397	+ 5.15059	+ 5.15735
0.80	+ 4.50743	+ 4.50667	+ 4.50819
0.70	+ 3.90932	+ 3.90922	+ 3.90943
0.60	+ 3.35879	+ 3.35879	+ 3.35880
0.50	+ 2.85493	+ 2.85492	+ 2.85493
0.40	+ 2.39677	+ 2.39677	+ 2.39677
0.30	+ 1.98329	+ 1.98329	+ 1.98329
0.20	+ 1.61344	+ 1.61344	+ 1.61344
0.10	+ 1.28610	+ 1.28610	+ 1.28610
0.08	+ 1.22559	+ 1.22559	+ 1.22559
0.06	+ 1.16675	+ 1.16675	+ 1.16675
0.05	+ 1.13798	+ 1.13798	+ 1.13798
0.04	+ 1.10954	+ 1.10954	+ 1.10954
0.02	+ 1.05390	+ 1.05390	+ 1.05390

TABLE II

β	$\bar{B}^{(2)*}_{\lambda;\,\text{Boltz.}}$	$\bar{B}^{(2)*}_{\lambda;\,\text{B.E.}}$	$\bar{B}^{(2)*}_{\lambda;\,\text{F.D.}}$
7.00	+ 332.988	− 810.211	+ 1476.19
6.00	+ 246.316	− 438.633	+ 931.265
5.00	+ 173.022	− 194.951	+ 540.996
4.00	+ 113.013	− 53.6704	+ 279.696
3.00	+ 66.2392	+ 10.7589	+ 121.720
2.00	+ 32.4509	+ 23.5854	+ 41.3163
1.00	+ 11.1677	+ 11.2161	+ 11.1193
0.90	+ 9.68791	+ 9.78497	+ 9.59085
0.80	+ 8.30942	+ 8.42122	+ 8.19762
0.70	+ 7.02633	+ 7.12137	+ 6.93129
0.60	+ 5.83584	+ 5.88510	+ 5.78659
0.50	+ 4.74033	+ 4.74390	+ 4.73677
0.40	+ 3.74816	+ 3.74318	+ 3.75315
0.30	+ 2.87201	+ 2.87186	+ 2.87216
0.20	+ 2.12379	+ 2.12380	+ 2.12379
0.10	+ 1.50593	+ 1.50593	+ 1.50593
0.08	+ 1.39677	+ 1.39677	+ 1.39677
0.06	+ 1.29298	+ 1.29298	+ 1.29298
0.05	+ 1.24119	+ 1.24119	+ 1.24119
0.04	+ 1.19126	+ 1.19126	+ 1.19126
0.02	+ 1.09613	+ 1.09613	+ 1.09613

TABLE III

β	$\bar{B}^{(2)*}_{\eta;\,Boltz.}$	$\bar{B}^{(2)*}_{\eta;\,B.E.}$	$\bar{B}^{(2)*}_{\eta;\,F.D.}$
7.00	+ 130.507	− 1159.70	+ 1420.71
6.00	+ 97.8804	− 697.485	+ 893.245
5.00	+ 70.1766	− 375.042	+ 515.394
4.00	+ 47.3243	− 167.658	+ 262.305
3.00	+ 29.1639	− 50.9042	+ 109.232
2.00	+ 15.3953	− 1.03124	+ 31.8217
1.00	+ 6.13430	+ 6.08301	+ 6.18559
0.90	+ 5.46090	+ 5.60569	+ 5.31610
0.80	+ 4.80887	+ 5.03620	+ 4.58153
0.70	+ 4.16865	+ 4.37774	+ 3.95955
0.60	+ 3.53769	+ 3.64812	+ 3.42726
0.50	+ 2.92532	+ 2.93335	+ 2.91730
0.40	+ 2.35465	+ 2.34343	+ 2.36586
0.30	+ 1.85849	+ 1.85816	+ 1.85882
0.20	+ 1.46825	+ 1.46825	+ 1.46825
0.10	+ 1.19414	+ 1.19414	+ 1.19414
0.08	+ 1.15103	+ 1.15103	+ 1.15103
0.06	+ 1.11080	+ 1.11080	+ 1.11080
0.05	+ 1.09164	+ 1.09164	+ 1.09164
0.04	+ 1.07303	+ 1.07303	+ 1.07303
0.02	+ 1.04119	+ 1.04119	+ 1.04119

TABLE IV

β	$\bar{C}^{(2)*}_{\mathcal{H};\mathrm{Boltz.}}$	$\bar{C}^{(2)*}_{\mathcal{H};\mathrm{B.E.}}$	$\bar{C}^{(2)*}_{\mathcal{H};\mathrm{F.D.}}$
7.00	+ 50.4717	+ 98.0002	+ 2.9432
6.00	+ 37.5013	+ 72.0006	+ 3.0019
5.00	+ 26.4817	+ 50.0013	+ 2.9621
4.00	+ 17.4893	+ 32.0039	+ 2.9746
3.00	+ 10.5091	+ 18.0153	+ 3.0028
2.00	+ 5.55036	+ 8.08795	+ 3.01276
1.00	+ 2.51114	+ 2.62999	+ 2.39228
0.90	+ 2.30060	+ 2.35902	+ 2.24217
0.80	+ 2.10411	+ 2.12836	+ 2.07986
0.70	+ 1.92051	+ 1.92886	+ 1.91215
0.60	+ 1.74905	+ 1.75152	+ 1.74658
0.50	+ 1.58945	+ 1.59012	+ 1.58878
0.40	+ 1.44174	+ 1.44189	+ 1.44158
0.30	+ 1.30620	+ 1.30623	+ 1.30617
0.20	+ 1.18380	+ 1.18380	+ 1.18379
0.10	+ 1.07715	+ 1.07715	+ 1.07715
0.08	+ 1.05830	+ 1.05830	+ 1.05830
0.06	+ 1.04058	+ 1.04058	+ 1.04058
0.05	+ 1.03222	+ 1.03222	+ 1.03222
0.04	+ 1.02425	+ 1.02425	+ 1.02425
0.02	+ 1.00995	+ 1.00995	+ 1.00995

TABLE V

β	$\bar{B}^{(2)*}_{\lambda;\varphi;B.E.}$	Λ
0.60	1.21630	1.2163
0.50	1.17580	1.1758
0.40	1.13196	1.1320
0.30	1.08869	1.0887
0.20	1.04833	1.0483
0.10	1.01425	1.014 ‡
0.08	1.00882	1.0088
0.06	1.00418	1.0042
0.05	1.00223	1.0023
0.04	1.00061	1.0006
0.02	0.99864	0.99868

‡ Interpolated

TABLE VI

β	$\bar{B}^{(2)*}_{\eta;\psi;B.E.}$	η_2
0.60	0.82375	0.82375
0.50	0.84240	0.84240
0.40	0.85410	0.85410
0.30	0.86732	0.86732
0.20	0.88723	0.88723
0.10	0.92129	0.9213‡
0.08	0.93126	0.93126
0.06	0.94296	0.94298
0.05	0.94965	0.94968
0.04	0.95706	0.95710
0.02	0.97480	0.97486

‡ Interpolated

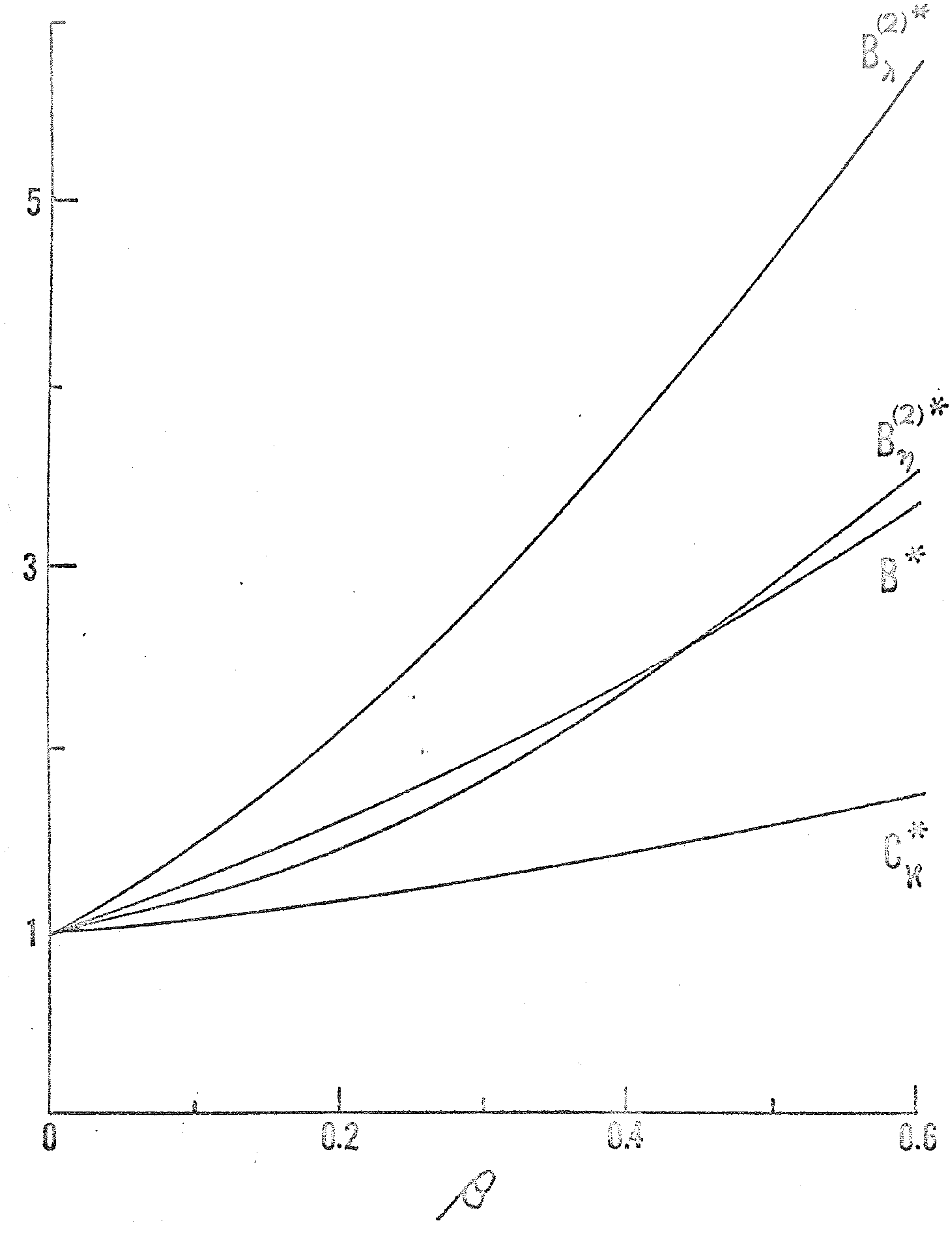

Figure 1. Calculated values of the four functions of $\beta = \frac{\hbar}{\sigma\sqrt{mkT}}$ for the rigid sphere potential.

Several convenient checks on the numerical methods are readily available. First, as β tends toward zero, all starred quantities must approach unity as a limit. For large values of β, computations may be compared with series expressions which follow directly from the definitions (5-37) and (5-38) and a consideration of the asymptotic behavior of Bessel functions. Some examples of such asymptotic series are those for the reduced rigid sphere second virial coefficient:

$$\bar{B}^*_{\text{Boltz.}} \sim \frac{9}{2} + 3\beta^2 - \frac{11}{2}\beta^{-2} + \frac{1921}{120}\beta^{-4} + \ldots$$

$$\bar{B}^*_{\text{B.E.}} \sim -\frac{3\sqrt{\pi}}{4}\beta^3 + 6\beta^2 + \frac{5}{2}\beta^{-2} - \frac{25}{12}\beta^{-4} + \ldots \qquad (5\text{-}42)$$

$$\bar{B}^*_{\text{F.D.}} \sim +\frac{3\sqrt{\pi}}{4}\beta^3 + 9 - \frac{27}{2}\beta^{-2} + \frac{341}{10}\beta^{-4} - \frac{11{,}837}{100}\beta^{-6} + \ldots$$

It may be noted that the expressions (5-42) differ from the low temperature series given in Hirschfelder, Curtiss, and Bird[4], which appear to be in error.

5.4 Classical Three-body Contributions

The three-body contributions to the first transport virial coefficients of a classical gas have been obtained in approximate form by Hoffman[14]. These expressions reduce to particularly simple forms for a gas of rigid spheres. No such simple reduction appears possible in the full quantum case, however. Moreover, for the rigid sphere potential, a semi-classical treatment would be invalid for reasons discussed in Appendix E. Consequently, in this section, we develop only the classical expressions for $B_\lambda^{(3)}$ and $B_\eta^{(3)}$ and compare the results with those of Hoffman.

From equation (E-14) and the definitions of $\mathcal{R}_1$ and $\mathcal{R}_2$, it follows trivially that

$$\mathcal{R}_1^{cl} = \mathcal{R}_2^{cl} = 0 \tag{5-43}$$

To develop the classical limits of $\mathcal{K}(\mathcal{Y}_e)$ and $\mathcal{L}(\mathcal{Y}_e)$, it is convenient to first rewrite their definitions (3-88) and (3-103) back in terms of the θ_2 operator:

$$\mathcal{K}(\mathcal{Y}_e) \equiv (15mK^2T^2)^{-1} \int d\underline{r}\, d\underline{p}_o\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2) \left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\}^2 \times$$

$$\times \left\{\underline{A}_o(\tilde{\underline{p}}_1) + \underline{A}_o(\tilde{\underline{p}}_2)\right\} \cdot \left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\} \Theta_2\, \mathcal{Y}_e\, F$$

(5-44)

$$\mathcal{L}(\mathcal{Y}_e) \equiv (10mKT)^{-1} \int d\underline{r}\, d\underline{p}_o\, d\underline{p}\, d\underline{P}\, \hat{f}_{1e}(\tilde{\underline{p}}_1)\, \hat{f}_{1e}(\tilde{\underline{p}}_2)\, \mathring{\underline{p}\underline{p}} :$$

$$: \left\{\underline{\underline{B}}_o(\tilde{\underline{p}}_1) + \underline{\underline{B}}_o(\tilde{\underline{p}}_2)\right\} \Theta_2\, \mathcal{Y}_e\, F$$

As discussed in Appendix E, $\mathcal{Y}_e$ is not a function of momentum in the classical case. Consequently,

$$\left\{\Theta_2 \mathcal{Y}_e F\right\}^{cl} = \mathcal{Y}_e^{cl} \left\{\Theta_2 F\right\}^{cl} \equiv y_{[o]} \left\{\Theta_2 F\right\}^{cl} \qquad (5\text{-}45)$$

where $y_{[o]}$, the classical limit of $\mathcal{Y}_e$ in Hoffman's notation, is discussed in Appendix E and defined by equation (E-19).

Since $F(\underline{r};\underline{p},\underline{p}_o)$ satisfies the two-particle Wigner equation, it must satisfy it independently for all orders of $\hbar$. Therefore,

$$\{\theta_2 F\}^{cl} = \frac{2}{m}\left\{\underline{p}\cdot\frac{\partial}{\partial\underline{r}}F\right\}^{cl} \tag{5-46}$$

Substituting equations (5-45) and (5-46) into (5-44) and integrating by parts on $\underline{r}$ then produces the following expressions for the classical limits of $\mathcal{K}(\mathcal{Y}_e)$ and $\mathcal{L}(\mathcal{Y}_e)$:

$$\mathcal{K}^{cl}(\mathcal{Y}_e) = -\frac{2}{15}(mKT)^{-2}\int d\underline{r}\,d\underline{p}_o\,d\underline{p}\,d\underline{P}\,\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\}^2 \times$$

$$\times F^{cl}\left\{\underline{A}_o(\tilde{\underline{p}}_1)+\underline{A}_o(\tilde{\underline{p}}_2)\right\}\cdot\left\{\tfrac{1}{2}\underline{P}-\underline{p}\right\}\left\{\underline{p}\cdot\frac{\partial}{\partial\underline{r}}\,y_{[0]}\right\}$$

$$\mathcal{L}^{cl}(\mathcal{Y}_e) = -(5m^2KT)^{-1}\int d\underline{r}\,d\underline{p}_o\,d\underline{p}\,d\underline{P}\,\hat{f}_{1e}(\tilde{\underline{p}}_1)\hat{f}_{1e}(\tilde{\underline{p}}_2)\,F^{cl}\times \tag{5-47}$$

$$\times\,\overset{\circ}{\underline{p}\underline{p}}:\left\{\underline{\underline{B}}_o(\tilde{\underline{p}}_1)+\underline{\underline{B}}_o(\tilde{\underline{p}}_2)\right\}\left\{\underline{p}\cdot\frac{\partial}{\partial\underline{r}}\,y_{[0]}\right\}$$

Using the results of equations (3-8) for $\underline{A}_o$ and $\underline{B}_o$, the $\underline{P}$ integration may be carried out. After removing terms from the integrand which are odd in $\underline{p}$ with the symmetry relations (3-22),

$$\mathcal{K}^{cl}(y_e) = \mathcal{L}^{cl}(y_e) = -\frac{(mKT)^{3/2}}{8\pi^2\sigma^2}\left(\Omega^{(2,2)*}\right)^{-1} \times$$

$$\times \int d\underline{r}\, d\underline{\gamma}_o\, d\underline{\gamma}\; e^{-\gamma_o^2}\, F^{cl}(\underline{\gamma}\cdot\underline{\gamma}_o)^2 \left\{\underline{\gamma}\cdot\frac{\partial}{\partial\underline{r}}\, y_{[o]}\right\} \tag{5-48}$$

where we have introduced the dimensionless variables

$$\underline{\gamma} \equiv \frac{\underline{p}}{\sqrt{mKT}} \qquad \underline{\gamma}_o \equiv \frac{\underline{p}_o}{\sqrt{mKT}} \tag{5-49}$$

and $\Omega^{(2,2)*}$ is the reduced form of the usual classical $\Omega^{(2,2)}$ integral:

$$\Omega^{(2,2)*} \equiv \frac{\Omega^{(2,2)}}{\left(\Omega^{(2,2)}\right)^{cl}} = \left(\frac{\pi m}{KT}\right)^{1/2} \frac{\Omega^{(2,2)}}{2\pi\sigma^2} \tag{5-50}$$

It follows from the fact that F is a distribution function defined on the relative motion space of two particles that the classical limit of F must simply be a delta function on a classical trajectory:

$$F^{cl} = (mKT)^{-3/2}\,\delta(\underline{\gamma}_0 - \underline{\gamma}') \tag{5-51}$$

where

$$(\gamma')^2 \equiv \gamma^2 + \varphi/KT \tag{5-52}$$

With this result, the $\underline{\gamma}_0$ integration in (5-48) may be performed trivially to yield, in Hoffman's notation,

$$\mathcal{K}^{cl}(\mathcal{Y}_e) = \mathcal{L}^{cl}(\mathcal{Y}_e) = -\frac{1}{8\pi^2}\left(\Omega^{(2,2)*}\right)^{-1} R \tag{5-53}$$

where

$$R \equiv \frac{1}{\sigma^2}\int d\underline{r}\, d\underline{\gamma}\, e^{-\gamma'^2} (\underline{\gamma}\cdot\underline{\gamma}')^2\, \underline{\gamma}\cdot\frac{\partial}{\partial \underline{r}}\, y_{[0]} \tag{5-54}$$

Combining equations (5-3), (5-43), and (5-53), we have finally

$$\left(B_\lambda^{(3)}\right)^{cl} = \left(B_\eta^{(3)}\right)^{cl} = -\frac{1}{8\pi^2}\left(\Omega^{(2,2)*}\right)^{-1} R \tag{5-55}$$

Hoffman has shown that, for a classical gas of rigid spheres, the integral R reduces to

$$\bar{R} = 8\pi^2\left(\frac{\bar{C}}{\bar{B}}\right)^{cl} \tag{5-56}$$

where C is the third virial coefficient. Then,

$$\left(\bar{B}_\lambda^{(3)}\right)^{cl} = \left(\bar{B}_\eta^{(3)}\right)^{cl} = -\left(\frac{\bar{C}}{\bar{B}}\right)^{cl} \tag{5-57}$$

Both equations (5-55) and (5-57) agree with the results which Hoffman obtained by a purely classical argument.

5.5 Discussion

The formalism developed in the preceding chapters has been shown to produce the accepted low density limits of the thermal conductivity and the shear viscosity, in both the full quantum and classical cases. The two-body contributions to the first transport virial coefficients were found in section 5.2 to agree with the results of Enskog for the case of a classical gas of rigid spheres. As a test of our expressions for the three-body contributions, $B_\lambda^{(3)}$ and $B_\eta^{(3)}$ were computed for a classical gas interacting through an arbitrary repulsive potential and for the particular case of the rigid sphere. Agreement with the previous results of Hoffman was found in each case. There is no three-body contribution to $C_\mathcal{H}$ for either a classical or a quantum gas.

The quantum two-body contributions to the first transport virial coefficients were computed for the rigid sphere potential. It may be seen from Tables V and VI that our results for the potential portions of these quantities agree very closely with those produced by the correlation function approach used by Herman. Such excellent numerical agreement immediately suggests an underlying analytic agreement. However, this seems not to be the case. The two treatments produce results which differ in the strong quantum region,* but are nearly identical in the region $\beta < 1$ which was considered by Herman and compared in the present study. This situation is not wholly unexpected since the two approaches are radically different and, understandably, involved slightly different mathematical techniques and approximations. In view of this, and ignoring the factor of two problems in Herman's work, the extent of the agreement is quite surprising.

The correlation function method does not yet seem to have produced expresssions for the full $B_{\lambda}^{(2)}$ and $B_{\eta}^{(2)}$, including kinetic contributions. Such a study would permit a further, and much more interesting, comparison. The reason for this is that, as may be seen from Chapter IV, our development of formal expressions for $B_{\lambda;\varphi}^{(2)}$ and $B_{\eta;\varphi}^{(2)}$ required only the solution to the lowest order Boltzmann equation. Therefore, the agreement of these results with

. . . .

* In the strong quantum region ($\beta \gg 1$):

$$\eta_2 \sim -5 - \frac{5}{3}\beta^{-2} + \ldots$$

$$\bar{B}^{(2)*}_{\eta;\varphi;\mathrm{B.E.}} \sim -5 + \frac{95}{6}\beta^{-2} + \ldots$$

$$\Lambda \sim -\frac{20}{9} + \frac{35}{9}\beta^{-2} + \ldots$$

$$\bar{B}^{(2)*}_{\lambda;\varphi;\mathrm{B.E.}} \sim -\frac{20}{9} + \frac{35}{3}\beta^{-2} + \ldots$$

Herman's for the rigid sphere case does not allow any inferences about the quality of our expressions for the full $B_{\lambda}^{(2)}$ and $B_{\eta}^{(2)}$ since these involved the solution to the second order Boltzmann equation in their kinetic contributions. It may be observed that, for the purpose of developing results for $B_{\lambda;\varphi}^{(2)}$ and $B_{\eta;\varphi}^{(2)}$, the Boltzmann equation approach used here is thus far simpler than the correlation function method.

It would be satisfying to appeal to experiment as a test of our results for the full $B_{\lambda}^{(2)}$ and $B_{\eta}^{(2)}$. Two problems prevent doing this in a detailed and meaningful way. First, determining the two-body contributions to B_{λ} and B_{η} from experimental data involves several assumptions which are questionable at best. Secondly, in the temperature region in which quantum effects become measurable, it is doubtful whether the rigid sphere potential adequately represents any real system.

Herman has attempted a rough correlation of his calculations with experimental data for the rare gases. His analysis of the experimental data available indicates that, for these gases, both $B_{\lambda}^{(2)}$ and $B_{\eta}^{(2)}$ are increasing functions of β. Herman's results, which included only potential contributions, suggest the opposite dependence in the case of $B_{\eta}^{(2)}$ and much smaller slopes than are observed experimentally in both cases. Including the kinetic contributions removes this apparent anomaly and produces more realistic slopes to the $B_{\lambda}^{(2)}$ versus β and $B_{\eta}^{(2)}$ versus β curves.

We consider it unwise, particularly in light of the unrealistic nature of the rigid sphere potential, to press further any attempt to fit our results for $\bar{\bar{B}}_{\lambda}^{(2)}$ and $\bar{\bar{B}}_{\eta}^{(2)}$ to experimental data, even for the rare gases. A better approach would be to consider a more realistic potential, then compare with experiment. Even this suggestion is hampered somewhat by the scarcity of reliable low temperature experimental data and the tenuous position of $B_{\lambda}^{(2)}$ and $B_{\eta}^{(2)}$ as experimental quantities.

A full quantum treatment of the three-body contributions to B_{λ} and B_{η}, for the case of rigid spheres or any other potential, would appear to be a difficult proposition. A semi-classical treatment, based on the methods outlined in Appendix E, is possible for non-singular potentials and might profitably be undertaken.

APPENDIX A

DEVELOPMENT OF $\hat{\hat{f}}_{1e}$

In this appendix, the results of de Boer[23] are shown to lead to an $\hat{\hat{f}}_{1e}$ of the form (2-56) for a gas of particles which interact through a purely repulsive potential. The treatment and notation are essentially those of de Boer.

To second order in the activity, the matrix form of the configurational probability density function for a single particle may be written

$$n_1(\underline{r}_1;\underline{r}_1') = b_1(\underline{r}_1;\underline{r}_1')z + 2b_2(\underline{r}_1;\underline{r}')z^2 \tag{A-1}$$

where the b_i are expressed in terms of the Slater sums:

$$b_1(\underline{r}_1;\underline{r}_1') \equiv W_1(\underline{r}_1;\underline{r}_1')$$

$$b_2(\underline{r}_1;\underline{r}_1') \equiv \frac{1}{2}\int_{\mathrm{tr}\,(2)} d\underline{r}_2 \left\{W_2(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') - W_1(\underline{r}_1;\underline{r}_1')W_1(\underline{r}_2;\underline{r}_2')\right\} \tag{A-2}$$

The Slater sum for a single particle is given by

$$W_1(\underline{r}_1;\underline{r}_1') = \left(\frac{\lambda}{h}\right)^3 \int d\underline{P}_1 \, \psi^*(\underline{r}_1';\underline{P}_1)\,\psi(\underline{r}_1;\underline{P}_1)\, e^{-P_1^2/2mkT} \tag{A-3}$$

Since there is no interaction, the wave functions are simply those for a free particle, and

$$\begin{aligned} W_1(\underline{r}_1;\underline{r}_1') &= \left(\frac{\lambda}{h}\right)^3 \int d\underline{P}_1 \, e^{\frac{i}{\hbar}\underline{P}_1\cdot(\underline{r}_1-\underline{r}_1')} \, e^{-P_1^2/2mkT} \\ &= e^{-\frac{\pi}{\lambda^2}(\underline{r}_1-\underline{r}')^2} \end{aligned} \tag{A-4}$$

The two-particle Slater sum is defined by

$$W_2(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') \equiv \lambda^6 \sum_\rho \Phi_\rho^*(\underline{r}_1'\underline{r}_2')\, e^{-\beta \mathcal{H}_2}\, \Phi_\rho(\underline{r}_1\underline{r}_2) \tag{A-5}$$

where the Φ_ρ are solutions to the Schrodinger equation:

$$\mathcal{H}_2 \Phi_\rho = E_\rho \Phi_\rho \tag{A-6}$$

For a purely repulsive intermolecular potential, all solutions to equation (A-6) lie in the continuum and the summation over states in (A-5) may be replaced by an integration over momenta.

Changing to center-of-mass and relative motion coordinates then allows the wave function to factor on this basis. The wave functions for the center-of-mass motion may then be written as plane waves to give

$$W_2(\underline{r},\underline{R};\underline{r}'\underline{R}') = \left(\frac{\Lambda}{h}\right)^6 \int d\underline{P}\, d\underline{p}\; \psi^*(\underline{r}';\underline{p})\, \psi(\underline{r};\underline{p})\, e^{-p^2/mKT} \times$$

$$\times\, e^{-P^2/4mKT}\, e^{\frac{i}{\hbar}\underline{P}\cdot(\underline{R}-\underline{R}')} \qquad \text{(A-7)}$$

The integration over the center-of-mass momentum may be carried out directly to yield

$$W_2(\underline{r}\underline{R};\underline{r}'\underline{R}') = g_0(\underline{r};\underline{r}')\, e^{-\frac{2\pi}{\Lambda^2}(\underline{R}-\underline{R}')^2} \qquad \text{(A-8)}$$

where $g_0(\underline{r};\underline{r}')$ is the matrix formulation of the quantum mechanical radial distribution function defined in (2-57).

With (A-4) and (A-8), the single particle configurational probability density function becomes

$$n_1(\underline{r}_1;\underline{r}_1') = n\, e^{-\frac{\pi}{\lambda^2}(\underline{r}_1-\underline{r}_1')^2} \Big\{ 1 - n\int d\underline{r}\, [g_0(\underline{r};\underline{r}) - 1] +$$

$$+ n\int d\underline{r}_2 \left[e^{\frac{\pi}{2\lambda^2}(\underline{r}_1-\underline{r}_1')^2} g_0(\underline{r}_2-\underline{r}_1';\underline{r}_2-\underline{r}_1) - 1 \right] \Big\} \qquad \text{(A-9)}$$

where

$$z \sim n - n^2 \int d\underline{r} \left\{ g_0(\underline{r};\underline{r}) - 1 \right\} + O(n^2) \qquad \text{(A-10)}$$

has been used to express $n_1(\underline{r}_1;\underline{r}_1')$ as an expansion in the number density.

The Wigner distribution function is related to the configurational probability density by

$$f_{1e}(\underline{P}_1) \equiv \left(\frac{2}{h}\right)^3 \int d\underline{s}\; e^{\frac{2i}{\hbar}\underline{s}\cdot\underline{P}_1}\, n_1(\underline{r}_1+\underline{s};\underline{r}_1-\underline{s}) \tag{A-11}$$

Substitution of (A-9) into (A-11) then leads directly to the form (2-56) for $\hat{\hat{f}}_{1e}$.

APPENDIX B

LEMMAS ON $\hat{\hat{f}}_{1e}$, F , AND $\underline{G}$

In chapters I, III, and IV, twelve integrals involving $\hat{\hat{f}}_{1e}$, F , and $\underline{G}$ were encountered. Since all twelve may be expressed in terms of the delta function or its derivatives, the integrals are considered together, in this appendix, in the form of lemmas. Lemmas 5, 6, 7, 9, 11, and 12 have been proved previously by Imam-Rahajoe[16] and their proofs are only outlined here for ease of reference.

Lemma B-1

$$\int d\underline{P}_1 \hat{\hat{f}}_{1e} = 0$$

Proof:

Using the definition (2-56) of $\hat{\hat{f}}_{1e}$ and the Fourier representation of the delta function,

$$\int d\underline{P}_1 \hat{\hat{f}}_{1e} = \left(\frac{2}{h}\right)^3 \int d\underline{r}\, d\underline{s}\, \delta(\underline{s})\, e^{-\frac{4\pi s^2}{\lambda^2}} \times$$

$$\times \left\{ e^{\frac{2\pi s^2}{\lambda^2}} g_0(\underline{r}+\underline{s};\underline{r}-\underline{s}) - g_0(\underline{r};\underline{r}) \right\}$$

and the result follows on completion of the trivial delta function integration.

Lemma B-2

$$\int d\underline{P}_1\, P_1^2\, \hat{\hat{f}}_{1e} = mKT\,\epsilon_1$$

Proof:

With the Fourier representation of the delta function, the LHS may be written as

$$-\frac{\hbar^2}{4}\int d\underline{r}\,d\underline{s}\; e^{-\frac{4\pi s^2}{\lambda^2}}\left\{e^{\frac{2\pi s^2}{\lambda^2}}\, g_o(\underline{r}+\underline{s};\underline{r}-\underline{s}) - g_o(\underline{r};\underline{r})\right\}\frac{\partial}{\partial \underline{s}}\cdot\frac{\partial}{\partial \underline{s}}\,\delta(\underline{s})$$

Integrating by parts on $\underline{s}$ twice and performing the trivial delta function integration, the lemma follows.

Lemma B-3

$$\int d\underline{P}_1\, P_1^4\, \hat{\hat{f}}_{1e} = (mKT)^2\left\{\epsilon_2 + 5\,\epsilon_1\right\}$$

Proof:

The LHS may be written as

$$\left(\frac{\hbar}{2}\right)^4 \int d\underline{r}\, d\underline{s}\; e^{-\frac{4\pi s^2}{\lambda^2}} \left\{ e^{\frac{2\pi s^2}{\lambda^2}} g_0(\underline{r}+\underline{s};\underline{r}-\underline{s}) - g_0(\underline{r};\underline{r}) \right\} \left(\frac{\partial}{\partial \underline{s}} \cdot \frac{\partial}{\partial \underline{s}} \right)^2 \delta(\underline{s})$$

After integrating by parts four times on $\underline{s}$, carrying out the trivial delta function integration, and introducing the definition (3-18) of the ϵ_i integrals, we obtain the desired result.

Lemma B-4

$$\int d\underline{P}_1\, P_1^6\, \hat{\hat{f}}_{1e} = (mKT)^3 \left\{ \frac{105}{4} \epsilon_1 + \frac{21}{2} \epsilon_2 + \epsilon_3 \right\}$$

Proof:

Expressed in terms of the Fourier delta function, the LHS becomes

$$-\left(\frac{\hbar}{2}\right)^6 \int d\underline{r}\, d\underline{s}\; e^{-\frac{4\pi s^2}{\lambda^2}} \left\{ e^{\frac{2\pi s^2}{\lambda^2}} g_0(\underline{r}+\underline{s};\underline{r}-\underline{s}) - g_0(\underline{r};\underline{r}) \right\} \times$$

$$\times \left(\frac{\partial}{\partial \underline{s}} \cdot \frac{\partial}{\partial \underline{s}} \right)^3 \delta(\underline{s})$$

After integrating by parts on $\underline{s}$ six times, and carrying out the delta function integration, introduction of the definition (3-18) completes the proof.

Lemma B-5

$$\int d\underline{p}\, F = \psi(\underline{r};\underline{p}_0)\,\psi^*(\underline{r};\underline{p}_0)$$

Proof:

With the definition (2-22) of $F(\underline{r};\underline{p};\underline{p}_0)$, the LHS may be written

$$\int d\underline{s}\; \psi^*(\underline{r}-\underline{s};\underline{p}_0)\,\psi(\underline{r}+\underline{s};\underline{p}_0)\,\delta(\underline{s})$$

Performing the trivial delta function integration then gives the lemma.

Lemma B-6

$$\int d\underline{p}\,\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} = 0$$

Proof:

Writing the LHS in terms of the delta function,

$$-\frac{\hbar}{2i}\int d\underline{s}\left\{\frac{\partial}{\partial \underline{s}}\delta(\underline{s})\right\}\cdot\frac{\partial}{\partial \underline{r}}\,\psi(\underline{r}+\underline{s};\underline{p}_0)\,\psi^*(\underline{r}-\underline{s};\underline{p}_0)$$

This may be integrated by parts on $\underline{s}$ to yield

$$\frac{\hbar}{2i}\int d\underline{s}\,\delta(\underline{s})\,\frac{\partial}{\partial \underline{s}}\cdot\frac{\partial}{\partial \underline{r}}\,\psi(\underline{r}+\underline{s};\underline{p}_0)\,\psi^*(\underline{r}-\underline{s};\underline{p}_0)$$

Performing the trivial delta function integration then gives finally

$$\frac{\hbar}{2i}\left\{\psi^*(\underline{r};\underline{p}_0)\frac{\partial}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{r}}\,\psi(\underline{r};\underline{p}_0)-\psi(\underline{r};\underline{p}_0)\frac{\partial}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{r}}\,\psi^*(\underline{r};\underline{p}_0)\right\}$$

which vanishes on substitution of the relative motion Schrodinger equation.

Lemma B-7

$$\int d\underset{\sim}{p}\, \underset{\sim}{p}\,\underset{\sim}{p}\, F = -\frac{\hbar^2}{4}\left\{\psi^* \frac{\partial}{\partial \underline{r}}\frac{\partial}{\partial \underline{r}}\psi + \psi\frac{\partial}{\partial \underline{r}}\frac{\partial}{\partial \underline{r}}\psi^* - \frac{\partial\psi}{\partial \underline{r}}\frac{\partial\psi^*}{\partial \underline{r}} - \frac{\partial\psi^*}{\partial \underline{r}}\frac{\partial\psi}{\partial \underline{r}}\right\}$$

where the $\underline{r}$ and $\underset{\sim}{p}_0$ dependence of the wave function has been suppressed in the notation.

Proof:

With the Fourier representation of the delta function, the LHS may be expressed as

$$-\frac{\hbar^2}{4}\int d\underline{s}\left\{\frac{\partial}{\partial \underline{s}}\frac{\partial}{\partial \underline{s}}\delta(\underline{s})\right\}\psi^*(\underline{r}-\underline{s};\underset{\sim}{p}_0)\,\psi(\underline{r}+\underline{s};\underset{\sim}{p}_0)$$

After integrating by parts on $\underline{s}$ twice to give

$$-\frac{\hbar^2}{4}\int d\underline{s}\,\delta(\underline{s})\frac{\partial}{\partial \underline{s}}\frac{\partial}{\partial \underline{s}}\,\psi^*(\underline{r}-\underline{s};\underset{\sim}{p}_0)\,\psi(\underline{r}+\underline{s};\underset{\sim}{p}_0)$$

the delta function integration may be carried out to complete the proof.

Lemma B-8

$$\int d\underline{r}\, d\underline{p}\, p^2\, \underline{p}\cdot\frac{\partial F}{\partial \underline{r}} = 0$$

Proof:

With equation (3-73), the $\underline{r}$ integration may be carried out directly to yield

$$\int d\underline{p}\, p^3 \left\{ \delta(p-p_0)\,\sigma\!\left(\cos^{-1}\hat{\underline{p}}_0\cdot\hat{\underline{p}}\right) - \hat{\underline{p}}_0\cdot\hat{\underline{p}}\;\delta(\underline{p}-\underline{p}_0)\,\Sigma \right\}$$

which vanishes on completion of the integration over the angles of $\underline{p}$ and use of the definition (3-72) of Σ.

Lemma B-9

$$\int d\underline{p}\, \underline{p}\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} = -\frac{m}{2}\,\frac{d\varphi}{d\underline{r}}\,\psi(\underline{r};\underline{p}_0)\,\psi^*(\underline{r};\underline{p}_0)$$

Proof:

The lemma follows directly by differentiation of lemma B-7 and substitution of the Schrodinger equation.

Lemma B-10

$$\int d\underline{p}_0\, A(p_0^2) \int d\underline{r}\, \underline{r}\, \underline{p} \cdot \frac{\partial F}{\partial \underline{r}} =$$

$$= \underline{p} \int d\underline{p}_0\, A(p_0^2) \int d\underline{r} \left\{ \delta(\underline{p}-\underline{p}_0) - F \right\}$$

where A is an arbitrary function of p_0^2.

Proof:

Using the divergence theorem, it may be simply shown that

$$\int d\underline{r}\, \underline{r}\, \underline{p} \cdot \frac{\partial F}{\partial \underline{r}} = \int d\underline{r} \left\{ \frac{\partial}{\partial \underline{r}} \cdot (\underline{p}\, \underline{r}\, F) - F \underline{p} \right\}$$

$$= - \underline{p} \int d\underline{r}\, F + \lim_{r \to \infty} r^2 \int_S d\theta\, d\phi\, \sin\theta\; \hat{\underline{k}} \cdot (\underline{p}\, \underline{r}\, F)$$

By substituting the asymptotic form of F given in equation (3-71) into the surface integral, this becomes

$$\int d\underline{r}\, \underline{r} p \cdot \frac{dF}{d\underline{r}} = -p \int d\underline{r}\, F \;+$$

$$+ \lim_{r \to \infty} r^2 \int_S d\theta\, d\phi\, \sin\theta\, \hat{\underline{K}} \cdot (p\underline{r})\, \delta(p - p_0) \;+$$

$$+ \lim_{r \to \infty} \int_S d\theta\, d\phi\, \sin\theta\, \hat{\underline{K}} \cdot (p\underline{r}) \left\{ \sigma(\theta_0)\, \delta(p - p_0 \hat{\underline{K}}) - \delta(\hat{p}_0 - \hat{\underline{K}})\, \delta(p - p_0) \Sigma \right\}$$

The first surface integral on the RHS has no poles, so the divergence theorem may be used to convert it back to a volume integral:

$$\int d\underline{r}\, \underline{r} p \cdot \frac{dF}{d\underline{r}} = p \int d\underline{r} \left\{ \delta(p - p_0) - F \right\} \;+$$

$$+ \lim_{r \to \infty} \int_S d\theta\, d\phi\, \sin\theta\, \hat{\underline{K}} \cdot (p\underline{r}) \left\{ \sigma(\theta_0)\, \delta(p - p_0 \hat{\underline{K}}) - \delta(\hat{p}_0 - \hat{\underline{K}})\, \delta(p - p_0) \Sigma \right\}$$

If we then multiply both sides of the equation by $A(p_0^2)$ and integrate over p_0 ,

$$\int d\underline{p}_0\, A(p_0^2) \int d\underline{r}\, \underline{r}\,\underline{p}\cdot\frac{\partial F}{\partial \underline{r}} = \underline{p}\int d\underline{p}_0\, A(p_0^2)\int d\underline{r}\left\{\delta(\underline{p}-\underline{p}_0)-F\right\} +$$

$$+\lim_{r\to\infty}\int d\underline{p}_0\, A(p_0^2)\int_S d\theta\, d\phi\, \sin\theta\; \hat{\underline{K}}\cdot(\underline{p}\,\underline{r})\; \times$$

$$\times\left\{\sigma(\theta_0)\,\delta(\underline{p}-p_0\hat{\underline{K}}) - \delta(\hat{\underline{p}}_0-\hat{\underline{K}})\,\delta(\underline{p}-\underline{p}_0)\sum\right\}$$

The second term on the RHS vanishes on completion of the trivial integrations over the angles of $\underline{K}$ and $\underline{p}_0$, and the lemma follows.

Lemma B-11

$$\int d\underline{p}\,\underline{p}\cdot\frac{d}{d\underline{r}}\,\underline{G} = \underline{p}_0\,\psi(\underline{r};\underline{p}_0)\,\psi^*(\underline{r};\underline{p}_0)$$

Proof:

Using the Fourier representation of the delta function, the LHS may be written as

$$\frac{\hbar^2}{4}\int d\underline{s}\left\{\frac{d}{d\underline{s}}\,\delta(\underline{s})\right\}\cdot\frac{d}{d\underline{r}}\left\{\psi^*(\underline{r}-\underline{s};\underline{p}_0)\frac{d}{d\underline{p}_0}\,\psi(\underline{r}+\underline{s};\underline{p}_0)-\right.$$

$$\left.-\psi(\underline{r}+\underline{s};\underline{p}_0)\frac{d}{d\underline{p}_0}\,\psi^*(\underline{r}-\underline{s};\underline{p}_0)\right\}$$

After an integration by parts and some rearrangement, this may be put in the form:

$$-\frac{\hbar^2}{4}\int d\underline{s}\,\delta(\underline{s})\frac{d}{d\underline{s}}\cdot\frac{d}{d\underline{r}}\frac{d}{d\underline{\sigma}}\,\psi^*(\underline{r}-\underline{s};\underline{p}_0-\underline{\sigma})\,\psi(\underline{r}+\underline{s};\underline{p}_0+\underline{\sigma})\Big|_{\underline{\sigma}=0}$$

It may be shown from the Schrodinger equation that

$$-\frac{\hbar^2}{m}\frac{d}{d\underline{s}}\cdot\frac{d}{d\underline{r}}\,\psi^*(\underline{r}-\underline{s};\underline{p}_0-\underline{\sigma})\,\psi(\underline{r}+\underline{s};\underline{p}_0+\underline{\sigma})=$$

$$=\left\{\varphi(\underline{r}-\underline{s})-\varphi(\underline{r}+\underline{s})+\frac{4}{m}\underline{\sigma}\cdot\underline{p}_0\right\}\psi^*(\underline{r}-\underline{s};\underline{p}_0-\underline{\sigma})\,\psi(\underline{r}+\underline{s};\underline{p}_0+\underline{\sigma})$$

Substitution into the LHS of the lemma then gives

$$\frac{m}{4}\int d\underline{s}\, \delta(\underline{s}) \frac{\partial}{\partial \underline{\sigma}} \left\{ \varphi(\underline{r}-\underline{s}) - \varphi(\underline{r}+\underline{s}) + \frac{4}{m}\, \underline{\sigma}\cdot \underline{p}_0 \right\} \times$$

$$\times\, \psi^*(\underline{r}-\underline{s};\underline{p}_0-\underline{\sigma})\, \psi(\underline{r}+\underline{s};\underline{p}_0+\underline{\sigma}) \Big|_{\underline{\sigma}=0}$$

and the lemma follows directly.

Lemma B-12

$$\int d\underline{p}\, p^2\, \underline{p}\cdot \frac{d}{d\underline{r}}\, G = \frac{\hbar^2}{4} \left\{ m \frac{d\varphi}{d\underline{r}} \cdot \underline{\underline{H}} \; - \right.$$

$$\left. - \underline{p}_0 \left[\psi^* \frac{d}{d\underline{r}} \cdot \frac{d}{d\underline{r}} \psi + \psi \frac{d}{d\underline{r}} \cdot \frac{d}{d\underline{r}} \psi^* - 2 \frac{d\psi^*}{d\underline{r}} \cdot \frac{d\psi}{d\underline{r}} \right] \right\}$$

where the tensor $\underline{\underline{H}}$ has been defined in equation (3-69).

Proof:

The same type of manipulations used in the proof of lemma B-11 allows the LHS to be written as

$$\frac{\hbar^4}{16}\int d\underline{s}\,\delta(\underline{s})\left\{\frac{\partial}{\partial \underline{s}}\frac{\partial}{\partial \underline{s}} \vdots \frac{\partial}{\partial \underline{s}}\frac{\partial}{\partial \underline{r}}\frac{\partial}{\partial \underline{\sigma}}\right\}\times$$

$$\times\,\psi^*(\underline{r}-\underline{s};\underline{p}_o-\underline{\sigma})\,\psi(\underline{r}+\underline{s};\underline{p}_o+\underline{\sigma})\Big|_{\underline{\sigma}=0}$$

Substitution of the identity employed in lemma B-11 then leads to

$$-\frac{m\hbar^2}{16}\int d\underline{s}\;\delta(\underline{s})\frac{\partial}{\partial \underline{s}}\cdot\frac{\partial}{\partial \underline{s}}\frac{\partial}{\partial \underline{\sigma}}\left\{\varphi(\underline{r}-\underline{s})-\varphi(\underline{r}+\underline{s})+\frac{4}{m}\,\underline{\sigma}\cdot\underline{p}_o\right\}\times$$

$$\times\,\psi^*(\underline{r}-\underline{s};\underline{p}_o-\underline{\sigma})\,\psi(\underline{r}+\underline{s};\underline{p}_o+\underline{\sigma})\Big|_{\underline{\sigma}=0}$$

Performing the indicated operations then gives the lemma.

APPENDIX C

LEMMAS ON RIGID SPHERE WAVE FUNCTIONS

In chapter V, four lemmas involving rigid sphere wave functions were introduced. Before beginning the proofs of these lemmas, it is necessary to construct a suitable expression for the rigid sphere wave function which is valid in the neighborhood of the boundary.

We first consider an intermolecular potential of the form:

$$\varphi = 0 \qquad r > \sigma$$

$$= M \qquad r < \sigma$$

where M is very large and will later be allowed to become infinite to obtain the rigid sphere limit. The radial Schrodinger equation (5-6) then assumes the approximate form:

$$\frac{d^2}{dr^2} R_\ell^{(i)} - \frac{mM}{\hbar^2} R_\ell^{(i)} = 0 \qquad r < \sigma$$

$$\frac{d^2}{dr^2} R_\ell^{(o)} + \left\{ \frac{p_0^2}{\hbar^2} - \frac{\ell(\ell+1)}{r^2} \right\} R_\ell^{(o)} = 0 \qquad r > \sigma$$

with solution

$$R_\ell^{(i)} = A_\ell^{(i)}(p_0) \exp\left\{\frac{r}{\hbar}\sqrt{mM}\right\} \qquad r < \sigma$$

$$R_\ell^{(o)} = \left(\frac{\pi r p_0}{2\hbar}\right)^{1/2} \left\{\cos\eta_\ell(M)\, J_{\ell+1/2}\left(\frac{r p_0}{\hbar}\right) + \right.$$

$$\left. +(-1)^\ell \sin\eta_\ell(M)\; J_{-\ell-1/2}\left(\frac{r p_0}{\hbar}\right)\right\} \qquad r > \sigma$$

where $\eta_\ell(M)$, as indicated, is a function of the step height M .

By matching wave functions and first derivatives at the boundary,

$$R_\ell^{(i)} \frac{dR^{(o)}}{dr}\bigg|_\sigma = R_\ell^{(o)} \frac{dR_\ell^{(i)}}{dr}\bigg|_\sigma$$

we obtain the proper functional form for $\eta_\ell(M)$:

$$\tan \eta_\ell(M) =$$

$$\frac{(-1)^\ell \left\{ \left(\frac{1}{\hbar}\sqrt{mM} - \frac{\ell}{\sigma} \right) J_{\ell+1/2}\left(\frac{p_0\sigma}{\hbar}\right) + \frac{p_0}{\hbar} J_{\ell-1/2}\left(\frac{p_0\sigma}{\hbar}\right) \right\}}{\left\{ \frac{p_0}{\hbar} J_{-\ell+1/2}\left(\frac{p_0\sigma}{\hbar}\right) - \left(\frac{1}{\hbar}\sqrt{mM} - \frac{\ell}{\sigma} \right) J_{-\ell-1/2}\left(\frac{p_0\sigma}{\hbar}\right) \right\}}$$

Substitution into the boundary condition then allows the function $A_\ell^{(i)}(p_0)$ to be uniquely determined. After lengthy manipulation, it may then be shown that

$$R_\ell^{(i)} = (-1)^{\ell+1} p_0 \left(\frac{\hbar}{mM\sigma}\right)^{1/2} \left(-\dot{\bar{\eta}}_\ell\right)^{1/2} \exp\left\{\frac{1}{\hbar}\sqrt{mM}(r-\sigma)\right\}$$

where $\bar{\eta}_\ell$ has been defined in equation (5-41) and is the usual rigid sphere phase shift. With this result, the lemmas can now be proved.

<u>Lemma C-1</u>

$$\int_{r.s.} dr\, r^n \frac{d\varphi}{dr} R_\ell R_j = (-1)^{\ell+j+1} \sigma^{n-1} \left(\frac{\hbar p_0^2}{m}\right) \left(-\dot{\bar{\eta}}_\ell\right)^{1/2} \left(-\dot{\bar{\eta}}_j\right)^{1/2}$$

$$-\infty < n < \infty$$

Proof:

The LHS may be integrated by parts to give

$$-\int_0^{\infty} dr\, \varphi \frac{d}{dr}\left\{ r^n R_\ell R_j \right\}$$

Based upon the step potential discussed earlier, for rigid spheres, the LHS then may be written

$$-\lim_{M\to\infty} M \int_0^{\sigma} dr \frac{d}{dr}\left\{ r^n R_\ell^{(i)} R_j^{(i)} \right\} = -\lim_{M\to\infty} M r^n R_\ell^{(i)} R_j^{(i)} \Big|_0^{\sigma}$$

This may be expressed equivalently as

$$-\lim_{\epsilon\to 0^+} \lim_{M\to\infty} M r^n R_\ell^{(i)} R_j^{(i)} \Big|_{\epsilon}^{\sigma}$$

Substituting the explicit form for $R_\ell^{(i)}$ and taking the limits in the order indicated then gives the lemma.

Lemms C-2

$$\int_{r.s.} dr\, r^n \frac{d\psi}{dr} R_j \frac{\partial R_\ell}{\partial p_0} =$$

$$= (-1)^{\ell+j+1} \sigma^{-n-1} \left(\frac{\hbar p_0^2}{m}\right)\left(-\dot{\bar{\eta}}_\ell\right)^{1/2}\left(-\dot{\bar{\eta}}_j\right)^{1/2} \left\{ p_0^{-1} + \frac{1}{2} \frac{\ddot{\bar{\eta}}_\ell}{\dot{\bar{\eta}}_\ell} \right\}$$

$$-\infty < n < \infty$$

Proof:

Using the same techniques involved in the proof of lemma C-1, the LHS of lemma C-2 may integrated by parts and written in terms of the step height M:

$$-\lim_{M\to\infty} M \int_0^\sigma dr \frac{d}{dr}\left\{ r^n R_j^{(i)} \frac{\partial R_\ell^{(i)}}{\partial p_0} \right\} = -\lim_{\epsilon\to 0^+} \lim_{M\to\infty} M r^n R_j^{(i)} \frac{\partial R_\ell^{(i)}}{\partial p_0} \Bigg|_\epsilon^\sigma$$

Taking the limits in the order indicated completes the proof.

Lemma C-3

$$\int_{r.s.} dr\, \varphi^n R_\ell R_j = 0 \qquad\qquad 1 \le n < \infty$$

Proof:

With the same methods used in the proofs of the first two lemmas, the LHS of C-3 may be expressed as

$$\lim_{\epsilon \to 0^+} \lim_{M \to \infty} M^n \int_0^{\sigma - \epsilon} dr\, R_\ell R_j$$

After substituting explicitly for the wave functions, the integration may be performed directly to yield:

$$\frac{\hbar^2 p_0^2}{2m^{3/2}} (-1)^{\ell + j} \left(-\dot{\eta}_\ell\right)^{1/2} \left(-\dot{\eta}_j\right)^{1/2} \times$$

$$\times \lim_{\epsilon \to 0^+} \lim_{M \to \infty} M^{n - 3/2} \left\{ e^{-\frac{2}{\hbar}\sqrt{mM}\,\epsilon} - e^{-\frac{2}{\hbar}\sqrt{mM}\,\sigma} \right\}$$

Taking the limits in the order indicated then gives the lemma.

Lemma C-4

$$R_j^{(i)} \frac{\partial R_\ell^{(i)}}{\partial r}\bigg|_{r.s.} = R_\ell^{(i)} \frac{\partial R_j^{(i)}}{\partial r}\bigg|_{r.s.}$$

$$R_j^{(i)} \frac{\partial^2 R_\ell^{(i)}}{\partial r \partial p_0}\bigg|_{r.s.} = \frac{\partial R_j^{(i)}}{\partial r} \frac{\partial R_\ell^{(i)}}{\partial p_0}\bigg|_{r.s.}$$

Proof:

The proof follows directly upon differentiation of the rigid sphere wave function in the limiting form discussed previously.

APPENDIX D

LEMMAS ON LEGENDRE POLYNOMIALS

In this appendix, we consider two relations involving Legendre polynomials which were used in Chapter V. Again, for ease of reference, the relations are developed in the form of lemmas.

Lemma D-1

$$\sum_{\ell,j} \beta_{\ell j} \int_{-1}^{+1} dx\, x(x^2-1)\left\{P_\ell P_j' - P_j P_\ell'\right\} =$$

$$= \frac{4}{3} \sum_{\ell} \left\{\beta_{\ell+2;\ell} - \beta_{\ell;\ell+2}\right\}(2\ell+3)\begin{pmatrix} \ell & \ell+2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$

Proof:

With the aid of the identity connecting derivatives of Legendre polynomials with the polynomials:

$$(x^2-1)P_j' = j\,x P_j - j\,P_{j-1}$$

the integral on the LHS of lemma D-1 may be shown to yield:

$$\frac{4}{3}(j-\ell)\begin{pmatrix}\ell & j & 2\\ 0 & 0 & 0\end{pmatrix}^2 + 2\ell\begin{pmatrix}j & \ell-1 & 1\\ 0 & 0 & 0\end{pmatrix}^2 - 2j\begin{pmatrix}\ell & j-1 & 1\\ 0 & 0 & 0\end{pmatrix}^2$$

Substitution of this result into the LHS of lemma D-1 and use of the triangle rule for the 3-j symbols then gives

$$\sum_{\ell}\left\{\frac{8}{3}\begin{pmatrix}\ell & \ell+2 & 2\\ 0 & 0 & 0\end{pmatrix}^2\beta_{\ell;\ell+2} - \frac{8}{3}\begin{pmatrix}\ell & \ell-2 & 2\\ 0 & 0 & 0\end{pmatrix}^2\beta_{\ell;\ell-2}\right.$$

$$\left.+2\ell\begin{pmatrix}\ell-2 & \ell-1 & 1\\ 0 & 0 & 0\end{pmatrix}^2\beta_{\ell;\ell-2} - 2(\ell+2)\begin{pmatrix}\ell & \ell+1 & 1\\ 0 & 0 & 0\end{pmatrix}^2\beta_{\ell;\ell+2}\right\}$$

Jumping the index by two in the second and third terms, the lemma follows directly.

<u>Lemma D-2</u>

For $\gamma_{\ell j}$ such that $\gamma_{\ell j} = \gamma_{j\ell}$,

$$\sum_{\ell,j} \gamma_{\ell j} \int_{-1}^{+1} dx \left\{ (P_j P_\ell'' - P_\ell' P_j')(1-2x^2)(1-x^2) + 2x^3 P_\ell' P_j \right\}$$

$$= \frac{8}{3} \sum_{\ell} \gamma_{\ell;\ell+2} (2\ell+3)^2 \begin{pmatrix} \ell & \ell+2 & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$

Proof:

After very lengthy, though straightforward, manipulations involving the differential equation satisfied by the Legendre polynomials, the integral on the LHS of lemma D-2 may be shown to give

$$-\frac{4}{3} \frac{\ell(\ell+1)}{(2\ell+1)} \delta_{j\ell} + \frac{8}{3} \left\{ \ell(\ell+1) + j(j+1) - \frac{3}{2} \right\} \begin{pmatrix} \ell & j & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$

This result may then be substituted into the LHS of lemma D-2. Use of the triangle rule for 3-j symbols then yields

$$\frac{4}{3}\sum_{\ell}\left\{(2\ell+3)^2\begin{pmatrix}\ell & \ell+2 & 2\\ 0 & 0 & 0\end{pmatrix}^2 \gamma_{\ell;\ell+2} + (2\ell-1)^2\begin{pmatrix}\ell & \ell-2 & 2\\ 0 & 0 & 0\end{pmatrix}^2 \gamma_{\ell;\ell-2}\right\}$$

With the defined symmetry of the $\gamma_{\ell j}$, increasing the index by two in the second term completes the proof.

APPENDIX E

PROPERTIES OF Y_e

In the first part of this appendix, we show that, for a gas of particles which interact through a purely repulsive potential, the low density limit of Y_e is unity. Later, the first density correction to Y_e is discussed for the classical case.

To derive the low density limit of Y_e, we temporarily define the formal density expansion of Y_e as

$$Y_e \equiv \alpha + n \mathcal{Y}_e + \mathcal{O}(n^2) + \dots \tag{E-1}$$

where α is, at this point, conceivably a function of $\underline{r}$, $\underline{p}$, and $\underline{P}$. Retaining only terms quadratic in the number density in the equilibrium form of equation (2-17) then defines α in terms of the low density limit of the pair distribution function, $\hat{\hat{f}}_{2e}$,

$$\hat{\hat{f}}_{2e} \equiv \alpha \int d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \Omega_{\alpha}^{(2)}\left(\underline{r}_1 \underline{r}_2 \underline{p}_1 \underline{p}_2 \middle| \underline{r}_{10} \underline{r}_{20} \underline{p}_{10} \underline{p}_{20}\right) \hat{f}_{1e}(\underline{p}_{10}) \hat{f}_{1e}(\underline{p}_{20}) \tag{E-2}$$

Changing to center-of-mass and relative motion coordinates and substituting the explicit expression (2-14) for the $\Omega^{(2)}_{\alpha\beta}$ operator, the trivial delta function integrations may be performed to give

$$\hat{\hat{f}}_{2e} \equiv \alpha \left(\frac{\lambda}{h}\right)^6 \int d\underline{p}_o \, e^{-p_o^2/mKT} \, F(\underline{r}; \underline{p}, \underline{p}_o) \tag{E-3}$$

Now, from the results of de Boer[23], the matrix form of the configurational probability density is defined by

$$n_2(\underline{r}\,\underline{R}; \underline{r}'\,\underline{R}') \equiv n^2 W_2(\underline{r}\,\underline{R}; \underline{r}'\,\underline{R}') + \mathcal{O}(n^3) + \ldots \tag{E-4}$$

where, for a purely repulsive potential, the second Slater sum is given by equation (A-8). The equilibrium pair distribution function is then expressed in terms of $n_2(\underline{r}\,\underline{R}; \underline{r}'\,\underline{R}')$ by

$$f_{2e}(\underline{r}; \underline{p}\,\underline{P}) \equiv \left(\frac{2}{h}\right)^6 \int d\underline{s}\, d\underline{\mathcal{S}} \; n_2(\underline{r}+\underline{s}; \underline{R}+\underline{\mathcal{S}}; \underline{r}-\underline{s}; \underline{R}-\underline{\mathcal{S}}) \times$$
$$\times \, e^{-\frac{2i}{\hbar}\{\underline{s}\cdot\underline{p} + \underline{\mathcal{S}}\cdot\underline{P}\}} \tag{E-5}$$

Combining equations (A-8), (E-4), and (E-5) and carrying out the $\mathcal{S}$ integration then yields:

$$\hat{\hat{f}}_{2e} = \left(\frac{\lambda}{h}\right)^6 \int dp_0\, e^{-p_0^2/mKT}\, F(r; p, p_0) \qquad \text{(E-6)}$$

Comparison of equations (E-3) and (E-6) then gives the result:

$$\alpha = 1 \qquad \text{(E-7)}$$

We now consider the first density correction to the classical Y_e. Wigner and Kirkwood[26] have developed a technique which is appropriate for constructing a semi-classical expansion for $\mathcal{Y}_e$. Using this formalism, terms through order $\hbar^2$ have been obtained. However, since $\mathcal{Y}_e$ is not analytic in $\hbar$ for singular potentials such as the rigid sphere, we develop only the classical term here.

From the results of Wigner and Kirkwood, the classical N-particle Slater sum may be written in matrix form as

$$W_N^{cl}(\underline{r}_1 \ldots \underline{r}_N; \underline{r}_1' \ldots \underline{r}_N') = e^{-\frac{V_N}{KT}} \prod_j^N e^{-\frac{\pi}{\lambda^2}(\underline{r}_j - \underline{r}_j')^2} \qquad \text{(E-8)}$$

where V_N refers to the N-particle potential. The classical configurational probability density function for a single particle, to second order in the activity, is given in matrix form by

$$n_1^{cl}(\underline{r}_1;\underline{r}_1') \equiv z W_1^{cl}(\underline{r}_1;\underline{r}_1') + \tag{E-9}$$

$$+ z^2 \int_{\substack{tr\\(2)}} d\underline{r}_2 \left\{ W_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') - W_1^{cl}(\underline{r}_1;\underline{r}_1') W_1^{cl}(\underline{r}_2;\underline{r}_2') \right\}$$

The analogous function for two particles, to third order in the activity, is

$$n_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') \equiv z^2 W_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') + \tag{E-10}$$

$$+ z^3 \int_{\substack{tr\\(3)}} d\underline{r}_3 \left\{ W_3^{cl}(\underline{r}_1\underline{r}_2\underline{r}_3;\underline{r}_1'\underline{r}_2'\underline{r}_3') - W_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') W_1^{cl}(\underline{r}_3;\underline{r}_3') \right\}$$

Combining the result (E-8) with equations (E-9) and (E-10) then gives

$$n_1^{cl} = e^{-\frac{\pi}{\lambda^2}(\underline{r}_1-\underline{r}_1')^2}\left\{z + z^2\int d\underline{r}_2\left[e^{-\frac{V_{12}}{KT}} - 1\right]\right\}$$

$$n_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2') = e^{-\frac{V_{12}}{KT}}\, e^{-\frac{\pi}{\lambda^2}(\underline{r}_1-\underline{r}_1')^2}\, e^{-\frac{\pi}{\lambda^2}(\underline{r}_2-\underline{r}_2')^2} \times \qquad \text{(E-11)}$$

$$\times\left\{z^2 + z^3\int d\underline{r}_3\left[e^{-\frac{V_{13}}{KT}}\, e^{-\frac{V_{23}}{KT}} - 1\right]\right\}$$

where additivity of potentials has been assumed and V_{ij} refers to the potential of interaction between particles i and j.

Equations (A-11) and (E-5) may then be used to relate $n_1^{cl}(\underline{r}_1;\underline{r}_1')$ and $n_2^{cl}(\underline{r}_1\underline{r}_2;\underline{r}_1'\underline{r}_2')$ to the classical Wigner distribution functions for one and two particles, respectively. Substituting (E-11) and performing the integrations over $\underline{s}$ and $\underline{\mathscr{S}}$,

$$f_{1e}^{cl} = \left(\frac{\lambda}{h}\right)^3 e^{-W_1^2}\left\{z + z^2\int d\underline{r}_2\left[e^{-V_{12}/KT} - 1\right]\right\}$$

$$f_{2e}^{cl} = \left(\frac{\lambda}{h}\right)^6 e^{-W_1^2 - W_2^2 - \frac{V_{12}}{KT}}\left\{z^2 + z^3\int d\underline{r}_3\left[e^{-\frac{V_{13}}{KT}}\, e^{-\frac{V_{23}}{KT}} - 1\right]\right\} \qquad \text{(E-12)}$$

In the classical case, the activity is related to the number density by

$$z \sim n - n^2 \int d\underline{r}_2 \left\{ e^{-\frac{V_{12}}{KT}} - 1 \right\} \tag{E-13}$$

Substitution of (E-13) into equations (E-12) then gives

$$f_{1e}^{cl} = n \left(\frac{\lambda}{h}\right)^3 e^{-W_1^2}$$

$$f_{2e}^{cl} = \left(\frac{\lambda}{h}\right)^6 e^{-W_1^2 - W_2^2 - \frac{V_{12}}{KT}} \left\{ n^2 + \right. \tag{E-14}$$

$$\left. + n^3 \int d\underline{r}_3 \left[e^{-\frac{V_{13}}{KT}} - 1 \right] \left[e^{-\frac{V_{23}}{KT}} - 1 \right] \right\}$$

where f_{1e}^{cl} is complete here through order n^2 (and demonstrably complete through all orders of the number density) and f_{2e}^{cl} is complete through terms cubic in n.

Retaining only terms cubic in the number density in the equilibrium form of equation (2-17) then defines $\mathcal{Y}_e$ in terms of the first density correction to the equilibrium pair distribution function:

$$\hat{\hat{\hat{f}}}_{2e} = \int d\underline{r}_{10}\, d\underline{r}_{20}\, d\underline{p}_{10}\, d\underline{p}_{20}\, \Omega^{(2)}_{\alpha}\left(\underline{r}_1 \underline{r}_2 \underline{p}_1 \underline{p}_2 \middle| \underline{r}_{10} \underline{r}_{20} \underline{p}_{10} \underline{p}_{20}\right) \times$$

$$\times \left\{ \mathcal{Y}_e \hat{f}_{1e}(\underline{p}_{10}) \hat{f}_{1e}(\underline{p}_{20}) + \hat{f}_{1e}(\underline{p}_{10}) \hat{\hat{f}}_{1e}(\underline{p}_{20}) + \hat{f}_{1e}(\underline{p}_{20}) \hat{\hat{f}}_{1e}(\underline{p}_{10}) \right\} \tag{E-15}$$

After changing to center-of-mass and relative motion coordinates and substituting the explicit expression (2-14) for the $\Omega^{(2)}_{\alpha}$ operator, the trivial delta function integrations may be performed. Then, by substituting the results of equations (E-14) and rearranging slightly, the classical analogue of equation (E-15) may be written:

$$\hat{\hat{\hat{f}}}{}^{cl}_{2e} = 2^{-\frac{3}{2}} (2\pi)^{-3} \left(\frac{\lambda}{h}\right)^3 \mathcal{Y}^{cl}_e \int d\underline{\rho}\, e^{-i\underline{\rho}\cdot\underline{p}}\, g^{cl}_o\left(\underline{r} + \frac{\hbar}{2}\underline{\rho}; \underline{r} - \frac{\hbar}{2}\underline{\rho}\right) \tag{E-16}$$

where $g^{cl}_o\left(\underline{r} + \frac{\hbar}{2}\underline{\rho}; \underline{r} - \frac{\hbar}{2}\underline{\rho}\right)$ refers to the classical limit of the matrix form of the radial distribution defined in equation (2-57).

From the result (E-8) for the classical limit of the second Slater sum, it is straightforward to show that

$$g_0^{cl}\left(\underline{r}+\frac{\hbar}{2}\underline{\rho};\underline{r}-\frac{\hbar}{2}\underline{\rho}\right)=e^{-\frac{V_{12}}{KT}}\,e^{-\frac{m\rho^2 KT}{4}} \tag{E-17}$$

Substituting equation (E-17) into (E-16) and carrying out the $\underline{\rho}$ integration then gives

$$\hat{\hat{\hat{f}}}{}_{2e}^{cl}=\left(\frac{\lambda}{h}\right)^6 e^{-\frac{V_{12}}{KT}}\,e^{-W_1^2}\,e^{-W_2^2}\,\mathcal{Y}_e^{cl} \tag{E-18}$$

Comparing (E-18) with the second of equations (E-14) then finally gives

$$\mathcal{Y}_e^{cl}=y_{[0]}=$$

$$=\int d\underline{r}_3\left\{e^{-\frac{V_{13}}{KT}}-1\right\}\left\{e^{-\frac{V_{23}}{KT}}-1\right\} \tag{E-19}$$

where $y_{[0]}$ is Hoffman's[14] notation for the same integral.

APPENDIX F

NUMERICAL RESULTS FOR RIGID SPHERE INTEGRALS

In this appendix, we list numerical data for several of the rigid sphere integrals encountered in Chapter V. Listings for $\bar{\sigma}_{12}^{*}$ are not given since this integral is identical to the quantity $\bar{B}^{(2)*}_{\eta;\varphi}$ which is detailed in Chapter V. The integrals $\bar{\sigma}_{30}^{*}$, $\bar{Q}_{3}^{*}$, and the temperature derivatives of $\bar{B}^{*}$ were computed directly from their definitions in equations (5-38). Values of the $\bar{\Omega}^{(2,2)*}$ integral were obtained using the form given in Hirschfelder, Curtiss, and Bird[4]:

$$\bar{\Omega}^{(2,2)*}_{\substack{B.E.\\F.D.}} = 4\beta^{8} \sum_{\substack{\ell\\ \text{even}\\ \text{odd}}} \frac{(\ell+1)(\ell+2)}{(2\ell+3)} \times \int_{0}^{\infty} dz\, z^{5}\, e^{-\beta^{2} z^{2}} \sin^{2}\left(\eta_{\ell+2}-\eta_{\ell}\right) \tag{F-1}$$

where their expression has been converted to our notation. The numerical results for the $\bar{\Omega}^{(2,2)*}$ integrals agree fairly well with the early results of Uehling[27], who lacked the advantage of a high speed electronic computer.

TABLE VII

β	$\bar{Q}^*_{3;Boltz.}$	$\bar{Q}^*_{3;B.E.}$	$\bar{Q}^*_{3;F.D.}$
7.00	+ 1019.61	+ 1977.18	+ 62.0317
6.00	+ 747.14	+ 1432.62	+ 61.6549
5.00	+ 516.973	+ 972.939	+ 61.0064
4.00	+ 329.366	+ 598.975	+ 59.7558
3.00	+ 184.827	+ 312.737	+ 56.9174
2.00	+ 84.0207	+ 119.188	+ 48.8534
1.00	+ 24.9478	+ 25.5857	+ 24.3099
0.90	+ 20.3727	+ 19.7268	+ 21.0185
0.80	+ 16.8878	+ 15.9648	+ 17.8107
0.70	+ 13.8712	+ 13.0334	+ 14.7089
0.60	+ 11.3229	+ 10.8812	+ 11.7646
0.50	+ 9.19482	+ 9.16271	+ 9.22692
0.40	+ 7.38332	+ 7.42818	+ 7.33845
0.30	+ 5.74460	+ 5.74592	+ 5.74328
0.20	+ 4.14023	+ 4.14020	+ 4.14025
0.10	+ 2.51562	+ 2.51562	+ 2.51562
0.08	+ 2.19556	+ 2.19556	+ 2.19556
0.06	+ 1.88135	+ 1.88135	+ 1.88135
0.05	+ 1.72712	+ 1.72712	+ 1.72712
0.04	+ 1.57414	+ 1.57414	+ 1.57414
0.02	+ 1.25974	+ 1.25974	+ 1.25974

TABLE VIII

β	$\overline{\sigma}^{*}_{30;\,Boltz.}$	$\overline{\sigma}^{*}_{30;\,B.E.}$	$\overline{\sigma}^{*}_{30;\,F.D.}$
7.00	+ 49.3153	+ 98.0001	+ 0.630555
6.00	+ 36.4080	+ 72.0003	+ 0.815768
5.00	+ 25.5426	+ 50.0008	+ 1.08447
4.00	+ 16.7414	+ 32.0028	+ 1.47993
3.00	+ 10.0276	+ 18.0128	+ 2.04234
2.00	+ 5.37064	+ 8.08357	+ 2.65770
1.00	+ 2.50366	+ 2.62968	+ 2.37763
0.90	+ 2.29605	+ 2.35798	+ 2.23412
0.80	+ 2.10096	+ 2.12659	+ 2.07533
0.70	+ 1.91807	+ 1.92679	+ 1.90934
0.60	+ 1.74713	+ 1.74966	+ 1.74460
0.50	+ 1.58801	+ 1.58868	+ 1.58733
0.40	+ 1.44073	+ 1.44088	+ 1.44057
0.30	+ 1.30558	+ 1.30561	+ 1.30555
0.20	+ 1.18348	+ 1.18349	+ 1.18348
0.10	+ 1.07706	+ 1.07706	+ 1.07706
0.08	+ 1.05824	+ 1.05824	+ 1.05824
0.06	+ 1.04055	+ 1.04055	+ 1.04055
0.05	+ 1.03220	+ 1.03220	+ 1.03220
0.04	+ 1.02424	+ 1.02424	+ 1.02424
0.02	+ 1.00995	+ 1.00995	+ 1.00995

TABLE IX

β	$T\frac{d}{dT}\bar{B}^*_{Boltz.}$	$T\frac{d}{dT}\bar{B}^*_{B.E.}$	$T\frac{d}{dT}\bar{B}^*_{F.D.}$
7.00	− 147.101	+ 389.994	− 684.195
6.00	− 108.132	+ 214.773	− 431.036
5.00	− 75.1781	+ 99.3447	− 249.701
4.00	− 48.2506	+ 31.7569	− 128.258
3.00	− 27.3644	+ 0.0665	− 54.7952
2.00	− 12.5249	− 7.65123	− 17.3985
1.00	− 3.60342	− 3.54792	− 3.65982
0.90	− 3.01966	− 2.99984	− 3.03947
0.80	− 2.48873	− 2.48353	− 2.49392
0.70	− 2.00960	− 2.00875	− 2.01044
0.60	− 1.58112	− 1.58106	− 1.58118
0.50	− 1.20210	− 1.20210	− 1.20210
0.40	− 0.871282	− 0.871282	− 0.871282
0.30	− 0.587212	− 0.587212	− 0.587212
0.20	− 0.348410	− 0.348410	− 0.348410
0.10	− 0.153282	− 0.153282	− 0.153282
0.08	− 0.119309	− 0.119309	− 0.119309
0.06	− 0.087037	− 0.087037	− 0.087037
0.05	− 0.071566	− 0.071566	− 0.071566
0.04	− 0.056410	− 0.056410	− 0.056410
0.02	− 0.027415	− 0.027415	− 0.027415

TABLE X

β	$T^2 \frac{d^2}{dT^2} \bar{B}^*_{Boltz.}$	$T^2 \frac{d^2}{dT^2} \bar{B}^*_{B.E.}$	$T^2 \frac{d^2}{dT^2} \bar{B}^*_{F.D.}$
7.00	+ 294.012	− 1121.86	+ 1709.89
6.00	+ 216.019	− 644.771	+ 1076.81
5.00	+ 150.035	− 323.135	+ 623.205
4.00	+ 96.0705	− 127.057	+ 319.198
3.00	+ 54.1544	− 26.6425	+ 134.951
2.00	+ 24.3585	+ 7.93623	+ 40.7808
1.00	+ 6.65601	+ 6.34724	+ 6.96478
0.90	+ 5.52698	+ 5.40344	+ 5.65051
0.80	+ 4.50812	+ 4.47090	+ 4.54534
0.70	+ 3.59723	+ 3.59005	+ 3.60441
0.60	+ 2.79168	+ 2.79103	+ 2.79233
0.50	+ 2.08876	+ 2.08875	+ 2.08877
0.40	+ 1.48570	+ 1.48570	+ 1.48570
0.30	+ 0.978977	+ 0.978977	+ 0.978977
0.20	+ 0.565106	+ 0.565106	+ 0.565106
0.10	+ 0.240265	+ 0.240265	+ 0.240265
0.08	+ 0.185521	+ 0.185521	+ 0.185521
0.06	+ 0.134223	+ 0.134223	+ 0.134223
0.05	+ 0.109947	+ 0.109947	+ 0.109947
0.04	+ 0.0862822	+ 0.0862822	+ 0.0862822
0.02	+ 0.0416569	+ 0.0416569	+ 0.0416569

TABLE XI

β	$T^3 \frac{d^3}{dT^3} \bar{B}^*_{Boltz.}$	$T^3 \frac{d^3}{dT^3} \bar{B}^*_{B.E.}$	$T^3 \frac{d^3}{dT^3} \bar{B}^*_{F.D.}$
7.00	− 882.006	+ 4220.52	− 5984.53
6.00	− 647.578	+ 2473.55	− 3768.71
5.00	− 450.012	+ 1280.95	− 2180.97
4.00	− 288.039	+ 540.643	− 1116.72
3.00	− 162.115	+ 147.094	− 471.324
2.00	− 72.4274	− 4.32839	− 140.526
1.00	− 19.2364	− 17.3692	− 21.1035
0.90	− 15.8851	− 15.0611	− 16.7091
0.80	− 12.8741	− 12.5931	− 13.1551
0.70	− 10.1967	− 10.1333	− 10.2601
0.60	− 7.84439	− 7.83733	− 7.85145
0.50	− 5.80839	− 5.80820	− 5.80858
0.40	− 4.08012	− 4.08012	− 4.08012
0.30	− 2.64749	− 2.64749	− 2.64749
0.20	− 1.49891	− 1.49891	− 1.49891
0.10	− 0.621479	− 0.621479	− 0.621479
0.08	− 0.476952	− 0.476952	− 0.476952
0.06	− 0.342852	− 0.342852	− 0.342852
0.05	− 0.280048	− 0.280048	− 0.280048
0.04	− 0.219162	− 0.219162	− 0.219162
0.02	− 0.105611	− 0.105611	− 0.105611

TABLE XII

β	$\bar{\Omega}^{(2,2)*}_{\text{Boltz.}}$	$\bar{\Omega}^{(2,2)*}_{\text{B.E.}}$	$\bar{\Omega}^{(2,2)*}_{\text{F.D.}}$
7.00	3.89411	7.77660	0.01162
6.00	3.86190	7.70326	0.02055
5.00	3.80746	7.57527	0.03964
4.00	3.71321	7.34086	0.08555
3.00	3.53331	6.85261	0.21401
2.00	3.14160	5.64451	0.63871
1.00	2.27192	2.75436	1.78952
0.90	2.15437	2.44718	1.86156
0.80	2.03291	2.18265	1.88318
0.70	1.90817	1.96844	1.84791
0.60	1.78071	1.79843	1.76300
0.50	1.65104	1.65472	1.64737
0.40	1.51962	1.52016	1.51907
0.30	1.38688	1.38693	1.38683
0.20	1.25337	1.25337	1.25337
0.10	1.12026	1.12026	1.12026
0.08	1.09399	1.09399	1.09399
0.06	1.06798	1.06798	1.06798
0.05	1.05483	1.05483	1.05483
0.04	1.04154	1.04154	1.04154
0.02	1.00469	1.00469	1.00469

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