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CLASSICAL THEORY OF DENSITY CORRECTIONS TO THE

GASEOUS TRANSPORT COEFFICIENTS OF MIXTURES

by

David Ellwyn Bennett III

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CLASSICAL THEORY OF DENSITY CORRECTIONS TO THE GASEOUS TRANSPORT COEFFICIENTS OF MIXTURES

by

David Ellwyn Bennett III

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CLASSICAL THEORY OF DENSITY CORRECTIONS TO THE GASEOUS TRANSPORT COEFFICIENTS OF MIXTURES*

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ABSTRACT

A modified Boltzmann equation for mixtures is developed which includes the effects of collisional transfer and three particle collisions. This equation is then solved by perturbation expansion techniques. General expressions for the fluxes are derived with the resulting transport coefficients expressed in terms of the perturbation coefficients. Finally, the various integrals encountered in the development are evaluated numerically.

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CHAPTER I

INTRODUCTION

In this study we are concerned with one of many problems currently being studied in the general field of non-equilibrium statistical mechanics. This is the problem of determining the transport coefficients of a classical, moderately dense, non-reacting, multicomponent gas mixture.

Historically, the basis of much of the current research can be traced directly back to Boltzmann's[1] development of an integro-differential equation for the single particle distribution function. For some time, the only solution to this equation was that obtained by Maxwell for the inverse fourth power potential.[2]

The first general solution was independently developed by Chapman[3] in 1916 and Enskog[4] in 1917, and led to expressions for the transport coefficients at low density. There are two extensions of this work which are related to the present development. The first, reported by Enskog[5] in 1922, extended the treatment to a dense gas of rigid spheres, and included corrections for both collisional transfer and three body collisions. The other is the general low density solution for a multicomponent system, reported by Curtiss and Hirschfelder[6,7] in 1949. The latter is one of the two papers upon which the present study is based.

Between 1935 and 1949, Bogoliubov,[8] Born and Green,[9] Kirkwood,[10] and Yvon[11] developed a set of equations for the h order distribution functions ($1\leq h\leq N$), now known as the B.B.G.K.Y. hierarchy (discussed in chapter II). Much of the currect research stems from this and the Chapman-Enskog developments, and include applications to various molecular models.[12] Of particular importance is the paper by Hoffman and Curtiss[13] on the first density corrections to the transport coefficients of a single component system. This completed several efforts[14] to accurately include the effects of more than two particles in a modified Boltzmann equation.

The present study resulted from a desire to combine the formulations of Curtiss and Hirschfelder with that of Hoffman and Curtiss. However, a simple combination and generalization is found to be insufficient, since many terms arise in our expressions that have no analog in either of the two parent treatments.

In this work, a modified Boltzmann equation for mixtures is developed, which includes the effects of collisional transfer and three particle interactions. This equation is then solved by perturbation expansion techniques. Expressions are then developed for the transport coefficients in terms of the perturbation solutions. Finally the various quantities appearing in our expressions are evaluated numerically. This then leads to numerical values for the transport second virial coefficients of a single component system. Self diffusion is considered in detail.

CHAPTER II

GENERALIZED BOLTZMANN EQUATION

In this chapter we develop the B.B.G.K.Y. hierarchy for mixtures and consider in particular the equation governing the time evolution of the lowest order distribution function, $f^{(1)}$. A truncation procedure is then applied to yield a closed equation for $f^{(1)}$.

2.1 Distribution Functions

The system considered consists of a large number, N, of molecules in a volume V. The system is composed of ν non reacting chemical species, each consisting of N_α molecules of species α such that

$$N = \sum_{\alpha=1}^{\nu} N_\alpha$$

The particles are assumed to interact according to spherically symmetric two body potentials $\varphi_{\alpha\beta}(r_{ij})$ which depend on both the magnitude of the separation distance and the chemical identity of each of the two molecules. Throughout this work Greek indices run over the various species while Latin indices number the individual molecules. Unless otherwise specified, the limits on sums over Greek indicies are 1 and ν, and the limits on Latin indices are 1 and N.

The state of the system is specified by 3N position and 3N velocity coordinates, which describe a point in a 6N dimensional position-velocity space. We assume that the evolution of the system is governed by the laws of classical mechanics and a set of initial conditions. Specifying these initial conditions as a point in the 6N dimensional space at a time t_o, the exact mechanistic evolution of the system for all post and future times could in principle be computed. Such a description is far too detailed for our needs.

Much more useful in this type of statistical problems are the concepts of ensembles and distribution functions. An ensemble consists of a large number of replicas of the system to be studied. The N particle distribution function $f^{(N)}$ is proportional to the probability of finding a member of the ensemble at a specified point in the 6N dimensional position-velocity space. The indistinguishability of the molecules of the same species requires that the ensemble and $f^{(N)}$ be symmetric with respect to the interchange of the coordinates of molecules of the same species. We choose to normalize $f^{(N)}$ so that

$$\int f^{(N)}(\underline{r}^{(N)}, \underline{v}^{(N)}, t)\, d\underline{r}^{(N)} d\underline{v}^{(N)} = \prod_{\alpha} N_{\alpha}! \qquad (2.1 - 1)$$

Since complete knowledge of $f^{(N)}$ is too detailed, we define lower order distribution functions $f^{(h)}(\underline{r}^{(h)}, \underline{v}^{(h)})$ of h particles by:

$$f^{(h)}(\underline{r}^{(h)}, \underline{v}^{(h)}, t) = \left\{\prod_{\alpha} h_{\alpha}!\right\}^{-1} \int f^{(N)}(\underline{r}^{(N)}, \underline{v}^{(N)}, t)\, d\underline{r}^{(N-h)} d\underline{v}^{(N-h)} \qquad (2.1 - 2)$$

where h_{α} is the number of particles of species α whose coordinates span the domain of integration. In particular, we have:

$$f_{\alpha}^{(1)}(\underline{r}^{(1)}, \underline{v}^{(1)}) = N_{\alpha}\left\{\prod_{\gamma} N_{\gamma}!\right\}^{-1} \int f^{(N)}(\underline{r}^{(N)}, \underline{v}^{(N)}, t)\, d\underline{r}^{(N-1)} d\underline{v}^{(N-1)} \qquad (2.1 - 3)$$

$$f_{\alpha\beta}^{(2)}(\underline{r}^{(2)}, \underline{v}^{(2)}) = N_{\alpha}N_{\beta}\left\{\prod_{\gamma} N_{\gamma}!\right\}^{-1} \int f^{(N)}(\underline{r}^{(N)}, \underline{v}^{(N)}, t)\, d\underline{r}^{(N-2)} d\underline{v}^{(N-2)} \qquad (2.1 - 4)$$

and

$$f^{(2)}_{\alpha\alpha}(\underline{r}^{(2)},\underline{v}^{(2)}) = N_\alpha(N_\alpha-1)\Big\{\prod_\gamma N_\gamma!\Big\}^{-1}\int f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t)\,d\underline{r}^{(N-2)}\,d\underline{v}^{(N-2)} \qquad (2.1 - 5)$$

The subscripts on $f^{(1)}_\alpha$ or $f^{(2)}_{\alpha\beta}$ indicate that

$$f^{(1)}_\alpha = f^{(1)}_\alpha(\underline{r}^{(1)},\underline{v}^{(1)}) = f^{(1)}_\alpha(\underline{r}_\alpha,\underline{v}_\alpha)$$

and

$$f^{(2)}_{\alpha\beta} = f^{(2)}_{\alpha\beta}(\underline{r}^{(2)},\underline{v}^{(2)}) = f^{(2)}(\underline{r}_\alpha,\underline{r}_\beta,\underline{v}_\alpha,\underline{v}_\beta)$$

To simplify the notation, the explicit indication of the time dependence of the distribution function is dropped.

Since we consider only two body forces, only the level of information contained in $f^{(1)}$ and $f^{(2)}$ is needed.

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

The time evolution of $f^{(N)}$ is governed by the Liouville equation:[15]

$$\left\{\frac{\partial}{\partial t} + \sum_k \frac{1}{m_k}\left[\frac{\partial H^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)})}{\partial \underline{v}_k}\cdot\frac{\partial}{\partial \underline{r}_k} - \frac{\partial H^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)})}{\partial \underline{r}_k}\cdot\frac{\partial}{\partial \underline{v}_k}\right]\right\} f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t) = 0 \qquad (2.2 - 1)$$

where the energy of the N particle system is:

$$H^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)}) = \frac{1}{2}\sum_i m_i v_i^2 + \frac{1}{2}\sum_{i\neq j}\sum \varphi_{ij} + \sum_i \varphi_i \qquad (2.2 - 2)$$

The terms φ_i represent conservative external potentials, giving rise to external forces of the form

$$-\frac{\partial \varphi_i}{\partial \underline{r}_i}$$

Carrying out the indicated differentiations explicitly, we obtain

$$\left\{\frac{\partial}{\partial t}+\sum_i \underline{v}_i\cdot\frac{\partial}{\partial \underline{r}_i}-\sum_i \frac{1}{m_i}\frac{\partial \varphi_i}{\partial \underline{r}_i}\cdot\frac{\partial}{\partial \underline{v}_i}\right\} f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t)$$

(2.2 - 3)

$$=\sum_{j\neq k}\sum \frac{1}{m_k}\frac{\partial \varphi_{jk}}{\partial \underline{r}_k}\cdot\frac{\partial}{\partial \underline{v}_k} f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t)$$

The equations for the time evolution of the lower order distribution functions $f^{(h)}$ are obtained by integrating the Liouville equation over the coordinates of the (N-h) remaining particles:

$$\left\{\frac{\partial}{\partial t}+\sum_{i=1}^{h} \underline{v}_i\cdot\frac{\partial}{\partial \underline{r}_i}-\sum_{\substack{i=1\\ i\neq j}}^{h}\sum_{j=1}^{h} \frac{1}{m_j}\frac{\partial \varphi_{ij}}{\partial \underline{r}_j}\cdot\frac{\partial}{\partial \underline{v}_j}-\sum_{i=1}^{h}\frac{1}{m_i}\frac{\partial \varphi_i}{\partial \underline{r}_i}\cdot\frac{\partial}{\partial \underline{v}_i}\right\} f^{(h)}(\underline{r}^{(h)},\underline{v}^{(h)},t)$$

(2.2 - 4)

$$=\sum_{\alpha}\sum_{i=1}^{h}\frac{1}{m_i}\int \frac{\partial \varphi_{\alpha i}}{\partial \underline{r}_i}\cdot\frac{\partial}{\partial \underline{v}_i} f^{(h+1}(\underline{r}^{(h+1)},\underline{v}^{(h+1)},t)\, d\underline{r}_\alpha d\underline{v}_\alpha$$

where the sum over α runs over the various species present in the group of (N-h) molecules. This set of equations is a generalization of the B.B.G.K.Y. hierarchy. The exact solution of any equation of this set would ultimately require the exact solution of the original Liouville equation.

2.3 Equation for $f^{(1)}$.

The lowest order equation of the hierarchy, corresponding to the species α, is

$$\left\{\frac{\partial}{\partial t}+\underline{v}_\alpha\cdot\frac{\partial}{\partial \underline{r}_\alpha}-\frac{1}{m_\alpha}\frac{\partial \phi_\alpha}{\partial \underline{r}_\alpha}\cdot\frac{\partial}{\partial \underline{v}_\alpha}\right\}f_\alpha^{(1)}=\frac{1}{m_\alpha}\sum_\beta\int\frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_\alpha}\cdot\frac{\partial f_{\alpha\beta}^{(2)}}{\partial \underline{v}_\alpha}\,d\underline{r}_\beta\,d\underline{v}_\beta \qquad (2.3-1)$$

$$1\le\alpha\le\nu$$

Note that the equation for a particular species α is coupled to all other species through the sum over β.

To write this equation in a more convenient form, we transform from the coordinates $(\underline{r}_\alpha, \underline{r}_\beta, \underline{v}_\alpha, \underline{v}_\beta)$ to the relative coordinates $(\underline{G}_{\alpha\beta}, \underline{g}_{\alpha\beta})$ and $(\underline{R}_{\alpha\beta}, \underline{r}_{\alpha\beta})$. The stream velocity $\underline{u}$ and the peculiar velocity $\underline{V}_\alpha$ are defined by

$$\underline{u} = \sum_\alpha n_\alpha m_\alpha \overline{\underline{v}_\alpha} \qquad (2.3-2)$$

and

$$\underline{V}_\alpha = \underline{v}_\alpha - \underline{u} \qquad (2.3-3)$$

where the average value of a quantity Ψ is given by

$$\overline{\Psi} = \frac{1}{n_\alpha}\int f_\alpha^{(1)}\,\Psi\,d\underline{v}_\alpha \qquad (2.3-4)$$

Utilizing these quantities, the relative coordinates are defined by:

$$\underline{g}_{\alpha\beta} = \underline{v}_\alpha - \underline{v}_\beta = \underline{V}_\alpha - \underline{V}_\beta \qquad (2.3-5)$$

$$\underline{G}_{\alpha\beta} = \frac{m_\alpha \underline{v}_\alpha + m_\beta \underline{v}_\beta}{M_{\alpha\beta}} - \underline{u} = \frac{m_\alpha \underline{V}_\alpha + m_\beta \underline{V}_\beta}{M_{\alpha\beta}} \qquad (2.3 - 6)$$

and

$$\underline{r}_{\alpha\beta} = \underline{r}_\alpha - \underline{r}_\beta \qquad (2.3 - 7)$$

$$\underline{R}_{\alpha\beta} = \frac{1}{2}(\underline{r}_\alpha + \underline{r}_\beta) \qquad (2.3 - 8)$$

where

$$M_{\alpha\beta} = m_\alpha + m_\beta$$

With these definitions we find that

$$\frac{1}{m_\alpha}\frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_\alpha}\cdot\frac{\partial}{\partial \underline{v}_\alpha} + \frac{1}{m_\beta}\frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_\beta}\cdot\frac{\partial}{\partial \underline{v}_\beta} = \frac{1}{\mu_{\alpha\beta}}\frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}} \qquad (2.3 - 9)$$

where $\mu_{\alpha\beta}$ is the reduced mass of the pair (α,β), defined by

$$\mu_{\alpha\beta} = \frac{m_\alpha m_\beta}{M_{\alpha\beta}} \qquad (2.3 - 10)$$

Upon combining equation (2.3 - 1) and 2.3 - 9), we note that the term containing $\frac{\partial}{\partial \underline{v}_\beta}$ gives zero upon converting to a surface integral in velocity space. Shifting the origin by replacing $\underline{r}_\beta$ with $\underline{r}_{\alpha\beta}$, we find that:

$$\left\{\frac{\partial}{\partial t}+\underline{v}_\alpha\cdot\frac{\partial}{\partial\underline{r}_\alpha}-\frac{1}{m_\alpha}\frac{\partial\varphi_\alpha}{\partial\underline{r}_\alpha}\cdot\frac{\partial}{\partial\underline{v}_\alpha}\right\}f_\alpha^{(1)}=\sum_\beta\frac{1}{\mu_{\alpha\beta}}\int\frac{\partial\varphi_{\alpha\beta}}{\partial\underline{r}_{\alpha\beta}}\cdot\frac{\partial f_{\alpha\beta}^{(2)}}{\partial\underline{g}_{\alpha\beta}}\,d\underline{r}_{\alpha\beta}\,d\underline{v}_\beta \quad (2.3-11)$$

In order to obtain a closed equation for $f^{(1)}$, $f^{(2)}$ must be expressed as a functional of $f^{(1)}$. An approximate expression for $f^{(2)}$ has been developed by Hoffman and Curtiss[13] based on the principle of molecular chaos. Starting from collision and post-collision configurations, the two particle trajectories are traced back in time until $f^{(2)}$ can be factored into a product of $f^{(1)}$'s. Then the coordinates are traced forward for the same time interval along one particle trajectories. Their results give

$$f_{\alpha\beta}^{(2)}(\underline{r}^{(2)},\underline{v}^{(2)})=Y_{\alpha\beta[0]}(\underline{R}_{\alpha\beta},\underline{r}_{\alpha\beta})\,f_\alpha^{(1)'}f_\beta^{(1)'} \quad (2.3-12)$$

as an approximate expression for $f_{\alpha\beta}^{(2)}$ as a functional of $f_\alpha^{(1)}$ and $f_\beta^{(1)}$, where the tracing procedure is denoted by a prime and the function $Y_{\alpha\beta[0]}$ is defined in terms of the quilibrium radial distribution function $y_{\alpha\beta[0]}$

$$y_{\alpha\beta[0]}=Y_{\alpha\beta[0]}\,e^{-\varphi_{\alpha\beta}/kT}$$

This expression may then be used to obtain a modified Boltzmann equation for $f^{(1)}$;

$$\frac{\partial f_\alpha^{(1)}}{\partial t} + \underline{v}_\alpha \cdot \frac{\partial f_\alpha^{(1)}}{\partial \underline{r}_\alpha} - \frac{1}{m_\alpha} \frac{\partial \Phi_\alpha}{\partial \underline{r}_\alpha} \cdot \frac{\partial f^{(1)}}{\partial \underline{v}_\alpha}$$

$$= \sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ Y_{\alpha\beta[0]} f_\alpha^{(1)'} f_\beta^{(1)'} \right\} d\underline{r}_{\alpha\beta} \, d\underline{v}_\beta \qquad (2.3 - 13)$$

This equation is the generalization to mixtures of the modified Boltzmann equation used by Hoffman and Curtiss.[13]

The next four chapters describe the solution of the above equations by perturbation methods and the use of these solutions to obtain expressions for the transport coefficients.

CHAPTER III

THE EQUATIONS OF CHANGE AND THE FLUXES

This chapter is concerned with the derivation of the equations of change, that is the equations describing the conservation of mass, momentum and energy in the system. The resulting fluxes are then expressed as functionals of the one particle distribution function $f_\alpha^{(1)}$.

3.1 General Equation

The starting point[16] is the N particle Liouville equation (2.2 - 1) and the definition of the average value of a dynamical variable $\psi(\underline{r}^{(N)},\underline{v}^{(N)})$:

$$\overline{\Psi} = \left\{\prod_\alpha N_\alpha!\right\}^{-1} \int \Psi(\underline{r}^{(N)},\underline{v}^{(N)})\, f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t)\, d\underline{r}^{(N)}\, d\underline{v}^{(N)} \qquad (3.1 - 1)$$

Taking the time derivative of both sides and using the Liouville equation to eliminate $\frac{\partial f^{(N)}}{\partial t}$, we integrate by parts each of the resulting terms. The integrated terms are zero since $f^{(N)}$ is zero for either large $\underline{r}^{(N)}$ or large $\underline{v}^{(N)}$, and we obtain the general equation of change:

$$\frac{\partial \overline{\Psi}}{\partial t} = \left\{\prod_\alpha N_\alpha!\right\}^{-1} \int f^{(N)}(\underline{r}^{(N)},\underline{v}^{(N)},t) \left\{ \sum_k \underline{v}_k \cdot \frac{\partial}{\partial \underline{r}_k} \right.$$

$$\left. - \sum_{j\neq k}\sum_k \frac{1}{m_k}\frac{\partial \phi_{jk}}{\partial \underline{r}_k}\cdot\frac{\partial}{\partial \underline{v}_k} - \sum_k \frac{1}{m_k}\frac{\partial \phi_k}{\partial \underline{r}_k}\cdot\frac{\partial}{\partial \underline{v}_k} \right\} \Psi(\underline{r}^{(N)},\underline{v}^{(N)})\, d\underline{r}^{(N)}\, d\underline{v}^{(N)} \qquad (3.1 - 2)$$

In general ψ may be a tensor of any order.

3.2 Equation of Continuity

The equations governing the conservation of mass are obtained by taking ψ to be a function of position of the form:

$$\psi = \sum_{k=1}^{N_\alpha} \delta(\underline{r}_k - \underline{r}) \tag{3.2 - 1}$$

The average value of ψ is then the number density $n_\alpha(r)$:

$$n_\alpha(\underline{r}) = \int f_\alpha^{(1)}(\underline{r}, \underline{v}_\alpha)\, d\underline{v}_\alpha \tag{3.2 - 2}$$

Utilizing the various definitions (2.3 - 2), (2.3 - 3), and (2.3 - 4), we obtain by straightforward means the equation of continuity for each species:

$$\frac{\partial n_\alpha}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot (n_\alpha \underline{u}) = -\frac{\partial}{\partial \underline{r}} \cdot (n_\alpha \overline{\underline{V}}_\alpha) \tag{3.2 - 3}$$

Multiplying by m_α and summing over the species gives the overall continuity equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot (\rho \underline{u}) = 0 \tag{3.2 - 4}$$

where

$$\rho = \sum_\alpha n_\alpha m_\alpha$$

is the mass density.

3.3 Equation of Momentum Conservation

The total linear momentum of the system is conserved. Taking ψ to be a total momentum of the form

$$\psi = \sum_{k} m_k \underline{v}_k \, \delta(\underline{r}_k - \underline{r}) \qquad (3.3 - 1)$$

leads to an equation governing the evolution of the stream velocity $\underline{u}$:

$$\rho\left\{\frac{\partial \underline{u}}{\partial t} + \underline{u}\cdot\frac{\partial}{\partial \underline{r}}\underline{u}\right\} = -\frac{\partial}{\partial \underline{r}}\cdot \underline{\underline{P}}_K - \underline{F}_\varphi - \sum_{\alpha} n_\alpha \frac{\partial \varphi_\alpha}{\partial \underline{r}} \qquad (3.3 - 2)$$

The kinetic portion of the pressure tensor, $\underline{\underline{P}}_K$, is given by the familiar expression:

$$\underline{\underline{P}}_K = \sum_{\alpha} m_\alpha \int f_\alpha^{(1)} \underline{V}_\alpha \underline{V}_\alpha \, d\underline{V}_\alpha \qquad (3.3 - 3)$$

The development of the collisional portion of the pressure tensor, which is contained in F_φ, parallels that of Irving and Kirkwood.[17] F_φ involves the combination of equation (3.3 - 1) and the second term on the right side of equation (3.1 - 2). Carrying out the differentiation with respect to $\underline{v}_k$, and all but two of the N integrations, we have

$$F_\varphi = \frac{1}{2}\sum_{\alpha}\sum_{\beta}\int f_{\alpha\beta}^{(2)} \left[\frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_\alpha}\delta(\underline{r}_\alpha - \underline{r}) + \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_\beta}\delta(\underline{r}_\beta - \underline{r})\right] d\underline{r}_\alpha d\underline{r}_\beta d\underline{v}_\alpha d\underline{v}_\beta \qquad (3.3 - 4)$$

Since $\varphi_{\alpha\beta}$ is of the form $\varphi_{\alpha\beta}(|\underline{r}_\alpha - \underline{r}_\beta|)$, we can write

$$\frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_\alpha} = -\frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_\beta} = \frac{\underline{r}_{\alpha\beta}}{r_{\alpha\beta}}\frac{\partial \varphi_{\alpha\beta}}{\partial r_{\alpha\beta}} \qquad (3.3 - 5)$$

The delta function of $\underline{r}_\beta$ can be expanded in a Taylor series about $\underline{r}_\alpha$. Making use of the symmetry of the delta function, we obtain:

$$\delta(\underline{r}_\beta-\underline{r})-\delta(\underline{r}_\alpha-\underline{r})=\frac{\partial}{\partial\underline{r}}\cdot\left\{\underline{r}_{\alpha\beta}\left[1+\frac{1}{2}\underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial\underline{r}}\right]\delta(\underline{r}_\alpha-\underline{r})\right\}+\cdots \qquad (3.3-6)$$

We now make the change of variable from $(\underline{r}_\alpha,\underline{r}_\beta)$ to $(\underline{r}_\alpha,\underline{r}_{\alpha\beta})$ to obtain:

$$F_\varphi=-\frac{\partial}{\partial\underline{r}}\cdot\underline{\underline{P}}_\varphi$$

where $\underline{\underline{P}}_\varphi$ is the collisional portion of the pressure tensor:

$$\underline{\underline{P}}_\varphi=\frac{1}{2}\sum_{\alpha,\beta}\int f^{(2)}_{\alpha\beta}\,\frac{\underline{r}_{\alpha\beta}\underline{r}_{\alpha\beta}}{r_{\alpha\beta}}\,\frac{\partial\phi_{\alpha\beta}}{\partial r_{\alpha\beta}}\left(1+\frac{1}{2}\underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial\underline{r}}\right)\delta(\underline{r}_\alpha-r)\,d\underline{r}_\alpha\,d\underline{r}_{\alpha\beta}\,d\underline{v}_\alpha\,d\underline{v}_\beta \qquad (3.3-7)$$

To obtain $\underline{\underline{P}}_\varphi$ as a functional of $f^{(1)}$, we use equation (2.3 - 12) and the bar notation[18] to denote the position dependence of $f^{(1)}_\beta$ on $\underline{r}_\alpha$:

$$\bar{f}^{(1)}_\beta=f^{(1)}_\beta(\underline{r}_\alpha,\underline{v}_\beta)$$

to write a Taylor series expansion of $f^{(2)}_{\alpha\beta}$ about $\underline{r}_\alpha$:

$$f^{(2)}_{\alpha\beta}=\bar{Y}_{\alpha\beta[0]}\bar{f}^{(1)'}_\alpha\bar{f}^{(1)'}_\beta+(\underline{R}_{\alpha\beta}-\underline{r}_\alpha)\cdot\frac{\partial\bar{Y}_{\alpha\beta[0]}}{\partial\underline{r}_\alpha}\bar{f}^{(1)'}_\alpha\bar{f}^{(1)'}_\beta$$

$$+\bar{Y}_{\alpha\beta[0]}\left\{(\underline{r}'_\alpha-\underline{r}_\alpha)\cdot\frac{\partial\bar{f}^{(1)'}_\alpha}{\partial\underline{r}_\alpha}\bar{f}^{(1)'}_\beta+(\underline{r}'_\beta-\underline{r}_\alpha)\cdot\frac{\partial\bar{f}^{(1)'}_\beta}{\partial\underline{r}_\alpha}\bar{f}^{(1)'}_\alpha\right\} \qquad (3.3-8)$$

Using only the leading term in the density expansion of $\bar{Y}_{\alpha\beta[0]}$

$$\bar{Y}_{\alpha\beta[0]}=1+n\,\bar{Y}^{(1)}_{\alpha\beta[0]}+\mathcal{O}(n^2) \qquad (3.3-9)$$

and the fact that $\underline{R}_{\alpha\beta} = \underline{R}'_{\alpha\beta}$, we can write:

$$f^{(2)}_{\alpha\beta} = \overline{Y_{\alpha\beta[0]}}\,\bar{f}^{(1)'}_{\alpha}\,\bar{f}^{(1)'}_{\beta} - \frac{1}{2}\underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial\underline{r}_{\alpha}}\left[\bar{f}^{(1)'}_{\alpha}\,\bar{f}^{(1)'}_{\beta}\right]$$

$$+\frac{1}{2}\underline{r}'_{\alpha\beta}\cdot\left[\frac{\partial\bar{f}^{(1)'}_{\alpha}}{\partial\underline{r}_{\alpha}}\,\bar{f}^{(1)'}_{\beta} - \bar{f}^{(1)'}_{\alpha}\,\frac{\partial\bar{f}^{(1)'}_{\beta}}{\partial\underline{r}_{\alpha}}\right] \tag{3.3 - 10}$$

The expression for $\underline{\underline{P}}_{\varphi}$ can now be simplified by carrying out the integration over $\underline{r}_{\alpha}$ to obtain:

$$\underline{\underline{P}}_{\varphi} = -\frac{1}{2}\sum_{\alpha,\beta}\int\frac{\underline{r}_{\alpha\beta}\underline{r}_{\alpha\beta}}{r_{\alpha\beta}}\frac{\partial\varphi_{\alpha\beta}}{\partial r_{\alpha\beta}}\Big\{Y_{\alpha\beta[0]}\,f^{(1)'}_{\alpha}\,f^{(1)'}_{\beta}$$

$$+\frac{1}{2}\underline{r}'_{\alpha\beta}\left[\frac{\partial f^{(1)'}_{\alpha}}{\partial\underline{r}}\,f^{(1)'}_{\beta} - f^{(1)'}_{\alpha}\,\frac{\partial f^{(1)'}_{\beta}}{\partial\underline{r}}\right]\Big\}\,d\underline{r}_{\alpha\beta}\,d\underline{v}_{\alpha}\,d\underline{v}_{\beta} \tag{3.3 - 11}$$

The f's are now all functions of $\underline{r}$ and $Y_{\alpha\beta[0]}$ has the form $Y_{\alpha\beta[0]}(\underline{r}, \underline{r}_{\alpha\beta})$

Writing the total pressure tensor $\underline{\underline{P}}$ as

$$\underline{\underline{P}} = \underline{\underline{P}}_{K} + \underline{\underline{P}}_{\varphi}$$

we have the final form for the equation of change governing momentum flow:

$$\frac{\partial\underline{u}}{\partial t} + \underline{u}\cdot\frac{\partial}{\partial\underline{r}}\underline{u} = -\frac{1}{\rho}\frac{\partial}{\partial\underline{r}}\cdot\underline{\underline{P}} - \frac{1}{\rho}\sum_{\alpha}n_{\alpha}\frac{\partial\varphi_{\alpha}}{\partial\underline{r}} \tag{3.3 - 12}$$

$\underline{\underline{P}}_{\varphi}$ contains the effects of collisional transfer, and through the function $Y_{\alpha\beta[0]}$ the effects of three body collisions.

3.4 Equation of Energy Balance

The equation describing the conservation of energy in the system is derived by taking ψ to be:

$$\psi = \frac{1}{2}\sum_{i} m_i v_i^2 \delta(\underline{r}_i - \underline{r}) + \frac{1}{2}\sum_{i \neq j}\sum \varphi_{ij}\,\delta(\underline{r}_j - \underline{r}) \tag{3.4 - 1}$$

The development then parallels that of the previous section. The total energy density u is the sum of kinetic and collisional terms:

$$u = u_K + u_\varphi \tag{3.4 - 2}$$

where

$$\rho u_K = \frac{1}{2}\sum_{\alpha} m_\alpha \int V_\alpha^2\, f_\alpha^{(1)}\, d\underline{v}_\alpha \tag{3.4 - 3}$$

and

$$\rho u_\varphi = \frac{1}{2}\sum_{\alpha\beta}\int f_{\alpha\beta}^{(2)}\,\varphi_{\alpha\beta}\,\delta(\underline{r}_\beta - \underline{r})\, d\underline{r}_\alpha\, d\underline{r}_\beta\, d\underline{v}_\alpha\, d\underline{v}_\beta \tag{3.4 - 4}$$

The time evolution of u is then given by the usual equation:

$$\rho\left\{\frac{\partial u}{\partial t} + \underline{u}\cdot\frac{\partial u}{\partial \underline{r}}\right\} = -\frac{\partial}{\partial \underline{r}}\cdot \underline{q} - \underline{\underline{P}} : \frac{\partial}{\partial \underline{r}}\underline{u} - \sum_{\alpha} m_\alpha \overline{\underline{V}}_\alpha \cdot \frac{\partial \phi_\alpha}{\partial \underline{r}} \tag{3.4 - 5}$$

The energy flux vector is the sum of two parts. The kinetic part is the usual

$$q_K = \frac{1}{2}\sum_{\alpha} m_\alpha \int V_\alpha^2\, \underline{V}_\alpha\, f_\alpha^{(1)}\, d\underline{V}_\alpha \tag{3.4 - 6}$$

After lengthy manipulations entirely analogous to those used in the development of $\underline{\underline{P}}_{\varphi}$, the collisional contribution to $\underline{q}$ is found to be:

$$
\begin{aligned}
\underline{q}_{\varphi} = -\frac{1}{2}\sum_{\alpha,\beta}\int \Big[\underline{G}_{\alpha\beta} + \frac{1}{2}\frac{(m_\beta - m_\alpha)}{M_{\alpha\beta}}\underline{g}_{\alpha\beta}\Big]\cdot
&\Bigg[\frac{\underline{r}_{\alpha\beta}\underline{r}_{\alpha\beta}}{r_{\alpha\beta}}\frac{\partial\varphi_{\alpha\beta}}{\partial r_{\alpha\beta}}\Big\{Y_{\alpha\beta(0)}f_\alpha^{(1)'}f_\beta^{(1)'} + \frac{1}{2}\underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial\underline{r}}\left(f_\alpha^{(1)'}f_\beta^{(1)'}\right) \\
&+ \frac{1}{2}\underline{r}_{\alpha\beta}'\cdot\left(\frac{\partial f_\alpha^{(1)'}}{\partial \underline{r}}f_\beta^{(1)'} - f_\alpha^{(1)'}\frac{\partial f_\beta^{(1)'}}{\partial\underline{r}}\right)\Big\} \\
&- \varphi_{\alpha\beta}\underline{\underline{U}}\Big\{Y_{\alpha\beta(0)}f_\alpha^{(1)'}f_\beta^{(1)'} + \underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial\underline{r}}\left(f_\alpha^{(1)'}f_\beta^{(1)'}\right) \\
&+ \frac{1}{2}\underline{r}_{\alpha\beta}'\cdot\left(\frac{\partial f_\alpha^{(1)'}}{\partial \underline{r}}f_\beta^{(1)'} - f_\alpha^{(1)'}\frac{\partial f_\beta^{(1)'}}{\partial\underline{r}}\right)\Big\}\Bigg]\, d\underline{r}_{\alpha\beta}\, d\underline{v}_\alpha\, d\underline{v}_\beta
\end{aligned}
\qquad (3.4-7)
$$

As with $\underline{\underline{P}}_{\varphi}$, this is a generalization to mixtures of the expression of Irving and Kirkwood.[17]

In later chapters, the energy flux vector and the pressure tensor are developed further, eventually relating the transport coefficients to the perturbation solutions.

CHAPTER IV

THE PERTURBATION EQUATIONS

In this chapter a perturbation equation is developed which is later split into fine separate integral equations, one associated with each of the gradients. Since the theory is developed only through first order, only quantities linear in the gradients are retained.

4.1 Development of the Perturbation Equations

The quantity $Y_{\alpha\beta[0]} f_\alpha^{(1)'} f_\beta^{(1)'}$ appearing in equation (2.3 - 13) is a function of $\underline{R}_{\alpha\beta}$, $\underline{r}'_\alpha$ and $\underline{r}'_\beta$. Since the left side of equation (2.3 - 13) contains $f_\alpha^{(1)}(\underline{r}_\alpha)$, we expand $Y_{\alpha\beta[0]} f_\alpha^{(1)'} f_\beta^{(1)'}$ about $\underline{r}_\alpha$ in a Taylor series.(13b) Utilizing the bar notation of section 3.3, the parameter ϵ is introduced to order the terms according to the power of the gradient. Equation (2.3 - 13) is then written:

$$\epsilon\left\{\frac{\partial}{\partial t} + \underline{v}_\alpha\cdot\frac{\partial}{\partial \underline{r}_\alpha} - \frac{1}{m_\alpha}\frac{\partial \phi_\alpha}{\partial \underline{r}_\alpha}\cdot\frac{\partial}{\partial \underline{v}_\alpha}\right\}\bar{f}_\alpha^{(1)} = \sum_\beta \frac{1}{\mu_{\alpha\beta}}\int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}}\cdot$$

$$\left\{\bar{Y}_{\alpha\beta[0]}\bar{f}_\alpha^{(1)'}\bar{f}_\beta^{(1)'} + \epsilon(\underline{R}_{\alpha\beta}-\underline{r}_\alpha)\cdot\frac{\partial \bar{Y}_{\alpha\beta[0]}}{\partial \underline{r}_\alpha}\bar{f}_\alpha^{(1)'}\bar{f}_\beta^{(1)'}\right. \qquad (4.1 - 1)$$

$$\left. + \epsilon(\underline{r}'_\alpha-\underline{r}_\alpha)\bar{Y}_{\alpha\beta[0]}\frac{\partial \bar{f}_\alpha^{(1)'}}{\partial \underline{r}_\alpha}\bar{f}_\beta^{(1)'} + \epsilon(\underline{r}'_\beta-\underline{r}_\alpha)\bar{Y}_{\alpha\beta[0]}\bar{f}_\alpha^{(1)'}\frac{\partial \bar{f}_\beta^{(1)'}}{\partial \underline{r}_\alpha}\right\}d\underline{r}_\alpha d\underline{r}_\beta + O(\epsilon^2)$$

The distribution function $f_\alpha^{(1)}$ can now be expanded in a perturbation series:

$$f_\alpha^{(1)} = f_{\alpha[0]}^{(1)} + \epsilon f_{\alpha[1]}^{(1)} + \ldots \qquad (4.1 - 2)$$

where $f^{(1)}_{\alpha[0]}$ is the equilibrium distribution function. Incorporating the perturbation series into equation (4.1 - 1), the parameter ϵ is used to obtain the zeroth order equation:

$$\sum_{\beta}\frac{1}{\mu_{\alpha\beta}}\int\frac{\partial\varphi_{\alpha\beta}}{\partial\underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial\underline{g}_{\alpha\beta}}\left\{\bar{Y}_{\alpha\beta[0]}\,\bar{f}^{(1)'}_{\alpha[0]}\,\bar{f}^{(1)'}_{\beta[0]}\right\}d\underline{r}_{\alpha\beta}\,d\underline{v}_{\beta}=0 \qquad (4.1 - 3)$$

and the first order equation:

$$\left\{\frac{\partial}{\partial t}+\underline{v}_{\alpha}\cdot\frac{\partial}{\partial\underline{r}_{\alpha}}-\frac{1}{m_{\alpha}}\frac{\partial\varphi_{\alpha}}{\partial\underline{r}_{\alpha}}\cdot\frac{\partial}{\partial\underline{v}_{\alpha}}\right\}\bar{f}^{(1)}_{\alpha[0]}-\sum_{\beta}\frac{1}{\mu_{\alpha\beta}}\int\frac{\partial\varphi_{\alpha\beta}}{\partial\underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial\underline{g}_{\alpha\beta}}$$

$$\left\{(\underline{R}_{\alpha\beta}-\underline{r}_{\alpha})\cdot\frac{\partial\bar{Y}_{\alpha\beta[0]}}{\partial\underline{r}_{\alpha}}\bar{f}^{(1)'}_{\alpha[0]}\,\bar{f}^{(1)'}_{\beta[0]}+(\underline{r}'_{\alpha}-\underline{r}_{\alpha})\bar{Y}_{\alpha\beta[0]}\frac{\partial\bar{f}^{(1)'}_{\alpha[0]}}{\partial\underline{r}_{\alpha}}\bar{f}^{(1)'}_{\beta[0]}\right.$$

$$\left.+(\underline{r}'_{\beta}-\underline{r}_{\alpha})\bar{Y}_{\alpha\beta[0]}\bar{f}^{(1)'}_{\alpha[0]}\frac{\partial\bar{f}^{(1)'}_{\beta[0]}}{\partial\underline{r}_{\alpha}}\right\}d\underline{r}_{\alpha\beta}\,d\underline{v}_{\beta} \qquad (4.1 - 4)$$

$$=\sum_{\beta}\frac{1}{\mu_{\alpha\beta}}\int\frac{\partial\varphi_{\alpha\beta}}{\partial\underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial\underline{g}_{\alpha\beta}}\left\{\bar{Y}_{\alpha\beta[0]}\left[\bar{f}^{(1)'}_{\alpha[1]}\,\bar{f}^{(1)'}_{\beta[0]}+\bar{f}^{(1)'}_{\alpha[0]}\,\bar{f}^{(1)'}_{\beta[1]}\right]\right\}d\underline{r}_{\alpha\beta}\,d\underline{v}_{\beta}$$

The equilibrium forms of $f^{(1)}_{\alpha}$ and $Y_{\alpha\beta}$ can be readily obtained from the equilibrium forms of the B.B.G.K.Y. equations for $f^{(1)}$ and $f^{(2)}$. Following the procedure of Hoffman and Curtiss,[13a] we can show that in the absence of external forces:

$$f^{(2)}_{\alpha\beta[0]} = Y_{\alpha\beta[0]}\,f^{(1)}_{\alpha[0]}\,f^{(1)}_{\beta[0]} \qquad (4.1 - 5)$$

where

$$f_{\alpha[0]}^{(1)} = n_\alpha \left(\frac{m_\alpha}{2\pi kT}\right)^{3/2} e^{-m_\alpha V_\alpha^2/2kT} \tag{4.1 - 6}$$

$$y_{\alpha\beta[0]} = Y_{\alpha\beta[0]}\, e^{-\varphi_{\alpha\beta}/kT} \tag{4.1 - 7}$$

and

$$Y_{\alpha\beta} = 1 + n \sum_\gamma x_\gamma \int d\underline{r}_\gamma \left(e^{-\varphi_{\alpha\gamma}/kT} - 1\right)\left(e^{-\varphi_{\beta\gamma}/kT} - 1\right) \tag{4.1 - 8}$$

Equation (4.1 - 4) can be simplified by density considerations. Since only terms through order n^2 are retained, we drop those terms arising from $Y_{\alpha\beta[0]}$ which are of order n^3. Using also the method of section 3.3, equation (4.1 - 4) reduces to

$$\left\{\frac{\partial}{\partial t} + \underline{v}_\alpha \cdot \frac{\partial}{\partial \underline{r}_\alpha} - \frac{1}{m_\alpha}\frac{\partial \varphi_\alpha}{\partial \underline{r}_\alpha}\cdot\frac{\partial}{\partial \underline{v}_\alpha}\right\} \bar{f}_{\alpha[0]}^{(1)} - \frac{1}{2}\sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}}$$

$$\left\{ \underline{r}_{\alpha\beta}\cdot\frac{\partial}{\partial \underline{r}}\left[\bar{f}_{\alpha[0]}^{(1)\prime}\bar{f}_{\beta[0]}^{(1)\prime}\right] + \underline{r}_{\alpha\beta}^{\prime}\left[\bar{f}_{\alpha[0]}^{(1)\prime}\frac{\partial \bar{f}_{\beta[0]}^{(1)\prime}}{\partial \underline{r}} - \frac{\partial \bar{f}_{\alpha[0]}^{(1)\prime}}{\partial r}\bar{f}_{\beta[0]}^{(1)\prime}\right]\right\}$$

$$\cdot\, d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \tag{4.1 - 9}$$

$$= \sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}}\left\{ Y_{\alpha\beta[0]}\left[\bar{f}_{\alpha[1]}^{(1)\prime}\bar{f}_{\alpha[0]}^{(1)\prime} + \bar{f}_{\alpha[0]}^{(1)\prime}\bar{f}_{\beta[1]}^{(1)\prime}\right]\right\} d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta$$

where now the bar notation indicates that all the f's are functions of $\underline{r}$. To simplify the notation, we henceforth use the abbreviation

$$f_\alpha = f_\alpha(\underline{r}, \underline{v}_\alpha) = \bar{f}^{(1)}_{\alpha[0]}(\underline{r}, \underline{v}_\alpha)$$

We define the perturbation function ϕ by the following product:

$$\bar{f}^{(1)}_{\alpha[1]} = \bar{f}^{(1)}_{\alpha[0]}\,\phi_\alpha = f_\alpha \phi_\alpha \tag{4.1 - 10}$$

Equation (4.1 - 9) can now be written as an inhomogeneous linear integral equation for the function ϕ:

$$J_\alpha = \sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ Y_{\alpha\beta[0]}\, f'_\alpha f'_\beta (\phi'_\alpha + \phi'_\beta) \right\} d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \tag{4.1 - 11}$$

where the inhomogeniety J_α is

$$J_\alpha = \left\{ \frac{\partial}{\partial t} + \underline{v}_\alpha \cdot \frac{\partial}{\partial \underline{r}} - \frac{1}{m_\alpha} \frac{\partial \phi_\alpha}{\partial r} \cdot \frac{\partial}{\partial \underline{v}_\alpha} \right\} f_\alpha - \sum_\beta \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}}$$

$$\left\{ \underline{r}_{\alpha\beta} \cdot \frac{\partial}{\partial \underline{r}} \left[f'_\alpha f'_\beta \right] + \underline{r}'_{\alpha\beta} \cdot \left[f'_\alpha \frac{\partial f'_\beta}{\partial \underline{r}} - \frac{\partial f'_\alpha}{\partial \underline{r}} f'_\beta \right] \right\} d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \tag{4.1 - 12}$$

After writing the inhomogeneous terms as a linear combination of the spatial gradients, the linearity in ϕ of equation (4.1 - 11) suggests that we write the perturbation as a linear combination of the same gradients. This will then be the basis of our five individual perturbation equations.

4.2 Evaluation of the Inhomogeneous Terms

In this section the inhomogeniety J_α, equation (4.1 - 12), is transformed into a linear combination of the macroscopic gradients.

The first term in the integral of equation (4.1 - 12) can be treated in the manner of Snider and Curtiss,[14a] yielding a generalization of their J_2:

$$J_{2\alpha} = -\sum_\beta \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ \underline{r}_{\alpha\beta} \cdot \frac{\partial}{\partial \underline{r}} \left[f_\alpha' f_\beta' \right] \right\} d\underline{r}_{\alpha\beta} \, d\underline{v}_\beta$$

$$= -\frac{\partial}{\partial \underline{r}} \cdot \left(\underline{V}_\alpha f_\alpha \sum_\beta B_{\alpha\beta} n_\beta \right) \qquad (4.2 - 1)$$

where the second virial coefficient $B_{\alpha\beta}$ for the potential $\varphi_{\alpha\beta}$ is given by the expression:

$$B_{\alpha\beta} = -\frac{2\pi}{3kT} \int_0^\infty \frac{\partial \varphi_{\alpha\beta}}{\partial r_{\alpha\beta}} e^{-\varphi_{\alpha\beta}/kT} r_{\alpha\beta}^3 \, dr_{\alpha\beta} \qquad (4.2 - 2)$$

Equation (4.2 - 1) may now be written:

$$-J_{2\alpha} = -f_\alpha \sum_\beta B_{\alpha\beta} n_\beta \frac{\partial}{\partial \underline{r}} \cdot \underline{u} + \sum B_{\alpha\beta} n_\beta \underline{V}_\alpha \cdot \frac{\partial f_\alpha}{\partial \underline{r}}$$

$$+ f_\alpha \underline{V}_\alpha \sum_\beta \left\{ B_{\alpha\beta} \frac{\partial n_\beta}{\partial \underline{r}} + n_\beta \frac{\partial B_{\alpha\beta}}{\partial T} \frac{\partial T}{\partial \underline{r}} \right\} \qquad (4.2 - 3)$$

The streaming portion of J_α can be evaluated using equation (4.1 - 6) for f_α. Using the dimensionless velocity $\underline{W}_\alpha$ defined by:

$$\underline{W}_\alpha = \left(\frac{m_\alpha}{2kT} \right)^{\frac{1}{2}} \underline{V}_\alpha \qquad (4.2 - 4)$$

we find that:

$$\left\{\frac{\partial}{\partial t} + \mathbf{v}_\alpha \cdot \frac{\partial}{\partial \mathbf{r}} - \frac{1}{m_\alpha}\frac{\partial \phi_\alpha}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{v}_\alpha}\right\} f_\alpha = f_\alpha \left\{ \frac{1}{kT}\mathbf{V}_\alpha \cdot \frac{\partial \phi_\alpha}{\partial \mathbf{r}} \right.$$

$$+ \frac{1}{n_\alpha}\left[\frac{\partial n_\alpha}{\partial t} + \mathbf{V}_\alpha \cdot \frac{\partial n_\alpha}{\partial \mathbf{r}} + \mathbf{u} \cdot \frac{\partial n_\alpha}{\partial \mathbf{r}}\right] + \left(W_\alpha^2 - \frac{3}{2}\right)\left[\frac{\partial \ln T}{\partial t}\right. \qquad (4.2 - 5)$$

$$\left. \left. + \mathbf{V}_\alpha \cdot \frac{\partial \ln T}{\partial \mathbf{r}} + \mathbf{u} \cdot \frac{\partial \ln T}{\partial \mathbf{r}}\right] + \frac{m_\alpha}{kT}\left[\mathbf{V}_\alpha \cdot \frac{\partial \mathbf{u}}{\partial t} + \mathbf{V}_\alpha \mathbf{V}_\alpha : \frac{\partial}{\partial \mathbf{r}}\mathbf{u} + \mathbf{V}_\alpha \mathbf{u} : \frac{\partial}{\partial \mathbf{r}}\mathbf{u}\right]\right\}$$

The equations of change are used to eliminate the time derivatives in equation (4.2 - 5). Since J_α is evaluated using the equilibrium distribution function, the fluxes appearing in the equations of change are also evaluated using the equilibrium distribution function. At equilibrium $\mathbf{q}$ and $\overline{\mathbf{V}_\alpha}$ are zero, while $\underline{\underline{P}}$ is the static pressure P times the unit tensor $\underline{\underline{U}}$. In this approximation the equations of change are

$$\frac{\partial n_\alpha}{\partial t} + \mathbf{u} \cdot \frac{\partial n_\alpha}{\partial \mathbf{r}} = 0 \qquad (4.2 - 6)$$

$$\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \frac{\partial}{\partial \mathbf{r}}\mathbf{u} = -\frac{1}{\rho}\left\{\frac{\partial P}{\partial \mathbf{r}} + \sum_\beta n_\beta \frac{\partial \phi_\beta}{\partial \mathbf{r}}\right\} \qquad (4.2 - 7)$$

$$\frac{\partial \ln T}{\partial t} + \mathbf{u} \cdot \frac{\partial \ln T}{\partial \mathbf{r}} = -\frac{1}{\rho \hat{C}_v}\left(\frac{\partial P}{\partial T}\right)_{\rho, \{x_\alpha\}} \frac{\partial}{\partial \mathbf{r}} \cdot \mathbf{u} \qquad (4.2 - 8)$$

Using the equilibrium distribution function, equations (3.3 - 3) and (3.3 - 11) give the static pressure

$$P = n k T (1 + n B) \tag{4.2 - 9}$$

where the second virial coefficient B is

$$B = \sum_{\alpha,\beta} B_{\alpha\beta} x_\alpha x_\beta \tag{4.2 - 10}$$

and the mole fraction x_α is

$$x_\alpha = \frac{n_\alpha}{n} \tag{4.2 - 11}$$

The streaming terms can thus be reduced to:

$$\left\{ \frac{\partial}{\partial t} + \underline{v}_\alpha \cdot \frac{\partial}{\partial \underline{r}} - \frac{1}{m_\alpha} \frac{\partial \varphi_\alpha}{\partial r} \cdot \frac{\partial}{\partial \underline{v}_\alpha} \right\} f_\alpha = f_\alpha \left\{ \frac{1}{kT} \underline{V}_\alpha \cdot \frac{\partial \varphi_\alpha}{\partial \underline{r}} \right.$$

$$+ 2 \underline{W}_\alpha \underline{W}_\alpha : \frac{\partial}{\partial \underline{r}} \underline{u} - \frac{1}{\rho \hat{C}_v} \left(\frac{\partial P}{\partial T} \right)_{\rho, \{x_\alpha\}} \left(W_\alpha^2 - \frac{3}{2} \right) \frac{\partial}{\partial \underline{r}} \cdot \underline{u} - \frac{\partial}{\partial \underline{r}} \cdot \underline{u} \tag{4.2 - 12}$$

$$\left. + \underline{V}_\alpha \cdot \frac{\partial \ln n_\alpha}{\partial \underline{r}} - \frac{m_\alpha}{\rho k T} \underline{V}_\alpha \cdot \frac{\partial P}{\partial \underline{r}} + \left(W_\alpha^2 - \frac{3}{2} \right) \underline{V}_\alpha \cdot \frac{\partial \ln T}{\partial \underline{r}} \right\}$$

Equation (4.2 - 9) is used to transform the term containing $\frac{\partial P}{\partial \underline{r}}$ to:

$$-\frac{n_\alpha m_\alpha}{\rho}\left(1+nB\right)\underline{V}_\alpha\cdot\frac{\partial \ln P}{\partial \underline{r}}$$

Several relations are required in order to transform the combination of $J_{2\alpha}$ and the streaming terms. The first is the straightforward identity:

$$\underline{V}_\alpha\cdot\frac{\partial \ln n_\alpha}{\partial \underline{r}} = \frac{n}{n_\alpha}\underline{V}_\alpha\frac{\partial X_\alpha}{\partial \underline{r}} + \underline{V}_\alpha\cdot\frac{\partial \ln n}{\partial \underline{r}} \qquad (4.2 - 13)$$

The second involves transforming derivatives of the temperature into derivatives of n, P and $\{x_\alpha\}$. Starting with equation (4.2 - 9), one can derive:

$$\frac{\partial \ln T}{\partial \underline{r}} = \left\{1 - nT\sum_{\beta,\gamma}\frac{\partial B_{\beta\gamma}}{\partial T}X_\beta X_\gamma\right\}\cdot\left\{\frac{\partial \ln P}{\partial \underline{r}}\right.$$

$$\left.-(1+nB)\frac{\partial \ln n}{\partial \underline{r}} - 2n\sum_{\beta,\gamma}B_{\beta\gamma}X_\beta\frac{\partial X_\gamma}{\partial \underline{r}}\right\} \qquad (4.2 - 14)$$

Using these expressions, we then cast the sum of the streaming terms, equation (4.2 - 12) and $-J_{2\alpha}$, equation (4.2 - 3), into the following form:

$$\left\{\frac{\partial}{\partial t} + \underline{v}_\alpha\cdot\frac{\partial}{\partial \underline{r}} - \frac{1}{m_\alpha}\frac{\partial \varphi_\alpha}{\partial \underline{r}}\cdot\frac{\partial}{\partial \underline{v}_\alpha}\right\}f_\alpha - J_{2\alpha} = f_\alpha\left\{\left(1+n\sum_\beta B_{\alpha\beta}X_\beta\right)\left(W_\alpha^2-\frac{3}{2}\right)\underline{V}_\alpha\cdot\frac{\partial \ln T}{\partial \underline{r}}\right.$$

$$+2\left(1+n\sum_\beta B_{\alpha\beta}X_\beta\right)\underline{W}_\alpha\underline{W}_\alpha:\left(\frac{\partial}{\partial \underline{r}}\underline{u} - \frac{1}{3}\frac{\partial}{\partial \underline{r}}\cdot\underline{u}\,\underline{\underline{U}}\right) \qquad (4.2 - 15)$$

$$\left.+\left[\frac{2}{3}\left(1+n\sum_\beta B_{\alpha\beta}X_\beta\right) - \frac{1}{\rho C_v}\left(\frac{\partial P}{\partial T}\right)_{\rho,\{X_\alpha\}}\right]\left(W_\alpha^2-\frac{3}{2}\right)\frac{\partial}{\partial \underline{r}}\cdot\underline{u} + \frac{n}{n_\alpha}\underline{V}_\alpha\cdot\underline{d}_\alpha\right\}$$

where $\underline{d}_\alpha$, the set of vectors governing diffusion, are defined by the relation:

$$\underline{d}_\alpha = \Big[n X_\alpha T \sum_\beta \frac{\partial B_{\alpha\beta}}{\partial T} X_\beta + X_\alpha \Big(1 + n \sum_\beta B_{\alpha\beta} X_\beta\Big) - n X_\alpha T \sum_{\beta,\gamma} \frac{\partial B_{\beta\gamma}}{\partial T} X_\beta X_\gamma$$

$$- \frac{n X_\alpha m_\alpha}{\rho}\big(1 + n B\big)\Big] \frac{\partial \ln P}{\partial \underline{r}} + n\Big[X_\alpha\Big(\sum_\beta B_{\alpha\beta} X_\beta - B\Big)$$

$$+ X_\alpha T \sum_{\beta,\gamma} \frac{\partial B_{\beta\gamma}}{\partial T} X_\beta X_\gamma - X_\alpha T \sum_\beta \frac{\partial B_{\alpha\beta}}{\partial T} X_\beta\Big] \frac{\partial \ln n}{\partial \underline{r}} \qquad (4.2 - 16)$$

$$+ \Big[\Big(1 + n \sum_\beta B_{\alpha\beta} X_\beta\Big)\frac{\partial X_\alpha}{\partial \underline{r}} + n X_\alpha \sum_\beta B_{\alpha\beta} \frac{\partial X_\beta}{\partial \underline{r}} - 2 n X_\alpha \sum_{\beta\gamma} B_{\beta\gamma} X_\beta \frac{\partial X_\gamma}{\partial \underline{r}}\Big]$$

$$+ \frac{n X_\alpha m_\alpha}{P \rho}\big(1 + n B\big)\Big[\frac{\rho}{m_\alpha} \frac{\partial \varphi_\alpha}{\partial \underline{r}} - n \sum_\beta X_\beta \frac{\partial \varphi_\beta}{\partial \underline{r}}\Big]$$

We note that the vectors $\underline{d}_\alpha$ readily satisfy the condition:

$$\sum_\alpha \underline{d}_\alpha = 0 \qquad (4.2 - 17)$$

The remainder of equation (4.1 - 11)

$$J_{1\alpha} = - \sum_\beta \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \Big\{ \underline{r}'_{\alpha\beta} \Big[f'_\alpha \frac{\partial f'_\beta}{\partial \underline{r}} - \frac{\partial f'_\alpha}{\partial \underline{r}} f'_\beta \Big] d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \qquad (4.2 - 18)$$

yields the collisional transfer effects. The derivatives of the distribution function can be evaluated explicitly using the definition of f_α, equation (4.1 - 6), and the expressions for the peculiar velocities in terms of the relative velocities, equations (2.3 - 5) and (2.3 - 6). The result is analogous to the J_1 of Snider and Curtiss,[14a] but contains terms which are zero for a single component system:

$$
\begin{aligned}
J_{1\alpha} = &-\sum_\beta \frac{1}{\mu_{\alpha\beta}} \frac{\partial}{\partial \underline{r}} \ln\left(\frac{x_\beta}{x_\alpha}\right) \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left(\underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \right) d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \\
&- \sum_\beta \frac{1}{4\mu_{\alpha\beta} kT} \frac{\partial \ln T}{\partial \underline{r}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \Big\{ \Big[(m_\beta - m_\alpha) G^2_{\alpha\beta} \\
&- 4\mu_{\alpha\beta} \underline{g}'_{\alpha\beta} \cdot \underline{G}_{\alpha\beta} + \frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}} \mu_{\alpha\beta} g'^2_{\alpha\beta} \Big] \underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \Big\} d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \qquad (4.2 - 19) \\
&- \sum_\beta \frac{1}{2\mu_{\alpha\beta} kT} \frac{\partial}{\partial \underline{r}} \underline{u} : \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \Big\{ \Big[(m_\beta - m_\alpha) \underline{G} - 2\mu_{\alpha\beta} \underline{g}'_{\alpha\beta} \Big] \underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \Big\} \\
&\cdot d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta
\end{aligned}
$$

$J_{1\alpha}$ consists of six individual integrals, three of which can be eliminated with the use of the identities:

$$\underline{G}_{\alpha\beta} f'_\alpha f'_\beta = -\frac{kT}{M_{\alpha\beta}} \frac{\partial}{\partial \underline{G}_{\alpha\beta}} \left(f'_\alpha f'_\beta \right) \qquad (4.2 - 20)$$

$$G^2_{\alpha\beta} f'_\alpha f'_\beta = \frac{kT}{M_{\alpha\beta}} \left[3 - \frac{\partial}{\partial \underline{G}_{\alpha\beta}} \cdot \underline{G}_{\alpha\beta} \right] f'_\alpha f'_\beta \qquad (4.2 - 21)$$

and

$$\frac{\partial}{\partial \underline{G}_{\alpha\beta}} = \frac{\partial}{\partial \underline{V}_\alpha} + \frac{\partial}{\partial \underline{V}_\beta} \qquad (4.2 - 22)$$

Lengthy but straightforward manipulations yield

$$J_{1\alpha} = -\sum_\beta \left\{ \frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}} \left[\underline{I}^{(3)}_{\alpha\beta} - \frac{3}{2} \underline{I}^{(1)}_{\alpha\beta} \right] + \frac{2\mu_{\alpha\beta}}{M_{\alpha\beta}} \frac{\partial}{\partial \underline{V}_\alpha} \cdot \underline{\underline{I}}^{(2)}_{\alpha\beta} \right.$$

$$\left. - \frac{kT}{2} \frac{(m_\alpha - m_\beta)}{M^2_{\alpha\beta}} \frac{\partial^2}{\partial V_\alpha^2} \underline{I}^{(1)}_{\alpha\beta} \right\} \frac{\partial \ln T}{\partial \underline{r}} \qquad (4.2 - 23)$$

$$- \sum_\beta \left\{ \frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}} \frac{\partial}{\partial \underline{V}_\alpha} \underline{I}^{(1)}_{\alpha\beta} - \frac{2\mu_{\alpha\beta}}{kT} \underline{\underline{I}}^{(2)}_{\alpha\beta} \right\} : \frac{\partial}{\partial \underline{r}} \underline{u}$$

$$- \sum_\beta \underline{I}^{(1)}_{\alpha\beta} \cdot \frac{\partial}{\partial \underline{r}} \ln \left(\frac{x_\beta}{x_\alpha} \right)$$

where

$$\underline{I}^{(1)}_{\alpha\beta} = \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left(\underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \right) d\underline{r}_{\alpha\beta} \, d\underline{V}_\beta \qquad (4.2 - 24)$$

$$\underline{\underline{I}}^{(2)}_{\alpha\beta} = \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left(\underline{g}'_{\alpha\beta} \underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \right) d\underline{r}_{\alpha\beta} \, d\underline{V}_\beta \qquad (4.2 - 25)$$

and

$$\underline{I}^{(3)}_{\alpha\beta} = \frac{1}{2\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left(\frac{\mu_{\alpha\beta} g'^2_{\alpha\beta}}{2kT} \underline{r}'_{\alpha\beta} f'_\alpha f'_\beta \right) d\underline{r}_{\alpha\beta} \, d\underline{V}_\beta \qquad (4.2 - 26)$$

The total inhomogeniety J_α can now be written in the standard form, plus a term involving the gradients of the mole fractions:

$$J_\alpha = -\underline{K}_\alpha \cdot \frac{\partial \ln T}{\partial \underline{r}} - \underline{\underline{L}}_\alpha : \left[\frac{\partial}{\partial \underline{r}} \underline{u} - \frac{1}{3}\frac{\partial}{\partial \underline{r}} \cdot \underline{u}\,\underline{\underline{U}}\right] - M_\alpha \frac{\partial}{\partial \underline{r}} \cdot \underline{u}$$

$$+ \frac{n}{M_\alpha} f_\alpha \underline{V}_\alpha \cdot \underline{d}_\alpha + \sum_\beta \underline{I}^{(1)}_{\alpha\beta} \cdot \frac{\partial}{\partial \underline{r}} \ln\left(\frac{x_\beta}{x_\alpha}\right) \qquad (4.2 - 27)$$

The quantities $\underline{K}_\alpha$, $\underline{\underline{L}}_\alpha$ and M_α are generalizations of those used by Hoffman and Curtiss:

$$\underline{K}_\alpha = -f_\alpha \left(1 + n\sum_\beta B_{\alpha\beta} x_\beta\right)\left(W_\alpha^2 - \frac{5}{2}\right)\underline{V}_\alpha$$

$$(4.2 - 28)$$

$$-\sum_\beta \left\{ \frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}} \left[\underline{I}^{(3)}_{\alpha\beta} - \frac{3}{2}\underline{I}^{(1)}_{\alpha\beta} - \frac{kT}{2M_{\alpha\beta}} \frac{\partial^2}{\partial \underline{V}_\alpha^2} \underline{I}^{(1)}_{\alpha\beta}\right] + \frac{2\mu_{\alpha\beta}}{M_{\alpha\beta}} \frac{\partial}{\partial \underline{V}_\alpha} \cdot \underline{\underline{I}}^{(2)}_{\alpha\beta} \right\}$$

$$\underline{\underline{L}}_\alpha = -2 f_\alpha \left(1 + n \sum_\beta B_{\alpha\beta} x_\beta\right)\left(\underline{W}_\alpha \underline{W}_\alpha - \frac{1}{3} W_\alpha^2 \underline{\underline{U}}\right)$$

$$-\sum_\beta \left\{ \frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}} \left[\frac{\partial}{\partial \underline{V}_\alpha} \underline{I}^{(1)}_{\alpha\beta} - \frac{1}{3} \frac{\partial}{\partial \underline{V}_\alpha} \cdot \underline{I}^{(1)}_{\alpha\beta} \underline{\underline{U}}\right] \right. \qquad (4.2 - 29)$$

$$\left. - \frac{2\mu_{\alpha\beta}}{kT} \left[\underline{\underline{I}}^{(2)}_{\alpha\beta} - \frac{1}{3} \underline{\underline{I}}^{(2)}_{\alpha\beta} : \underline{\underline{U}}\,\underline{\underline{U}}\right] \right\}$$

and

$$M_\alpha = -f_\alpha\left[\frac{2}{3}\left(1+n\sum_\beta B_{\alpha\beta}X_\beta\right) - \frac{1}{\rho \hat{C}_v}\left(\frac{\partial P}{\partial T}\right)_{\rho,\{x_\alpha\}}\right]\left(\omega_\alpha^2 - \frac{3}{2}\right)$$

(4.2 - 30)

$$-\frac{1}{3}\sum_\beta\left[\frac{(m_\alpha - m_\beta)}{M_{\alpha\beta}}\frac{\partial}{\partial \underline{V}_\alpha}\cdot \underline{\underline{I}}^{(1)}_{\alpha\beta} - \frac{2\mu_{\alpha\beta}}{kT}\underline{\underline{I}}^{(2)}_{\alpha\beta} : \underline{\underline{U}}\right]$$

The separation of the inhomogeniety associated with diffusion into two separate terms, the terms in the $\underline{d}_\alpha$ and the terms in $\frac{\partial X_\alpha}{\partial \underline{r}}$, is a formality, which has been introduced as a matter of convenience.

4.3 Perturbation Function ϕ

The perturbation is now written as a linear combination of the same gradients as appear in the inhomogeniety J_α, equation (4.2 - 27):

$$\phi_\alpha = -\underline{A}_\alpha\cdot\frac{\partial \ln T}{\partial \underline{r}} - \underline{\underline{B}}_\alpha : \left(\frac{\partial}{\partial \underline{r}}\underline{u} - \frac{1}{3}\frac{\partial}{\partial \underline{r}}\cdot\underline{u}\,\underline{\underline{U}}\right) - E_\alpha\frac{\partial}{\partial \underline{r}}\cdot\underline{u}$$

(4.3 - 1)

$$+ n\sum_\beta \underline{C}_{\alpha\beta}\cdot\underline{d}_\beta + n\sum_\beta \underline{E}_{\alpha\beta}\cdot\frac{\partial X_\beta}{\partial \underline{r}}$$

The five gradients we have chosen for ϕ_α are not independent. However, we require only that the separated equations be solvable, and hence that the sum of the solutions, that is ϕ_α, be a solution to the original equation (4.1 - 11). Since ϕ_α is a function only of $\underline{V}_\alpha$, so also will be $\underline{A}_\alpha$, $\underline{B}_\alpha$, E_α, $\underline{C}_{\alpha\beta}$ and $\underline{E}_{\alpha\beta}$.

We define the integral operator Δ_α of equation (4.1 - 11) to be:

$$\Delta_\alpha(\xi) = \sum_\beta \frac{1}{\mu_{\alpha\beta}}\int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}}\left[Y_{\alpha\beta(0)} f_\alpha' f_\beta'(\xi_\alpha' + \xi_\beta')\right] d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \quad (4.3 - 2)$$

Since equation (4.1 - 11) is linear, we now separate it into five equations. The equation governing thermal conductivity is:

$$\underline{K}_\alpha = \Delta_\alpha(\underline{A}) \tag{4.3 - 3}$$

Shear and bulk viscosity involve the equations for $\underline{\underline{B}}_\alpha$ and E_α:

$$\underline{\underline{L}}_\alpha = \Delta_\alpha(B) \tag{4.3 - 4}$$

and

$$M_\alpha = \Delta_\alpha(E) \tag{4.3 - 5}$$

The two quantities governing diffusion are determined by the equations:

$$\frac{1}{m_\alpha} f_\alpha \underline{V}_\alpha \cdot \underline{d}_\alpha = \Delta_\alpha\left(\sum_\gamma \underline{C}_{\alpha\gamma} \cdot \underline{d}_\gamma\right) \tag{4.3 - 6}$$

and

$$\frac{1}{m}\sum_\beta \underline{\underline{I}}^{(1)}_{\alpha\beta} \cdot \frac{\partial}{\partial \underline{r}} \ln\left(\frac{X_\beta}{X_\alpha}\right) = \Delta_\alpha\left(\sum_\gamma \underline{E}_{\alpha\gamma} \cdot \frac{\partial X_\gamma}{\partial \underline{r}}\right) \tag{4.3 - 7}$$

The vectors $\{\underline{d}_\alpha\}$ are not independent. Hence we desire an equation, in place of equation (4.3 - 6), which does not involve the $\underline{d}_\alpha$. It can readily be shown[18] that a solution of

$$\frac{1}{m_\alpha} f_\alpha \underline{V}_\alpha \left\{ \delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho} \right\} = \Delta_\alpha\left(\underline{C}_{\alpha\gamma}\right) \tag{4.3 - 8}$$

is also a solution of equation (4.3 - 6). In a similar manner, a solution of

$$\frac{1}{M}\sum_{\beta}{}' \frac{1}{X_\alpha X_\beta} \underline{\underline{I}}^{(1)}_{\alpha\beta}\left(X_\alpha \delta_{\beta\gamma} - X_\beta \delta_{\alpha\gamma}\right) = \Delta_\alpha\left(E_{\alpha\gamma}\right) \qquad (4.3 - 9)$$

is a solution of equation (4.3 - 7).

This gives five separate sets of equations, solutions of which can be used to construct a solution to the original equation (4.1 - 11).

4.4 Orthogonality and Auxiliary Conditions

The equations to be solved, equations (4.3 - 3, 4, 5, 8, and 9), are all inhomogeneous linear integral equations. The existence of solutions to these equations is proved by showing that for each equation the inhomogeneiety is orthogonal to the solutions of the corresponding homogeneous equation. The solutions of the homogeneous equations are the well known summational invariants m_α, $m_\alpha \underline{V}_\alpha$ and $m_\alpha V_\alpha^2$. For an arbitrary inhomogeniety J_α, the orthogonality conditions are:

$$\int J_\alpha \, d\underline{V}_\alpha = 0 \qquad (4.4 - 1)$$

$$\sum_\alpha{}' m_\alpha \int J_\alpha \underline{V}_\alpha \, d\underline{V}_\alpha = 0 \qquad (4.4 - 2)$$

and

$$\sum_\alpha{}' m_\alpha \int J_\alpha V_\alpha^2 \, d\underline{V}_\alpha = 0 \qquad (4.4 - 3)$$

We now show that each of the five inhomogenieties satisfies the above three conditions. These fifteen separate conditions can be reduced to seven by the use of the tensor properties of the integrals.(14a)

The only non-trivial condition on the thermal conductivity term $\underline{K}_\alpha$ is

$$\sum_\alpha m_\alpha \int \underline{K}_\alpha V_\alpha \, d\underline{V}_\alpha = 0$$

The first of the five terms of $\underline{K}_\alpha$, equation (4.2 - 28), gives zero on straightforward integration. The second and third terms can be symmetrized on α and β, following which integration over the angles of $\underline{G}_{\alpha\beta}$ gives zero. The fourth term is zero upon application of the same method, following the conversion of $\frac{\partial^2}{\partial V_\alpha^2}$ to $\frac{\partial^2}{\partial G_{\alpha\beta}^2}$ by successive use of the identity (4.2 - 22). The last term may be written in terms of $\underline{G}_{\alpha\beta}$ with the use of equations (4.2 - 20) and (4.2 - 22), and $\frac{\partial}{\partial g_{\alpha\beta}}$ converted into a surface integral which equals zero.

The three conditions on $\underline{\underline{L}}_\alpha$ are all satisfied because $\underline{\underline{L}}_\alpha$ is traceless.

The first of two conditions on M is:

$$\int M_\alpha \, d\underline{V}_\alpha = 0$$

Using equation (4.2 - 30), the first term is zero on direct integration. The second can be converted to a surface integral over $\underline{V}_\alpha$ which is zero, and similarly the third term on converting $\frac{\partial}{\partial g_{\alpha\beta}}$ to a surface integral.

The second condition on M is:

$$\sum_\alpha m_\alpha \int M_\alpha V_\alpha^2 \, d V_\alpha = 0$$

The second of the three terms can be transformed with the use of equations (4.2 - 20), (4.2 - 22), (2.3 - 5) and (2.3 - 6) into a quantity which is symmetric with respect to the interchange of α and β, times $(m_\alpha - m_\beta)$. The sum is therefore zero. Following the method of Snider and Curtiss[14a] and using the relation

$$\rho \hat{C}_v = n C_v \tag{4.3 - 4}$$

we can show that the first and third terms are equal, but opposite in sign, hence giving a zero sum.

The only non trivial condition involving equation (4.3 - 8) is condition (4.4 - 2) which may be written as:

$$\sum_\alpha \frac{m_\alpha}{m_\alpha}\left(\delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho}\right)\int f_\alpha \underline{V}_\alpha \underline{V}_\alpha \, d\underline{V}_\alpha = 0$$

Direct integration shows this to be zero.

Likewise, only condition (4.4 - 2) is involved with equation (4.3 - 9), and when written out in detail is:

$$0 = \sum_{\alpha,\beta} \frac{(X_\alpha \delta_{\beta\gamma} - X_\beta \delta_{\alpha\gamma})}{2\mu_{\alpha\beta} X_\alpha X_\beta} \int m_\alpha \underline{V}_\alpha \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left(\underline{r}'_{\alpha\beta} f'_\alpha f'_\beta\right) d\underline{r}_{\alpha\beta}\, d\underline{g}_{\alpha\beta}\, d\underline{G}_{\alpha\beta}$$

Symmetrizing with respect to α and β, and integrating over the angles of $\underline{G}_{\alpha\beta}$ gives zero.

Thus we have shown that each of the five sets of inhomogenieties satisfies the orthogonality conditions. Hence each of the five sets of equations possesses a solution. This justifies the separation in section 4.3 of the set of equations (4.1 - 11), into five sets of equations (4.3 - 3, 4, 5, 8, and 9).

The uniqueness of the solutions is fixed by a procedure analogous to that of Hoffman and Curtiss.[13b] We require that the non-equilibrium portion of the distribution function, namely the product $f\phi$, be orthogonal to the summational invariants. Stated explicitly, the perturbation function is required to satisfy the conditions:

$$\int f_{\alpha[0]}^{(1)} \phi_\alpha \, d\underline{V}_\alpha = 0 \qquad (4.4-5)$$

$$\sum_\alpha m_\alpha \int f_{\alpha[0]}^{(1)} \phi_\alpha \underline{V}_\alpha \, d\underline{V}_\alpha = 0 \qquad (4.4-6)$$

$$\sum_\alpha m_\alpha \int f_{\alpha[0]}^{(1)} \phi_\alpha V_\alpha^2 \, d\underline{V}_\alpha = 0 \qquad (4.4-7)$$

These are referred to as the auxiliary conditions. These conditions will be used in a later chapter to obtain unique solutions to each equation.

CHAPTER V

SOLUTION OF THE PERTURBATION EQUATIONS

In this chapter we discuss the solution of the five perturbation equations. The first section treats the $\underline{C}_{\alpha\beta}$ equation in detail to illustrate the method[18] while later sections summarize the results for the remaining equations. The various integrals, labeled $R^{(i)}$, encountered in this and the next chapter are tabulated in Appendix A.

5.1 Generalized $\underline{d}$

The unknown coefficients $\underline{C}_{\alpha\beta}$ associated with the generalized diffucion vectors $\underline{d}_{\alpha}$ are determined by:

$$\frac{1}{m_\alpha} f_\alpha \underline{V}_\alpha \left\{ \delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho} \right\}$$

$$= \sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ Y_{\alpha\beta(0)} f_\alpha' f_\beta' \left(\underline{C}_{\alpha\gamma}' + \underline{C}_{\beta\gamma}' \right) \right\} d\underline{r}_{\alpha\beta}\, d\underline{V}_\beta \tag{5.1 - 1}$$

The functions $\underline{C}_{\alpha\gamma}$ are functions only of the vector $\underline{V}_\alpha$, or more conveniently $\underline{W}_\alpha$; hence we may write

$$\underline{C}_{\alpha\gamma} = C_{\alpha\gamma}(W_\alpha^2)\, \underline{W}_\alpha \tag{5.1 - 2}$$

Following the usual Chapman-Enskog procedure, we expand the scalar $C_{\alpha\gamma}(W_\alpha^2)$ in terms of Sonine polynomials $S_{\frac{3}{2}}^{(m)}(W_\alpha^2)$:[19]

$$C_{\alpha\gamma}(W_\alpha^2) = \sum_m c_{\alpha\gamma}^{(m)}\, S_{\frac{3}{2}}^{(m)}(W_\alpha^2) \tag{5.1 - 3}$$

The second auxiliary condition, equation (4.4 - 6), imposes a restriction only on the $c_{\alpha\gamma}^{(0)}$:

$$\sum_{\alpha} n_\alpha m_\alpha^{\frac{1}{2}} C_{\alpha\gamma}^{(0)} = 0 \qquad (5.1 - 4)$$

The standard variational method may now be applied. First we truncate the series (5.1 - 3) keeping only the lowest term $C_{\alpha\gamma} = C_{\alpha\gamma}^{(0)}$, where the superscript is dropped to simplify the notation. Multiplying equation (5.1 - 1) by $S_{\frac{3}{2}}^{(\ell)}(W_\alpha^2)$, we now integrate over $\underline{V}_\alpha$. With the aid of equations (4.1 - 6) and (4.2 - 4), the inhomogeneous portion may be written in terms of the orthogonality condition for $S_{\frac{3}{2}}^{(\ell)}(W_\alpha^2)$:

$$\frac{4kT}{3m_\alpha\sqrt{\pi}}\left\{\delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho}\right\}\int S_{\frac{3}{2}}^{(\ell)}(W_\alpha^2)\, S_{\frac{3}{2}}^{(0)}(W_\alpha^2)\, W_\alpha^3 e^{-W_\alpha^2}\, d(W_\alpha^2)$$

where

$$S_{\frac{3}{2}}^{(0)}(W_\alpha^2) = 1 \qquad (5.1 - 5)$$

The inhomogeniety is then

$$\frac{kT}{m_\alpha}\delta_{\ell 0}\left\{\delta_{\alpha\gamma} - \frac{\rho_\alpha}{\rho}\right\}$$

The identity

$$\frac{1}{\mu_{\alpha\beta}}\frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}}\cdot\frac{\partial}{\partial \underline{g}_{\alpha\beta}} = \underline{g}_{\alpha\beta}\cdot\frac{\partial}{\partial \underline{r}_{\alpha\beta}} - \underline{g}'_{\alpha\beta}\cdot\frac{\partial}{\partial \underline{r}'_{\alpha\beta}} \qquad (5.1 - 6)$$

can be applied to equation (5.1 - 1) to yield

$$\frac{kT}{m_\alpha}\left\{\delta_{\alpha\gamma}-\frac{\rho_\alpha}{\rho}\right\} \tag{5.1 - 7}$$

$$=\sum_\beta \int g_{\alpha\beta}\cdot\frac{\partial}{\partial \underline{r}_{\alpha\beta}}\left\{ Y_{\alpha\beta[0]} f_\alpha' f_\beta' \underline{V}_\alpha\cdot\left(c_{\alpha\gamma}\underline{W}_\alpha'+c_{\beta\gamma}\underline{W}_\beta'\right)\right\} d\underline{r}_{\alpha\beta} d\underline{V}_\alpha d\underline{V}_\beta$$

$$-\sum_\beta \int g_{\alpha\beta}\cdot\frac{\partial Y_{\alpha\beta[0]}}{\partial \underline{r}_{\alpha\beta}} f_\alpha' f_\beta' \underline{V}_\alpha\cdot\left(c_{\alpha\gamma}\underline{W}_\alpha'+c_{\beta\gamma}\underline{W}_\beta'\right) d\underline{r}_{\alpha\beta} d\underline{V}_\alpha d\underline{V}_\beta$$

where the quantity $g'_{\alpha\beta}\cdot\frac{\partial Y_{\alpha\beta[0]}}{\partial \underline{r}'_{\alpha\beta}}$ is transformed into $g_{\alpha\beta}\cdot\frac{\partial Y_{\alpha\beta[0]}}{\partial \underline{r}_{\alpha\beta}}$ with the use of the same identity. Using the method outlined by Hoffman and Curtiss,[13b] the first integral can be written in terms of the $\Omega^{(\ell,s)}_{\alpha\beta}$ integrals. The relations (2.3 - 5) and (2.3 - 6) can be inverted and written in terms of dimensionless velocities:

$$\underline{W}_\alpha=\left(\frac{m_\alpha}{M_{\alpha\beta}}\right)^{\frac{1}{2}}\underline{\Gamma}_{\alpha\beta}+\left(\frac{m_\beta}{M_{\alpha\beta}}\right)^{\frac{1}{2}}\underline{\gamma}_{\alpha\beta} \tag{5.1 - 8}$$

$$\underline{W}_\beta=\left(\frac{m_\beta}{M_{\alpha\beta}}\right)^{\frac{1}{2}}\underline{\Gamma}_{\alpha\beta}-\left(\frac{m_\alpha}{M_{\alpha\beta}}\right)^{\frac{1}{2}}\underline{\gamma}_{\alpha\beta} \tag{5.1 - 9}$$

where

$$\underline{\Gamma}_{\alpha\beta}=\left(\frac{M_{\alpha\beta}}{2kT}\right)^{\frac{1}{2}}\underline{G}_{\alpha\beta} \tag{5.1 - 10}$$

$$\underline{\gamma}_{\alpha\beta}=\left(\frac{\mu_{\alpha\beta}}{2kT}\right)^{\frac{1}{2}}\underline{g}_{\alpha\beta} \tag{5.1 - 11}$$

Using these, we may carry out the integration over $\underline{r}_{\alpha\beta}$ in the second part of equation (5.1 - 7) to yield:

$$\frac{kT}{m_\alpha}\left\{\delta_{\alpha\gamma}-\frac{\rho_\alpha}{\rho}\right\} = -\frac{2}{3}n^2\sum_\beta x_\alpha x_\beta\left[4\left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}}\Omega^{(11)}_{\alpha\beta}\right.$$

(5.1 - 12)

$$\left.+\frac{nkT}{(\pi^3\mu_{\alpha\beta}m_\alpha)^{\frac{1}{2}}}R^{(1)}_{\alpha\beta}\right]\cdot\left[\left(\frac{m_\beta}{M_{\alpha\beta}}\right)c_{\alpha\gamma}-\left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{\frac{1}{2}}c_{\beta\gamma}\right]$$

We define the diffusion coefficient $D_{\alpha\beta}$ by

$$D_{\alpha\beta} = -n\left(\frac{kT}{2m_\alpha}\right)^{\frac{1}{2}}c_{\alpha\beta} \qquad (5.1 - 13)$$

and the usual binary diffusion coefficient $\mathcal{D}_{\alpha\beta}$ by:

$$\mathcal{D}_{\alpha\beta} = \frac{1}{n}\mathcal{D}^{(-1)}_{\alpha\beta} = \frac{3kT}{16n\mu_{\alpha\beta}\Omega^{(11)}_{\alpha\beta}} \qquad (5.1 - 14)$$

Utilizing these, equation (5.1 - 12) can be written in the form:

$$\delta_{\alpha\gamma}-\frac{\rho_\alpha}{\rho} = \sum_\beta x_\alpha x_\beta\left[\frac{n}{\mathcal{D}^{(-1)}_{\alpha\beta}}+\frac{2n^2}{3}\left(\frac{2\mu_{\alpha\beta}}{\pi^3 kT}\right)^{\frac{1}{2}}R^{(1)}_{\alpha\beta}\right](D_{\alpha\gamma}-D_{\beta\gamma})$$

(5.1 - 15)

while the auxiliary condition, equation (5.1 - 4), becomes

$$\sum_\alpha \rho_\alpha D_{\alpha\gamma} = 0 \qquad (5.1 - 16)$$

These two sets of equations may now be combined to give the set:

$$\left\{\frac{\rho_\alpha}{\rho} - \delta_{\alpha\gamma}\right\} = \sum_{\beta \neq \alpha} \left\{ X_\alpha X_\beta \left[\frac{n}{\mathcal{D}_{\alpha\beta}^{(-1)}} + \frac{2n^2}{3}\left(\frac{2\mu_{\alpha\beta}}{\pi^3 kT}\right)^{\frac{1}{2}} R_{\alpha\beta}^{(1)} \right]\right.$$

(5.1 - 17)

$$\left. + \sum_{\gamma \neq \alpha} \frac{X_\gamma X_\beta m_\beta}{m_\alpha} \left[\frac{n}{\mathcal{D}_{\alpha\gamma}^{(-1)}} + \frac{2n^2}{3}\left(\frac{2\mu_{\alpha\gamma}}{\pi^3 kT}\right)^{\frac{1}{2}} R_{\alpha\gamma}^{(1)} \right] \right\} D_{\beta\gamma}$$

We now introduce a density expansion of $D_{\alpha\beta}$ of the form:

$$D_{\alpha\beta} = \frac{1}{n} D_{\alpha\beta}^{(0)} + D_{\alpha\beta}^{(1)} + \Theta(n) \qquad (5.1 - 18)$$

Equation (5.1 - 17) can be divided into two density independent equations. The lowest order equation was previously used by Curtiss:[18]

$$\sum_{\beta \neq \alpha} \left\{ \frac{X_\alpha X_\beta}{\mathcal{D}_{\alpha\beta}^{(-1)}} + \sum_{\gamma \neq \alpha} \frac{X_\beta X_\gamma m_\beta}{m_\alpha \mathcal{D}_{\alpha\gamma}^{(-1)}} \right\} D_{\beta\gamma}^{(0)} = \frac{\rho_\alpha}{\rho} - \delta_{\alpha\gamma} \qquad (5.1 - 19)$$

while the first order equation is:

$$-\frac{2}{3}\sum_{\beta \neq \alpha} \left[X_\alpha X_\beta \left(\frac{2\mu_{\alpha\beta}}{\pi^3 kT}\right)^{\frac{1}{2}} R_{\alpha\beta}^{(1)} + \sum_{\gamma \neq \alpha} \frac{X_\gamma X_\beta m_\beta}{m_\alpha} \left(\frac{2\mu_{\alpha\gamma}}{\pi^3 kT}\right)^{\frac{1}{2}} R_{\alpha\gamma}^{(1)} \right] D_{\beta\gamma}^{(0)}$$

(5.1 - 20)

$$= \sum_{\beta \neq \alpha} \left[\frac{X_\alpha X_\beta}{\mathcal{D}_{\alpha\beta}^{(-1)}} + \sum_{\gamma \neq \alpha} \frac{X_\gamma X_\beta m_\beta}{m_\alpha \mathcal{D}_{\alpha\gamma}^{(-1)}} \right] D_{\beta\gamma}^{(1)}$$

These two equations can be easily solved for the special case of a two component system. The solutions of equation (5.1 - 19) are of course identical to those of Curtiss:

$$D_{11}^{(0)} = n^3 n_2 m_2^2 \mathcal{D}_{12} / \rho^2 n_1 \qquad (5.1 - 21)$$

$$D_{12}^{(0)} = D_{21}^{(0)} = - n^3 m_1 m_2 \mathcal{D}_{12} / \rho^2 \qquad (5.1 - 22)$$

$$D_{22}^{(0)} = n^3 n_1 m_1^2 \mathcal{D}_{12} / \rho^2 n_2 \qquad (5.1 - 23)$$

The solutions of equation (5.1 - 20) can be summarized in the form:

$$D_{\alpha\beta}^{(1)} = - \frac{2}{3} n \left(\frac{2 \mu_{\alpha\beta}}{\pi^3 kT} \right)^{\frac{1}{2}} R_{12}^{(1)} \mathcal{D}_{12} D_{\alpha\beta}^{(0)} \qquad (5.1 - 24)$$

where α and β take the values 1 and/or 2.

This completes the solution of equation (5.1 - 1). We show in section 6.3 that the diffusion coefficients $D_{\alpha\beta}$ are symmetric.

5.2 Gradients of the Mole Fractions

The solution of equation (4.3 - 9) is virtually identical with that of section 5.1, with only the inhomogeniety being different. Rewriting equation (4.3 - 9) in detail we have:

$$\frac{1}{n} \sum_{\beta} \underline{\underline{I}}_{\alpha\beta}^{(1)} \left[\frac{X_\alpha \delta_{\beta\gamma} - X_\beta \delta_{\alpha\gamma}}{X_\alpha X_\beta} \right] = \sum_{\beta} \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \phi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left[Y_{\alpha\beta(0)} f_\alpha' f_\beta' (E_{\alpha\gamma} + E_{\beta\gamma}) \right] \cdot d\underline{r}_{\alpha\beta} \, d\underline{V}_\beta \qquad (5.2 - 1)$$

Making a Sonine polynomial expansion and integrating over $\underline{V}_\alpha$, we can introduce a new diffusion coefficient $\tilde{D}_{\alpha\beta}$ defined by

$$\tilde{D}_{\alpha\beta} = -n\left(\frac{kT}{2m_\alpha}\right)^{\frac{1}{2}} F_{\alpha\gamma} \tag{5.2 - 2}$$

Introducing a density expansion for $\tilde{D}_{\alpha\beta}$, only the lowest order term is needed:

$$\tilde{D}_{\alpha\beta} = \tilde{D}^{(0)}_{\alpha\beta} + \mathcal{O}(n) \tag{5.2 - 3}$$

We can now write equation (5.2 - 1) as a density independent equation:

$$\sum_\beta \frac{(X_\beta \delta_{\alpha\gamma} - X_\alpha \delta_{\beta\gamma})}{6\pi^{3/2}\, kT} R^{(16)}_{\alpha\beta}$$
$$= \sum_{\beta\neq\alpha}\left[\frac{X_\alpha X_\beta}{\mathcal{D}^{(-1)}_{\alpha\beta}} + \sum_{\varphi\neq\alpha} \frac{X_\varphi X_\beta m_\beta}{m_\alpha \mathcal{D}^{(-1)}_{\alpha\varphi}}\right] \tilde{D}^{(0)}_{\beta\gamma} \tag{5.2 - 4}$$

where we have used the auxiliary condition:

$$\sum_\alpha \rho_\alpha \tilde{D}_{\alpha\gamma} = 0 \tag{5.2 - 5}$$

to insure uniqueness of the solutions.

Again we consider the case of a two component system. The solutions to equation (5.2 - 4) are

$$\tilde{D}^{(0)}_{11} = -n^2 \rho_2 \mathcal{D}_{12} R^{(16)}_{12} / 6\pi^{3/2} \rho m_1 kT \tag{5.2 - 6}$$

$$\tilde{D}_{12}^{(0)} = n^2 m_2 \mathcal{A}_{12} R_{12}^{(16)} / 6\pi^{3/2} \rho k T \tag{5.2 - 7}$$

$$\tilde{D}_{21}^{(0)} = n^2 m_1 \mathcal{A}_{12} R_{12}^{(16)} / 6\pi^{3/2} \rho k T \tag{5.2 - 8}$$

and

$$\tilde{D}_{22}^{(0)} = -n^2 \rho_1 \mathcal{A}_{12} R_{12}^{(16)} / 6\pi^{3/2} \rho n_2 k T \tag{5.2 - 9}$$

This completes the solution of the diffusion equation, the results of which will be used in section 6.3 to evaluate the diffusion velocities.

5.3 Thermal Conductivity

The equation governing thermal conductivity is considerably more complicated than the two previously considered. The starting point is equation (4.3 - 3):

$$\underline{K}_\alpha = \tag{5.3 - 1}$$

$$\sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ Y_{\alpha\beta(0)} f_\alpha' f_\beta' \left[\underline{A}_\alpha' + \underline{A}_\beta' \right] \right\} d\underline{r}_{\alpha\beta} d\underline{V}_\beta$$

In evaluating the integrals of $\underline{K}_\alpha$, we find that the zeroth and first order integrals can be separated according to powers of the density:

$$\int S_{\frac{3}{2}}^{(0)}(W_\alpha^2) \underline{V}_\alpha \cdot \underline{K}_\alpha d\underline{V}_\alpha = n^2 K_{\alpha 0}^{(2)} \tag{5.3 - 2}$$

and

$$\int S_{\frac{3}{2}}^{(1)}(W_\alpha^2)\underline{V}_\alpha \cdot \underline{K}_\alpha \, d\underline{V}_\alpha = n K_{\alpha 1}^{(1)} + n^2 K_{\alpha 1}^{(2)} \qquad (5.3 - 3)$$

The $K^{(i)}$'s are density independent quantities and are given in Appendix B.

The coefficients $\underline{A}_\alpha$ are expanded in terms of Sonine polynomials of order $\frac{3}{2}$ and only the first two terms in the series are retained:

$$\underline{A}_\alpha = \underline{W}_\alpha \left\{ a_{\alpha 0} + a_{\alpha 1} S_{\frac{3}{2}}^{(1)}(W_\alpha^2) \right\} \qquad (5.3 - 4)$$

The only auxiliary condition on the coefficients $a_{\alpha i}$ is:

$$\sum_\alpha n_\alpha m_\alpha^{\frac{1}{2}} a_{\alpha 0} = 0 \qquad (5.3 - 5)$$

This will be used later in the development. The coefficients $a_{\alpha i}$ are then expanded in a density series:

$$a_{\alpha i} = \frac{1}{n_\alpha} a_{\alpha i}^{(0)} + a_{\alpha i}^{(1)} + \mathcal{O}(n) \qquad (5.3 - 6)$$

Application of the above expansions to equation (5.3 - 1) yields four density independent equations, which can be written very compactly in the form:

$$0 = \sum_\gamma \left\{ \mathcal{H}_{\alpha\gamma 0}^{(100)} a_{\gamma 0}^{(0)} + \mathcal{H}_{\alpha\gamma 0}^{(101)} a_{\gamma 1}^{(0)} \right\} \qquad (5.3 - 7)$$

$$K^{(1)}_{\alpha 1} = \sum_{\gamma}{}' \left\{ \mathcal{H}^{(100)}_{\alpha\gamma 1} a^{(0)}_{\gamma 0} + \mathcal{H}^{(101)}_{\alpha\gamma 1} a^{(0)}_{\gamma 1} \right\} \tag{5.3 - 8}$$

$$\begin{aligned} K^{(2)}_{\alpha 0} - \sum_{\gamma} \left\{ \mathcal{H}^{(200)}_{\alpha\gamma 0} a^{(0)}_{\gamma 0} + \mathcal{H}^{(201)}_{\alpha\gamma 1} a^{(0)}_{\gamma 1} \right\} \\ = \sum_{\gamma} \left\{ \mathcal{H}^{(210)}_{\alpha\gamma 0} a^{(1)}_{\gamma 0} + \mathcal{H}^{(211)}_{\alpha\gamma 0} a^{(1)}_{\gamma 1} \right\} \end{aligned} \tag{5.3 - 9}$$

$$\begin{aligned} K^{(2)}_{\alpha 1} - \sum_{\gamma}{}' \left\{ \mathcal{H}^{(200)}_{\alpha\gamma 1} a^{(0)}_{\gamma 0} + \mathcal{H}^{(201)}_{\alpha\gamma 1} a^{(0)}_{\gamma 1} \right\} \\ = \sum_{\gamma} \left\{ \mathcal{H}^{(210)}_{\alpha\gamma 1} a^{(1)}_{\gamma 0} + \mathcal{H}^{(211)}_{\alpha\gamma 1} a^{(1)}_{\gamma 1} \right\} \end{aligned} \tag{5.3 - 10}$$

The coefficients $\mathcal{H}$ are functions of known quantities including integrals and several more $R^{(i)}$ integrals, and are tabulated in Appendix B. In the coefficients $\mathcal{H}^{(jkl)}_{\alpha\gamma i}$, j is the order in the density of the equation from which it came and k is the order in the density of the $a^{(k)}_{\alpha l}$ which it multiplies. l is the Sonine polynomial degree of the $a^{(k)}_{\alpha l}$ which it multiplies, while i is the degree of the Sonine polynomial used to form the matrix element.

Equations (5.3 - 7 and 8) are indeterminate in that the matrix of the $\mathcal{H}$'s is zero. The auxiliary condition (5.3 - 5) removes the indeterminancy and leads to a unique solution of the pair of equations.

The solutions of equations (5.3 - 7, 8, 9, and 10) then represent a generalization to mixtures of the work of Hoffman and Curtiss.

5.4 Shear Viscosity

The evaluation of the coefficient of shear viscosity requires the solution of:

$$\underline{\underline{L}}_\alpha = \sum_\beta \frac{1}{\mu_{\alpha\beta}} \int \frac{\partial q_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} \cdot \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \left\{ Y_{\alpha\beta[0]} f_\alpha' f_\beta' \left(\underline{\underline{B}}_\alpha' + \underline{\underline{B}}_\beta' \right) \right\} d\underline{r}_{\alpha\beta} d\underline{V}_\beta \qquad (5.4 - 1)$$

The tensorial dependence in $\underline{\underline{B}}_\alpha$ can be separated off and the remainder expanded in terms of Sonine polynomials of order $\frac{5}{2}$. We retain only the lowest order term, giving:

$$\underline{\underline{B}}_\alpha = b_\alpha \left(\underline{W}_\alpha \underline{W}_\alpha - \frac{1}{3} W_\alpha^2 \underline{\underline{U}} \right) \qquad (5.4 - 2)$$

The coefficient b_α is then expanded in a density series

$$b_\alpha = \frac{1}{n_\alpha} b_\alpha^{(0)} + b_\alpha^{(1)} + \mathcal{O}(n) \qquad (5.4 - 3)$$

The integral of $\underline{\underline{L}}_\alpha$ with $S_{\frac{5}{2}}^{(0)}(\omega_\alpha^2)$ is:

$$\int S_{\frac{5}{2}}^{(0)}(W_\alpha^2) \underline{V}_\alpha \underline{V}_\alpha : \underline{\underline{L}}_\alpha d\underline{V}_\alpha = n x_\alpha L_\alpha^{(1)} + n^2 \sum_\beta x_\alpha x_\beta L_{\alpha\beta}^{(2)} \qquad (5.4 - 4)$$

Using the above expansions, we write equation (5.4 - 1) as two density independent equations:

$$x_\alpha L_\alpha^{(1)} = - \sum_\gamma \mathcal{L}_{\alpha\gamma}^{(0)} b_\gamma^{(0)} \qquad (5.5 - 5)$$

and

$$\sum_\beta x_\alpha x_\beta L_{\alpha\beta}^{(2)} = - \sum_\gamma \left[\mathcal{L}_{\alpha\gamma}^{(1)} b_\gamma^{(1)} + \mathcal{L}_{\alpha\gamma}^{(2)} b_\gamma^{(0)} \right] \qquad (5.5 - 6)$$

The quantities $L^{(1)}_{\alpha}$, $L^{(2)}_{\alpha\beta}$ and $\mathcal{L}^{(i)}_{\alpha\beta}$ are tabulated in Appendix B.

These equations then represent a generalization to mixtures of the work of Hoffman and Curtiss. No new integrals are introduced, so that if the thermal condictivity were calculated, very little additional effort would be required for the viscosity.

5.5 Bulk Viscosity

The solution of this equation is slightly different from the others in that the solution is needed only to lowest order in the density. This means that the terms leading to the R integrals are dropped.

The starting point is equation (4.3 - 5):

$$M_{\alpha}=\sum_{\beta}\frac{1}{\mu_{\alpha\beta}}\int\frac{\partial\varphi_{\alpha\beta}}{\partial r_{\alpha\beta}}\cdot\frac{\partial}{\partial g_{\alpha\beta}}\left\{Y_{\alpha\beta[0]}f_{\alpha}'f_{\beta}'\left(E_{\alpha}'+E_{\beta}'\right)\right\}d r_{\alpha\beta}\,dV_{\beta} \tag{5.5 - 1}$$

The integrals of the inhomogeniety M_{α} are:

$$\int S^{(0)}_{\frac{1}{2}}(\omega_{\alpha}^{2})M_{\alpha}\,d\underline{V}_{\alpha}=0 \tag{5.5 - 2}$$

$$\int S^{(1)}_{\frac{1}{2}}(\omega_{\alpha}^{2})M_{\alpha}\,d\underline{V}_{\alpha}=n^{2}M^{(1)}_{\alpha} \tag{5.5 - 3}$$

and

$$\int S^{(2)}_{\frac{1}{2}}(\omega_{\alpha}^{2})M_{\alpha}\,d\underline{V}_{\alpha}=n^{2}M^{(2)}_{\alpha} \tag{5.5 - 4}$$

where the density independent quantities $M_\alpha^{(i)}$ are given in Appendix B.

The Sonine polynomial expansion of E_α is

$$E_\alpha = E_{\alpha 0} + E_{\alpha 1} S_{\frac{1}{2}}^{(1)}(W_\alpha^2) + E_{\alpha 2} S_{\frac{1}{2}}^{(2)}(W_\alpha^2) \tag{5.5 - 5}$$

The auxiliary conditions then require that

$$E_{\alpha 0} = 0 \tag{5.5 - 6}$$

and

$$\sum_\alpha{}' E_{\alpha 1} X_\alpha = 0 \tag{5.5 - 7}$$

Using the expansion of E_α, equation (5.5 - 1) can be written as a pair of equations in terms of the square bracket integrals:[20]

$$M_\alpha^{(l)} = -\sum_\gamma \left[\mathcal{M}_{\alpha\gamma 1}^{(l)} E_{\gamma 1} + \mathcal{M}_{\alpha\gamma 2}^{(l)} E_{\gamma 2} \right] \quad (l = 1, 2) \tag{5.5 - 8}$$

where

$$\mathcal{M}_{\alpha\gamma i}^{(l)} = \sum_\beta{}' X_\alpha X_\beta \Big\{ \left[S_{\frac{1}{2}}^{(l)}(W_\alpha^2); S_{\frac{1}{2}}^{(i)}(W_\alpha^2) \right]_{\alpha\beta} \delta_{\alpha\gamma} + \left[S_{\frac{1}{2}}^{(l)}(W_\alpha^2); S_{\frac{1}{2}}^{(i)}(W_\beta^2) \right]_{\alpha\beta} \delta_{\beta\gamma} \Big\} \quad \begin{pmatrix} l = 1, 2 \\ i = 1, 2 \end{pmatrix} \tag{5.5 - 9}$$

Upon evaluating the various square bracket integrals, we then have the low density contribution to the bulk viscosity of mixtures.

This then completes the solution of the five perturbation equations. The various integrals encountered are considered in Chapter VII.

CHAPTER VI

THE TRANSPORT COEFFICIENTS

In this chapter we develop expressions for the fluxes in terms of the transport coefficients and relate these coefficients to the solutions of the perturbation equations.

6.1 Pressure Tensor

The perturbation expansion of $f_\alpha^{(1)}$, equations (4.1 - 2) and 4.1 - 10), may be used to evaluate the kinetic portion of the pressure tensor, equation (3.3 - 3):

$$\underline{\underline{P}}_K = \sum_\alpha m_\alpha \int f_\alpha (1 + \phi_\alpha) \underline{V}_\alpha \underline{V}_\alpha d\underline{V}_\alpha \qquad (6.1 - 1)$$

The equilibrium part is integrated directly to give the usual:

$$n k T \underline{\underline{U}} \qquad (6.1 - 2)$$

The non-equilibrium part may be simplified by noting that only the terms in $\underline{\underline{B}}_\alpha$ and E_α of ϕ_α remain after integrating over the angles of $\underline{V}_\alpha$.

The term contributing to the bulk viscosity is:

$$-\left(\frac{\partial}{\partial \underline{r}} \cdot \underline{u}\right) \sum_\alpha m_\alpha \int \underline{V}_\alpha \underline{V}_\alpha f_\alpha E_\alpha d\underline{V}_\alpha$$

The summation is precisely the auxiliary condition on E_α, and hence is zero.

The contribution to the shear viscosity can be written in terms of the dimensionless velocity $\underline{W}_\alpha$:

$$-\sum_{\alpha} \frac{2 n_\alpha kT b_\alpha}{\pi^{3/2}} \int e^{-W_\alpha^2} \underline{W}_\alpha \underline{W}_\alpha \underline{W}_\alpha \underline{W}_\alpha d\underline{W}_\alpha : \left(\frac{\partial}{\partial \underline{r}} \underline{u} - \frac{1}{3} \frac{\partial}{\partial \underline{r}} \cdot \underline{u} \underline{\underline{U}}\right)$$

The angular portion of this integral has been evaluated by Snider and Curtiss,[14a] and the remainder is relatively simple. Introducing the rate of shear tensor:

$$\underline{\underline{S}} = \frac{1}{2}\left[\left(\frac{\partial}{\partial \underline{r}} \underline{u}\right) + \widetilde{\left(\frac{\partial}{\partial \underline{r}} \underline{u}\right)}\right] - \frac{1}{3}\left(\frac{\partial}{\partial \underline{r}} \cdot \underline{u}\right) \underline{\underline{U}} \qquad (6.1 - 3)$$

and using the density expansion of b_α, equation (5.4 - 3), the final form of $\underline{\underline{P}}_K$ is:

$$\underline{\underline{P}}_K = n kT \underline{\underline{U}} - kT \sum_{\alpha} \left(b_\alpha^{(0)} + n_\alpha b_\alpha^{(1)}\right) \underline{\underline{S}} \qquad (6.1 - 4)$$

The collisional portion of $\underline{\underline{P}}$ is evaluated in an entirely analogous manner. Combining the perturbation expansion with equation (3.3 - 11), we have:

$$\underline{\underline{P}}_\phi = -\frac{1}{2} \sum_{\alpha,\beta} \int \frac{1}{r_{\alpha\beta}} \frac{\partial \phi_{\alpha\beta}}{\partial r_{\alpha\beta}} \underline{r}_{\alpha\beta} \underline{r}_{\alpha\beta} \Big\{ Y_{\alpha\beta[0]} f_\alpha' f_\beta' \left(1 + \phi_\alpha' + \phi_\beta'\right)$$

$$+ \frac{1}{2} \underline{r}_{\alpha\beta}' \cdot \left(\frac{\partial f_\alpha'}{\partial \underline{r}} f_\beta' - f_\alpha' \frac{\partial f_\beta'}{\partial \underline{r}}\right) \Big\} d\underline{r}_{\alpha\beta} d\underline{V}_\alpha d\underline{V}_\beta \qquad (6.1 - 5)$$

The equilibrium portion may be simplified by neglecting the n^3 contribution from $Y_{\alpha\beta[0]}$, which then yields the second virial coefficient:

$$n^2 kT \, B \, \underline{\underline{U}} \qquad (6.1 - 6)$$

As in the case of $\underline{\underline{P}}_K$, the perturbation part of $\underline{\underline{P}}_\phi$ can be simplified to only the shear and bulk viscosity contributions, and density considerations eliminate the factor $Y_{\alpha\beta(0)}$:

$$\frac{1}{2}\sum_{\alpha\beta} \int \frac{1}{r_{\alpha\beta}} \frac{\partial \varphi_{\alpha\beta}}{\partial r_{\alpha\beta}} \underline{r}_{\alpha\beta}\underline{r}_{\alpha\beta} f_\alpha f_\beta \, e^{-\varphi_{\alpha\beta}/kT} \Big\{ (E'_\alpha + E'_\beta) \frac{\partial}{\partial \underline{r}} \cdot \underline{u} \qquad (6.1 - 7)$$

$$+ (\underline{\underline{B}}'_\alpha + \underline{\underline{B}}'_\beta) : \left(\frac{\partial}{\partial \underline{r}} \underline{u} - \frac{1}{3} \frac{\partial}{\partial \underline{r}} \cdot \underline{u} \, \underline{\underline{U}} \right) \Big\} d\underline{r}_{\alpha\beta} d\underline{V}_\alpha d\underline{V}_\beta$$

Using the expression for $\underline{\underline{B}}_\alpha$ and introducing the concepts of isotropic cartesian tensors, the shear viscosity part can be evaluated, giving:

$$n^2 \sum_{\alpha,\beta} \frac{x_\alpha x_\beta m_\beta b_\alpha}{5\pi^{3/2} M_{\alpha\beta}} \left[R^{(6)}_{\alpha\beta} + 2\pi^{3/2} kT \left(\frac{5}{2} B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T} \right) \right] \underline{\underline{S}}$$

We note that the kinetic contribution to the shear viscosity is known only through order n. Therefore only the lowest order term in the density expansion of b_α is retained, and we have:

$$\underline{\underline{S}} \frac{n}{5\pi^{3/2}} \sum_{\alpha,\beta} \frac{m_\beta x_\beta}{M_{\alpha\beta}} b_\alpha^{(0)} \left[R^{(6)}_{\alpha\beta} + 2\pi^{3/2} kT \left(\frac{5}{2} B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T} \right) \right] \qquad (6.1 - 8)$$

The bulk viscosity contribution is calculated similarly. Using the expansion (5.5 - 5) and the identity

(5.1 - 9)

$$\left[\frac{1}{2}\left(\frac{\phi_{\alpha\beta}}{kT}\right)^2-\left(\frac{\phi_{\alpha\beta}}{kT}\right)\right]e^{-\phi_{\alpha\beta}/kT}=\left[\frac{1}{2}kT^3\frac{\partial^2}{\partial T^2}+kT^2\frac{\partial}{\partial T}\right]\left(e^{-\phi_{\alpha\beta}/kT}-1\right)$$

we find that the integral reduces to

$$-\mathcal{K}_{\phi 1}\left(\frac{\partial}{\partial \underline{r}}\cdot\underline{u}\right)\underline{\underline{U}} \tag{6.1 - 10}$$

where $\mathcal{K}_{\phi 1}$ is part of the coefficient of bulk viscosity:

$$\mathcal{K}_{\phi 1}=2n^2kT\sum_{\alpha,\beta}x_\alpha x_\beta\Big\{E_{\alpha 2}\frac{m_\beta^2}{M_{\alpha\beta}^2}\left(\frac{1}{2}T^2\frac{\partial^2}{\partial T^2}+T\frac{\partial}{\partial T}\right)$$

(6.1 - 11)

$$+E_{\alpha 1}\frac{m_\beta}{M_{\alpha\beta}}\left(T\frac{\partial}{\partial T}+1\right)\Big\}B_{\alpha\beta}$$

The last part of equation (6.1 - 5) can be evaluated using the quantity Δ_1 as defined by Snider and Curtiss.(14a) The contributions of the gradients of n_α and T are zero as they yield tensor integrals of odd order. By density considerations only the trace of $\frac{\partial}{\partial \underline{r}}\underline{u}$ contributes, and can be written in terms of another $R^{(i)}$ integral

$$-\mathcal{K}_{\phi 2}\left(\frac{\partial}{\partial \underline{r}}\cdot\underline{u}\right)\underline{\underline{U}} \tag{6.1 - 12}$$

where

$$\mathcal{K}_{\phi 2}=-n^2\sum_{\alpha\beta}\frac{x_\alpha x_\beta}{9\pi^{3/2}}\left(\frac{\mu_{\alpha\beta}}{2kT}\right)^{\frac{1}{2}}R^{(7)}_{\alpha\beta} \tag{6.1 - 13}$$

We now write $\underline{\underline{P}}_\phi$ in the form:

$$\underline{\underline{P}}_\phi = n^2 kTB\underline{\underline{U}} - \kappa\left(\frac{\partial}{\partial \underline{r}}\cdot \underline{u}\right)\underline{\underline{U}}$$

(6.1 - 14)

$$+ \frac{n}{5\pi^{3/2}} \sum_{\alpha,\beta} \frac{m_\beta x_\beta}{M_{\alpha\beta}} b_\alpha^{(0)} \left[R_{\alpha\beta}^{(6)} + 2\pi^{3/2} kT\left(\frac{5}{2}B_{\alpha\beta} + T\frac{\partial B_{\alpha\beta}}{\partial T}\right)\right]\underline{\underline{S}}$$

where

$$\kappa = \kappa_{\phi 1} + \kappa_{\phi 2} \qquad (6.1 - 15)$$

is the coefficient of bulk viscosity. Combining $\underline{\underline{P}}_K$ and $\underline{\underline{P}}_\phi$, we obtain the standard form of the pressure tensor:

$$\underline{\underline{P}} = nkT(1+nB)\underline{\underline{U}} - 2\eta\underline{\underline{S}} - \kappa\left(\frac{\partial}{\partial \underline{r}}\cdot \underline{u}\right)\underline{\underline{U}} \qquad (6.1 - 16)$$

where the coefficient of shear viscosity η for mixtures is given by

$$\eta = \frac{kT}{2}\sum_\alpha \left(b_\alpha^{(0)} + n x_\alpha b_\alpha^{(1)}\right) - \frac{n}{10\pi^{3/2}} \sum_{\alpha\beta} \frac{m_\beta x_\beta}{M_{\alpha\beta}} b_\alpha^{(0)} \left[R_{\alpha\beta}^{(6)}\right.$$

(6.1 - 17)

$$\left. + 2\pi^{3/2} kT\left(\frac{5}{2}B_{\alpha\beta} + T\frac{\partial B_{\alpha\beta}}{\partial T}\right)\right]$$

The coefficient η can be written in the form of a density expansion:

$$\eta = \eta^{(0)}(1 + nB_\eta + \cdots) \qquad (6.1 - 18)$$

For the special case of a single component system, B_η is:

$$B_\eta = \frac{1}{2}B - \frac{2}{3}T\frac{\partial B}{\partial T} - \frac{2}{15}T^2\frac{\partial^2 B}{\partial T^2} + \frac{R^{(15)}}{10\pi^{3/2}kT}$$

$$- \frac{R^{(6)}}{10\pi^{3/2}kT} - \frac{1}{4\pi^{3/2}}\left(\frac{kT}{m}\right)^{\frac{1}{2}} R^{(2)}/\Omega^{(22)} \qquad (6.1 - 19)$$

This agrees with the results of Hoffman and Curtiss.

The difference in the order of the density dependence between the shear and bulk viscosity results from the fact that the kinetic portion of η is known only through order n, while the kinetic contribution to κ is zero to all orders. In contrast, the collisional part of both is known through order n^2. For reference purposes, the n^2 part of η_ϕ is:

$$n^2\sum_{\alpha\beta}\frac{x_\alpha x_\beta}{10\pi^{3/2}}\left\{\left(\frac{\mu_{\alpha\beta}}{2kT}\right)^{\frac{1}{2}} R^{(8)}_{\alpha\beta} - \frac{m_\beta}{M_{\alpha\beta}} b_\alpha^{(1)}\left[R^{(6)}_{\alpha\beta}\right.\right.$$

$$\left.\left. + 2\pi^{3/2}kT\left(\frac{5}{2}B_{\alpha\beta} + T\frac{\partial B_{\alpha\beta}}{\partial T}\right)\right]\right\} \qquad (6.1 - 20)$$

Thus we see that the basic form of $\underline{P}$, equation (6.1 - 16), is unchanged. The new expressions for η and κ are generalizations to mixtures of the results of Hoffman and Curtiss.[13]

6.2 Energy Flux Vector

The evaluation of the energy flux vector $\underline{q}$ is entirely analogous to that of the pressure tensor, except that since $\underline{q}$ is a vector, only the vector part of Φ contributes. The kinetic part of $\underline{q}$ can be evaluated in a straight forward manner to give:

(6.2 - 1)

$$q_K = -\lambda_K'' \frac{\partial T}{\partial \underline{r}} - \frac{5}{2} kT \sum_{\alpha\beta} x_\alpha \left\{ \left(D_{\alpha\beta}^{(0)} + n D_{\alpha\beta}^{(1)} \right) \underline{d}_\beta + n \tilde{D}_{\alpha\beta}^{(0)} \frac{\partial x_\beta}{\partial \underline{r}} \right\}$$

where the coefficient λ_K'' is given by:

$$\lambda_K'' = \frac{5}{2} k \sum_\alpha \left(\frac{kT}{2m_\alpha} \right)^{\frac{1}{2}} \left\{ \left(a_{\alpha 0}^{(0)} - a_{\alpha 1}^{(0)} \right) + n x_\alpha \left(a_{\alpha 0}^{(1)} - a_{\alpha 1}^{(1)} \right) \right\} \qquad (6.2 - 2)$$

The equilibrium contributions to $\underline{q}$, arising from the perturbation expansion of $f_\alpha^{(1)}$, all give zero, as is expected.

The collisional portion $\underline{q}_\phi$ of the energy flux vector can be considerably simplified by tensorial and density arguments to the form:

$$q_\phi = -\frac{1}{2} \sum_{\alpha\beta} \int \left[\underline{G}_{\alpha\beta} + \frac{(m_\beta - m_\alpha)}{2 M_{\alpha\beta}} \underline{g}_{\alpha\beta} \right] \cdot \left[\frac{1}{r_{\alpha\beta}} \frac{\partial \phi_{\alpha\beta}}{\partial r_{\alpha\beta}} \underline{r}_{\alpha\beta} \underline{r}_{\alpha\beta} - \phi_{\alpha\beta} \underline{\underline{U}} \right] \cdot$$

(6.2 - 3)

$$\left\{ f_\alpha' f_\beta' \left(\phi_\alpha' + \phi_\beta' \right) + \frac{1}{2} \underline{r}_{\alpha\beta}' \cdot \left(\frac{\partial f_\alpha'}{\partial \underline{r}} f_\beta' - f_\alpha' \frac{\partial f_\beta'}{\partial \underline{r}} \right) \right\} d\underline{r}_{\alpha\beta} d\underline{V}_\alpha d\underline{V}_\beta$$

Further development parallels that for $\underline{\underline{P}}_\phi$. The final form of $\underline{q}$ is

$$q_\phi = -\lambda_\phi'' \frac{\partial T}{\partial \underline{r}} - 2nkT \sum_{\alpha\beta\gamma} x_\alpha x_\beta \left\{ \frac{m_\alpha}{M_{\alpha\beta}} \left(-B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T} \right) \right.$$

(6.2 - 4)

$$\left. + \frac{(m_\beta - m_\alpha) R_{\alpha\beta}^{(16)}}{6 M_{\alpha\beta} \pi^{3/2} kT} \right\} D_{\alpha\gamma}^{(0)} \underline{d}_\gamma$$

where

$$\lambda_\phi'' = -nk \sum_{\alpha,\beta} x_\alpha a_{\alpha 0}^{(0)} \frac{(2m_\alpha kT)^{\frac{1}{2}}}{M_{\alpha\beta}} \left[-B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T} \right] \qquad (6.2 - 5)$$

$$+ n k \sum_{\alpha\beta}' \frac{X_\beta \mu_{\alpha\beta} a_{\alpha 1}^{(0)}}{3 M_{\alpha\beta}} \left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}} \left[7T \frac{\partial B_{\alpha\beta}}{\partial T} + 5T^2 \frac{\partial^2 B_{\alpha\beta}}{\partial T^2} + \frac{R_{\alpha\beta}^{(6)}}{\pi^{3/2} kT}\right]$$

$$- n k \sum_{\alpha\beta}' \frac{X_\beta (m_\beta - m_\alpha)}{12 \pi^{3/2} M_{\alpha\beta} kT} \left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}} \left\{ a_{\alpha 0}^{(0)} R_{\alpha\beta}^{(11)} + a_{\alpha 1}^{(0)} \left(\frac{m_\beta}{M_{\alpha\beta}}\right) R_{\alpha\beta}^{(22)} \right\}$$

As in the case of $\underline{\underline{P}}_K$ and $\underline{\underline{P}}_\phi$, we know $\underline{q}_\phi$ to one higher order of the density than $\underline{q}_K$. The n^2 contribution to λ_ϕ'' is:

$$\lambda_\phi^{''(2)} + n^2 k \sum_{\alpha\beta}' \frac{X_\alpha X_\beta}{6 \pi^{3/2} kT} \left(\frac{kT}{2\mu_{\alpha\beta}}\right)^{\frac{1}{2}} \left[\frac{2\mu_{\alpha\beta}}{M_{\alpha\beta}} R_{\alpha\beta}^{(21)} - \frac{(m_\beta - m_\alpha)^2}{2 M_{\alpha\beta}^2} R_{\alpha\beta}^{(10)}\right] \qquad (6.2 - 6)$$

where $\lambda_\phi^{''(2)}$ is obtained from equation (6.2 - 5) by replacing X_β with $n X_\alpha X_\beta$ and $a_{\alpha i}^{(0)}$ with $a_{\alpha i}^{(1)}$. The remaining n^2 part of $\underline{q}_\phi$ is:

$$- n^2 kT \sum_{\alpha,\beta,\gamma}' X_\alpha X_\beta \left\{ \frac{2 m_\alpha}{M_{\alpha\beta}} \left(- B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T}\right) \right.$$

$$\left. + \frac{(m_\beta - m_\alpha) R_{\alpha\beta}^{(11)}}{3 M_{\alpha\beta} \pi^{3/2} kT} \right\} \cdot \left\{ D_{\alpha\gamma}^{(1)} \underline{d}_\gamma + D_{\alpha\gamma}^{(0)} \frac{\partial X_\gamma}{\partial \underline{r}} \right\} \qquad (6.2 - 7)$$

$$+ n^2 \sum_{\alpha\beta}' \frac{X_\alpha (m_\beta - m_\alpha)}{6 \pi^{3/2} M_{\alpha\beta}} \left(\frac{kT}{2\mu_{\alpha\beta}}\right)^{\frac{1}{2}} R_{\alpha\beta}^{(9)} \frac{\partial X_\beta}{\partial \underline{r}}$$

Combining the collisional and kinetic parts of $\underline{q}$, we have the final form:

$$\underset{\sim}{q} = -\lambda'' \frac{\partial T}{\partial \underset{\sim}{r}} - \frac{5}{2} kT \sum_{\alpha,\gamma} X_\alpha \left\{ D_{\alpha\gamma}^{(0)} \underset{\sim}{d}_\gamma + n \left[D_{\alpha\gamma}^{(1)} \underset{\sim}{d}_\gamma + \tilde{D}_{\alpha\gamma}^{(0)} \frac{\partial X_\gamma}{\partial \underset{\sim}{r}} \right] \right\}$$

(6.2 - 8)

$$-2nkT \sum_{\alpha,\beta,\gamma} X_\alpha X_\beta \left\{ \frac{m_\alpha}{M_{\alpha\beta}} \left(-B_{\alpha\beta} + T \frac{\partial B_{\alpha\beta}}{\partial T} \right) + \frac{(m_\beta - m_\alpha) R_{\alpha\beta}^{(16)}}{6 M_{\alpha\beta} \pi^{3/2} kT} \right\} D_{\alpha\gamma}^{(0)} \underset{\sim}{d}_\gamma$$

where

$$\lambda'' = \lambda''_K + \lambda''_\phi$$

As with η, λ'' can be written in a density series:

$$\lambda'' = \lambda''^{(0)} \left(1 + n B_\lambda + \cdots \right) \qquad (6.2 - 9)$$

For a single component system, B_λ is:

$$B_\lambda = B - \frac{1}{5} T^2 \frac{\partial^2 B}{\partial T^2} + \frac{R^{(15)}}{15 \pi^{3/2} kT} - \frac{R^{(6)}}{15 \pi^{3/2} kT}$$

$$- \frac{1}{4\pi^{3/2}} \left(\frac{kT}{m} \right)^{\frac{1}{2}} R^{(2)} / \Omega^{(22)} \qquad (6.2 - 10)$$

Except for an apparent sign error, this result agrees with the work of Hoffmann and Curtiss.[21]

Using the results of the next section, we form the quantity $\sum_\alpha m_\alpha \overline{\underset{\sim}{V}_\alpha}$ to simplify our expression for $\underset{\sim}{q}$. Defining a new quantity λ', which is not the usual thermal conductivity, by

$$\lambda' = \lambda'' - \frac{5}{2} k \sum_\alpha' \left(\frac{kT}{2m_\alpha} \right)^{\frac{1}{2}} \left(a_{\alpha 0}^{(0)} + n_\alpha a_{\alpha 0}^{(1)} \right) \qquad (6.2 - 11)$$

we have

$$q = -\lambda' \frac{\partial T}{\partial \underline{r}} + \frac{5}{2} kT \sum_{\alpha} n_\alpha \overline{V}_\alpha - 2nkT \sum_{\alpha,\beta,\gamma}' X_\alpha X_\beta \Big\{ \frac{m_\alpha}{M_{\alpha\beta}} \Big(-B_{\alpha\beta} \tag{6.2 - 12}$$

$$+ T \frac{\partial B_{\alpha\beta}}{\partial T} \Big) + \frac{(m_\beta - m_\alpha) R^{(16)}_{\alpha\beta}}{6 M_{\alpha\beta} \pi^{3/2} kT} \Big\}$$

The thermal conductivity is usually defined as the coefficient of $\frac{\partial T}{\partial \underline{r}}$ when the energy flux vector $\underline{q}$ is expressed as function of $\frac{\partial T}{\partial \underline{r}}$ and $\{\overline{V}_\alpha\}$.

This is analogous to equation (7.4 - 30) of reference 6 and represents a generalization to mixtures of that result. We note that the thermal conductivity requires only the solutions of the perturbation equations and no additional integrals.

6.3 Diffusion Velocities

The third quantity necessary for the phenomenological description of the system is the diffusion velocity defined by:

$$\overline{V}_\alpha = \frac{1}{n_\alpha} \int f_\alpha^{(1)} \underline{V}_\alpha \, d\underline{V}_\alpha \tag{6.3 - 1}$$

Using the perturbation expansion, equations (4.1 - 2) and (4.1 - 10), the expression for ϕ, equation (4.3 - 1), and the density expansions for the perturbation coefficients, $\overline{V}_\alpha$ is found to be:

$$\overline{V}_\alpha = - \frac{D_\alpha^T}{n_\alpha m_\alpha} \frac{\partial \ln T}{\partial \underline{r}} - \sum_{\beta}' \left(\frac{1}{n_\alpha} D^{(0)}_{\alpha\beta} + D^{(1)}_{\alpha\beta} \right) \underline{d}_\beta - \sum_{\beta}' \tilde{D}^{(0)}_{\alpha\beta} \frac{\partial X_\beta}{\partial \underline{r}} \tag{6.3 - 2}$$

where the coefficient of thermal diffusion D_α^T is:

$$D_\alpha^T = n_\alpha m_\alpha \left(\frac{kT}{2m_\alpha} \right)^{\frac{1}{2}} \left(\frac{1}{n_\alpha} a^{(0)}_{\alpha 0} + a^{(1)}_{\alpha 0} \right) \tag{6.3 - 3}$$

The fact that $D_{\gamma\varsigma}$ ($=\frac{1}{m}D^{(0)}_{\gamma\varsigma} + D^{(1)}_{\gamma\varsigma}$) is symmetric can be readily shown by arguments similar to those of Curtiss.[18] Using equation (5.1 - 2), $D_{\gamma\varsigma}$ can be written in the form:

$$D_{\gamma\varsigma} = -\frac{1}{6} m \sum_{\alpha,\beta} \int \left(C_{\alpha\varsigma} \underline{W}_\alpha + C_{\beta\varsigma} \underline{W}_\beta \right) \frac{\partial \varphi_{\alpha\beta}}{\partial \underline{r}_{\alpha\beta}} : \frac{\partial}{\partial \underline{g}_{\alpha\beta}} \Big[Y_{\alpha\beta} f_\alpha' f_\beta' \cdot \left(C_{\alpha\gamma} \underline{W}_\alpha' + C_{\beta\gamma} \underline{W}_\beta' \right) \Big] d\underline{r}_{\alpha\beta}\, d\underline{V}_\alpha\, d\underline{V}_\beta \qquad (6.3 - 4)$$

which is symmetric under the interchange of γ and ς.

Next we consider the specialization of equation (6.3 - 2) to a system at constant temperature and pressure in the absence of external forces. Using the equation of state to eliminate $\frac{\partial \ln m}{\partial \underline{r}}$ from the expression for $\underline{d}_\alpha$ we have:

$$\overline{\underline{V}}_\alpha = -\sum_\beta \left(\frac{1}{m} D^{(0)}_{\alpha\beta} + D^{(1)}_{\alpha\beta} \right) \underline{d}_\beta - \sum_\beta \tilde{D}^{(0)}_{\alpha\beta} \frac{\partial X_\beta}{\partial \underline{r}} \qquad (6.3 - 5)$$

where

$$\underline{d}_\beta = \left(1 + m \sum_\gamma B_{\beta\gamma} X_\gamma \right) \frac{\partial X_\beta}{\partial \underline{r}} + m X_\beta \sum_\gamma B_{\beta\gamma} \frac{\partial X_\gamma}{\partial \underline{r}} - 2 m X_\beta \sum_{\varsigma\gamma} B_{\varsigma\gamma} X_\varsigma \frac{\partial X_\gamma}{\partial \underline{r}} \qquad (6.3 - 6)$$

We can further restrict ourselves to consideration of a two component system. Straight forward manipulations show that:

$$\overline{\underline{V}}_1 = -\frac{1}{m} \left(D^{(0)}_{11} - D^{(0)}_{12} \right) \left(1 + m B_{\Delta 12} \right) \frac{\partial X_1}{\partial \underline{r}} \qquad (6.3 - 7)$$

where

$$\mathcal{B}_{D12} = 2x_1x_2\left(\mathcal{B}_{11}+\mathcal{B}_{22}\right)+\left(x_2-x_1\right)^2\mathcal{B}_{12} + \frac{D_{11}^{(1)}-D_{12}^{(1)}+\tilde{D}_{11}^{(0)}-\tilde{D}_{12}^{(0)}}{D_{11}^{(0)}-D_{12}^{(0)}} \qquad (6.3-8)$$

The expression for B_{D12} can be reduced further. Using the expressions from sections 5.1 and 5.2 for the D's, we have

$$\frac{D_{11}^{(1)}-D_{12}^{(1)}}{D_{11}^{(0)}-D_{12}^{(0)}} = -\frac{2}{3}\left(\frac{2\mu_{12}}{\pi^3 kT}\right) R_{12}^{(1)} \Delta_{12}^{(-1)} \qquad (6.3-9)$$

and

$$\frac{\tilde{D}_{11}^{(0)}-\tilde{D}_{12}^{(0)}}{D_{11}^{(0)}-D_{12}^{(0)}} = \frac{R_{12}^{(16)}}{6\pi^{3/2} kT} \qquad (6.3-10)$$

For the special case of rigid spheres, these integrals can be readily evaluated,[22] giving

$$\frac{D_{11}^{(1)}-D_{12}^{(1)}}{D_{11}^{(0)}-D_{12}^{(0)}} = -\left[\frac{Y_{12}-1}{n}\right]_{RS} \qquad (6.3-11)$$

$$= -\frac{\pi}{12}\left[x_1\sigma_{11}^3\left(8-\frac{3\sigma_{11}}{\sigma_{12}}\right)+x_2\sigma_{22}^3\left(8-\frac{3\sigma_{22}}{\sigma_{12}}\right)\right]$$

$$\frac{\tilde{D}_{11}^{(0)}-\tilde{D}_{12}^{(0)}}{D_{11}^{(0)}-D_{12}^{(0)}} = -\frac{2\pi}{3}\sigma_{12}^3 \qquad (6.3-12)$$

and hence

$$\mathcal{B}_{D12} = \frac{4\pi}{3}x_1x_2\left(\sigma_{11}^3-2\sigma_{12}^3+\sigma_{22}^3\right)$$

$$-\frac{\pi}{12}\left[x_1\sigma_{11}^3\left(8-\frac{3\sigma_{11}}{\sigma_{12}}\right)+x_2\sigma_{22}^3\left(8-\frac{3\sigma_{22}}{\sigma_{12}}\right)\right] \qquad (6.3-13)$$

At this point our results can be compared with the original Chapman Enskog theory as extended to a dense gas of rigid spheres by H. H. Thorne.[23] Forming the quantity $\overline{\underline{V}}_1 - \overline{\underline{V}}_2$ from equations (6.3 - 7) and (6.3 - 8), and using equation (6.3 - 13) for B_{D12} for rigid spheres, we have

$$\overline{\underline{V}}_1 - \overline{\underline{V}}_2 = -\frac{3}{8 x_1 x_2 \sigma_{12}^3}\left(\frac{kT}{2\pi\mu_{12}}\right)^{\frac{1}{2}}\left[\frac{1}{n} + B_{D12}\right]\frac{\partial x_1}{\partial \underline{r}} \qquad (6.3 - 14)$$

which is exactly Thorne's result at constant temperature and pressure.

Another special case is that of self-diffusion. From equations (6.3 - 8, 9, and 10) we have

$$B_D = B + \frac{R^{(16)}}{6\pi^{3/2} kT} - \frac{2}{3}\left(\frac{2\mu}{\pi^3 kT}\right)^{\frac{1}{2}} R^{(1)} \Delta^{(-1)} \qquad (6.3 - 15)$$

which for rigid spheres has the especially simple form

$$B_D = -\left[\frac{Y-1}{n}\right] = -\frac{5}{12}\pi\sigma^3 \qquad (6.3 - 16)$$

This concludes the analytic treatment of the density corrections to the transport coefficients for mixtures. The next chapter is concerned with evaluating numerically the various integrals developed in the preceding chapters.

CHAPTER VII

NUMERICAL RESULTS AND SUMMARY

In this chapter the reduction of the $R^{(i)}$ integrals to a form suitable for numerical computation is reviewed and the numerical methods used are outlined. The results are discussed and compared with previous calculations. Finally, a summary of this work is presented.

7.1 Evaluation of the $R^{(i)}$ Integrals

The set of integrals, $R^{(i)}$, given in Appendix A, are of the same form and structure as those developed by Hoffman and Curtiss,[13] in that a detailed knowledge of the dynamics of a two particle collision is required. The set can be divided into two classes, those which involve $y_{\alpha\beta[0]}$ and those which do not.

For the numerical calculations, the Lennard-Jones potential and the reduced variables of Hoffman and Curtiss were used to write the integrals in the following dimensionless form:

$$\int dr^* d\xi^* dg'^* \frac{\partial(\theta, g^*)}{\partial(\xi^*, g'^*)} \sin\theta \, r^{*2} g^{*2} e^{-g'^{*2}/T^*} F^{(i)} \quad (7.1 - 1)$$

where $F^{(i)}$ represents the remaining factors of the integrand. For the set that does not contain $y_{\alpha\beta[0]}$, that is numbers 6 through 22, $F^{(i)}$ involves the integration variables and the angles between the vectors associated with the collision.

The set that includes $y_{\alpha\beta[0]}$, numbers 1 through 5, is similar to the others, but is composition dependent through $y_{\alpha\beta[0]}$, equation (4.1 - 8):

$$Y_{\alpha\beta[0]} = 1 + n\sum_{\gamma} x_\gamma \int d\underline{r}_\gamma \left(e^{-\phi_{\alpha\gamma}/kT} - 1\right)\left(e^{-\phi_{\beta\gamma}/kT} - 1\right) \quad (7.1 - 2)$$

The integral is a function of $(T, \underline{r}_{\alpha\beta}, \epsilon_{\alpha\beta}, \epsilon_{\alpha\gamma}, \epsilon_{\beta\gamma}, \sigma_{\alpha\beta}, \sigma_{\alpha\gamma}, \sigma_{\beta\gamma})$, and can be written in the form:

$$Y_{\alpha\beta[0]}\left[T^*_{\alpha\beta}, \underline{r}^*_{\alpha\beta}, \frac{\epsilon_{\alpha\gamma}}{\epsilon_{\alpha\beta}}, \frac{\epsilon_{\beta\gamma}}{\epsilon_{\alpha\beta}}, \frac{\sigma_{\alpha\gamma}}{\sigma_{\alpha\beta}}, \frac{\sigma_{\beta\gamma}}{\epsilon_{\alpha\beta}}\right] \quad (7.1 - 3)$$

For a single component system this has the especially simple form:

$$Y_{\alpha\alpha[0]}\left[T^*_{\alpha\alpha}, \underline{r}^*_{\alpha\alpha}, 1, 1, 1, 1\right]$$

and is the function curve fit by Hoffman and Curtiss. The calculations presented here are for single component systems only. To extend the computations to mixtures, it would be necessary to calculate and then curve fit $Y_{\alpha\beta[0]}$ as a function of T^* , $\underline{r}^*_{\alpha\beta}$ and the four additional parameters.

The numerical results (Table I) are expressed in terms of $R^{(i)*}$:

$$R^{(i)*} = R^{(i)}/R^{(i)}_{RS} \quad (7.1 - 4)$$

where $R^{(i)}_{RS}$ is the value of $R^{(i)}$ for a single component system of rigid spheres, in the cases in which this is non-zero. For the cases in which the rigid sphere value is zero, $R^{(i)}_{RS}$ is taken to be an appropriate constant to render $R^{(i)*}$ dimensionless. The constants $R^{(i)}_{RS}$ are listed in Appendix A.

For a mixture of rigid spheres, $R^{(1)}$ through $R^{(5)}$ can be expressed in

TABLE I

R FOR THE LENNARD-JONES POTENTIAL

T	1	2	8	30	100
1	1.346	.2880	.4549	.3708	.2606
2	1.486	.3151	.5046	.4164	.2946
3	.5075	.2899	.4015	.3414	.2412
4	4.070	1.255	1.549	1.260	.8835
5	1.800	.4554	.6960	.5678	.3982
6	- .1594	.3360	.5163	.4427	.3509
7	1.945	1.065	.5734	.3821	.2639
8	1.645	1.028	.5638	.3861	.2725
9	.4916	.1427	.005085	-.01156	-.01216
10	.1228	.03842	.02045	.02099	.01681
11	-1.295	- .6166	-.1170	$.1778 \cdot 10^{-4}$	.02604
12	.3488	.6433	.5882	.4521	.3466
13	- .5633	.1416	.4828	.4606	.3793
14	- .3098	.1783	.4745	.4488	.3688
15	-3.664	-1.537	.2645	.5958	.5713
16	-1.221	- .3398	.3905	.4743	.4134
17	-1.570	- .9831	-.1977	.02226	.06677
18	-1.257	- .3035	.3831	.4596	.4010
19	- .2243	- .01720	.1345	.1438	.1222
20	- .8140	- .1520	.2942	.3318	.2854
21	1.782	1.030	.5808	.4057	.2877
22	- .05639	- .06212	-.04525	-.04070	-.03458

terms of $(\gamma_{d\rho\xi o3} - 1)/n$. These quantities are also listed in Appendix A, and $(\gamma_{d\rho 1 o3} - 1)/n$ for a binary mixture is given by equation (6.3 - 11).

The numerical methods used in this work differ only slightly from those used previously.[13c,24] For the integration over g'^* an Hermite quadrature of N_g points was used. For the integration over ξ^*, a Gauss quadrature of $N_{\xi 1}$ points was used from a to b, and from c to ∞, a Chebyshev routine[25] of $N_{\xi 2}$ terms was used after folding the interval (c,∞) into (0,1) where a, b, and c are the three turning points in (g'^*, ξ^*) space. A Chebyshev quadrature of N_r terms was used for the r^* integration and one of $N_{\rho 1}$ terms for the complete ρ^* integration. The incomplete ρ^* integration employed a Gauss quadrature of $N_{\rho 2}$ points.

Calculations in which the set $(N_g, N_{\xi 1}, N_{\xi 2}, N_{\rho 1}, N_r, N_{\rho 2})$ was (10,16,16,24,24,12) required about one minute per temperature on a CDC 3600, giving values with an accuracy of 1% to 5%. An accuracy of .1% or better was obtained by taking the set of values to be (16,24,24,48,48,20), which required six minutes for each temperature. These latter results are the values presented in Table I. Four significant figures are given for each value. The maximum error is about one in the third figure. This program is listed in Appendix C.

7.2 Comparison with Previous Numerical Results

As a check on the numerical results, the transport second virial coefficients for viscosity and thermal conductivity were calculated for a single component system. The second virial coefficient for self diffusion was then evaluated. Using the expressions from Chapter VI, these coefficients can be written in terms of reduced quantities

$$B_\eta^* = B_\eta/\sigma^3 = \frac{2\pi}{3}\Big[\frac{1}{2}B^* - \frac{2}{3}B_1^* - \frac{2}{15}B_2^* - \frac{3}{5}R^{(15)*} + \frac{9}{10}R^{(6)*}\Big] - \frac{5\pi}{12}R^{(2)*}/\Omega^{(22)*} \qquad (7.2 - 1)$$

$$B_\lambda^* = B_\lambda/\sigma^3 = \frac{2\pi}{3}\Big[B^* - \frac{1}{5}B_2^* - \frac{2}{5}R^{(15)*} + \frac{3}{5}R^{(6)*}\Big] - \frac{5\pi}{12}R^{(2)*}/\Omega^{(22)*} \qquad (7.2 - 2)$$

$$B_\mathcal{D}^* = B_\mathcal{D}/\sigma^3 = \frac{2\pi}{3}\Big[B^* - R^{(16)*}\Big] - \frac{5\pi}{12}R^{(1)*}/\Omega^{(11)*} \qquad (7.2 - 3)$$

The last term in each expression is the contribution of three body collisions. The remaining terms represent the effects of collisional transfer. They are labeled B_{SC}; in the cases of η and λ, they are the corrections developed by Snider and Curtiss.[14a] Each of these contributions, along with the total, is tabulated in Table II. The total values are also presented graphically in Figure I.

The values of B_η are in good agreement with those of Hoffman and Curtiss. For the case of thermal conductivity, the collisional transfer contributions of the previous work appear to be in error.[26] After the corrections are made, our results and those of Hoffman and Curtiss are in satisfactory agreement.

The numerical results for self diffusion show that $B_\mathcal{D}$ is negative for all temperatures, approaching zero in the high termperature limit.

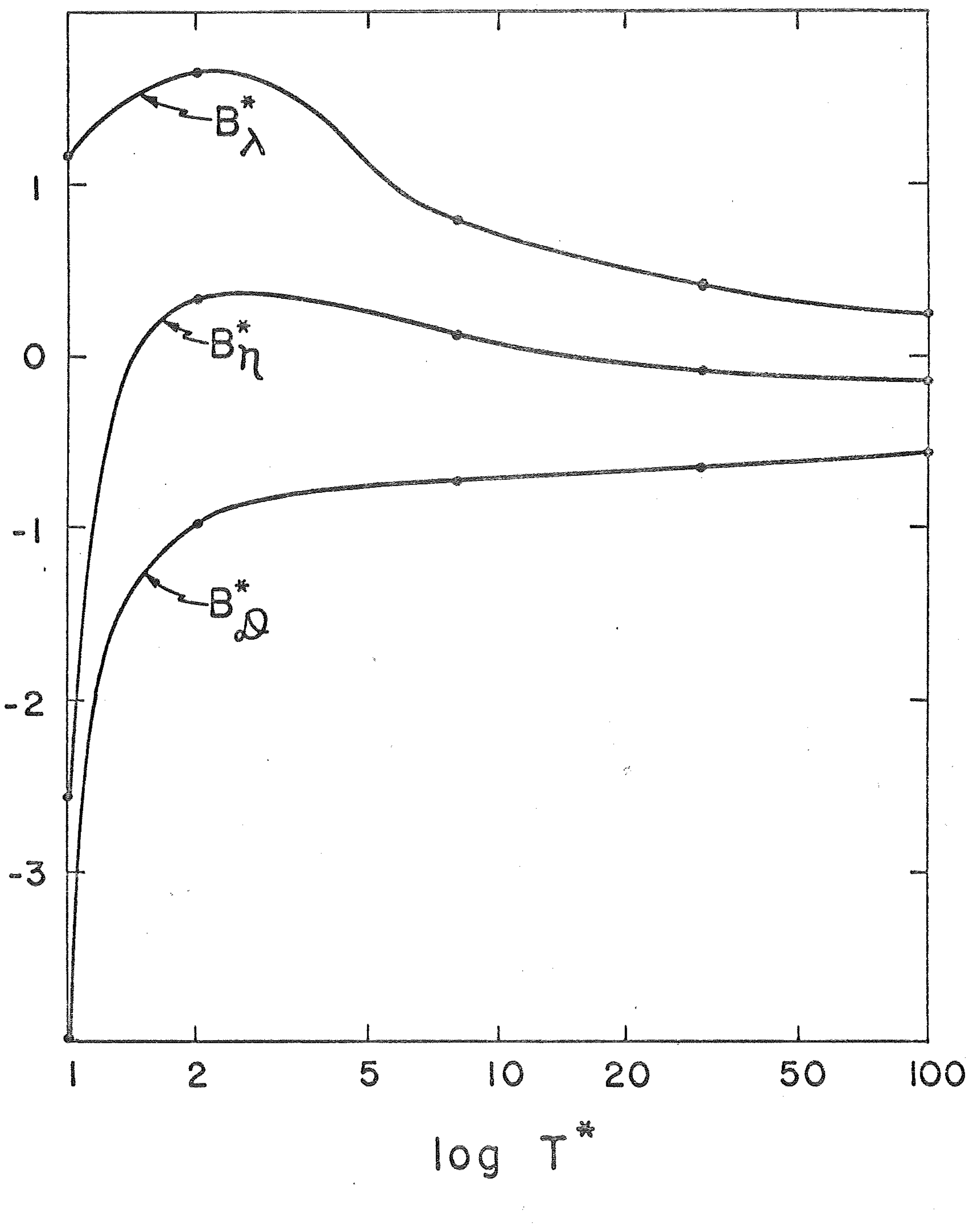
TABLE II

SECOND VIRIAL COEFFICIENTS FOR THE TRANSPORT PROPERTIES.

T	1	2	8	30	100
$B^*_{\eta Sc}$	-1.315	.6926	.9000	.6822	.5151
$B^*_{\lambda Sc}$	2.387	1.987	1.561	1.191	.9107
$B^*_{\Delta Sc}$	-2.758	- .6029	.0480	.1101	.1062
$5\pi R^{(2)*}/12\,\Omega^{(22)*}$	1.225	.3510	.7736	.7782	.6556
$5\pi R^{(1)*}/12\,\Omega^{(11)*}$	1.224	.3507	.7720	.7789	.6599
B^*_{η}	-2.540	.3416	.1264	- .09597	-.1406
B^*_{λ}	1.162	1.636	.7876	.4128	.2551
B^*_{Δ}	-3.982	- .9536	-.7240	- .6687	-.5538

FIGURE I

SECOND VIRIAL COEFFICIENT FOR THE TRANSPORT PROPERTIES



As discussed by Hoffman and Curtiss,[13c] the contributions of bound pairs are not included. These corrections probably become increasingly significant in the lower temperature region. Experimental results[27] for self diffusion are inconclusive at the present time; for the case of binary diffusion $B_{\mathcal{D}}$ appear to be negative at all temperatures.

7.3 Summary

The purpose of this work is the determinatinn of the first density corrections to the transport coefficients of gas mixtures. This is accomplished by developing and then solving a modified Boltzmann equation which includes the effects of both collisional transfer and three body collisions.

In Chapter II the classical BBGKY hierarchy for mixtures is developed from the N particle Liouville equation. The application of the principle of molecular chaos to the lowest order equation of the hierarchy truncates the hierarchy and yields a closed equation for the single particle distribution function.

The macroscopic equations of change for mixtures are derived in Chapter III. This leads to expressions for the fluxes in terms of the first and second order distribution functions. In the manner of Chapter II, the principle of molecular chaos is used to write the fluxes as functionals of the lowest order distribution function only.

In Chapter IV the lowest order distribution function is expanded about the equilibrium function, retaining only terms linear in the gradients. An inhomogeneous linear integral equation is then developed for the perturbation function. The inhomogeniety is written in the usual form except for additional terms proportional to the gradients of the mole fraction. The perturbation is written as a linear combination of the same gradients and the integral equation is separated into five separate perturbation equations. Each of the five equations is shown to independently satisfy the orthogonality conditions and thus be solvable.

The five equations are solved in Chapter V by the usual technique of expanding the perturbation functions in terms of Sonnine polynomials and using a variational principle. The expansion coefficients are then expanded in powers of the density to give sets of density independent equations.

In Chapter VI the fluxes and thence the transport coefficients are written in terms of the density expansion coefficients of the previous chapter. The transport second virial coefficients are written explicitly for a single component system.

For Chapter VII a computer program was written to calculate the integrals developed in the previous chapters. The Lennard-Jones potential was used, but the contributions of bound states have not been considered. The values of the transport second virial coefficients are given for five reduced temperatures for a single component system. For thermal conductivity an error in previous work is corrected and new values are presented.

The diffusion second virial coefficient is considered in detail. Explicit expressions for binary and self diffusion are given for the restricted case of rigid spheres and for the general case. Numerical values are presented for the case of self diffusion.

Appendix A

This appendix is a tabulation of the $R^{(i)}$ integrals developed in this work. Expressed as integrals over a relative position-velocity space, they are:

$$R^{(1)} = \frac{1}{m}\int \underline{\gamma}\cdot\frac{\partial V}{\partial \underline{r}}\, e^{-\gamma'^2}(\underline{\gamma}\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(2)} = \frac{1}{m}\int \underline{\gamma}\cdot\frac{\partial V}{\partial \underline{r}}\, e^{-\gamma'^2}(\underline{\gamma}\cdot\underline{\gamma}')^2\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(3)} = \frac{1}{m}\int \underline{\gamma}\cdot\frac{\partial V}{\partial \underline{r}}\, e^{-\gamma'^2}\left(\frac{5}{2}-\gamma'^2\right)(\underline{\gamma}\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(4)} = \frac{1}{m}\int \underline{\gamma}\cdot\frac{\partial V}{\partial \underline{r}}\, e^{-\gamma'^2}\left(\frac{5}{2}-\gamma^2\right)(\underline{\gamma}\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(5)} = \frac{1}{m}\int \underline{\gamma}\cdot\frac{\partial V}{\partial \underline{r}}\, e^{-\gamma'^2}\left(\frac{5}{2}-\gamma^2\right)\left(\frac{5}{2}-\gamma'^2\right)(\underline{\gamma}\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(6)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r}\, e^{-\gamma'^2}(\underline{r}\cdot\underline{\gamma}')^2\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(7)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r}\, e^{-\gamma'^2}\, r^2(\underline{r}'\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(8)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r}\, e^{-\gamma'^2}\left\{(\underline{r}\cdot\underline{\gamma}')(\underline{r}\cdot\underline{r}') - \frac{1}{3}r^2(\underline{r}'\cdot\underline{\gamma}')\right\} d\underline{r}\, d\gamma$$

$$R^{(9)} = \int e^{-\gamma'^2}\left\{\frac{1}{r}\frac{\partial \phi}{\partial r}(\underline{r}\cdot\underline{\gamma})(\underline{r}\cdot\underline{r}') - \phi(\underline{r}'\cdot\underline{\gamma})\right\} d\underline{r}\, d\underline{\gamma}$$

$$R^{(10)} = \int e^{-\gamma'^2}\left(\frac{3}{2}-\gamma'^2\right)\left\{\frac{1}{r}\frac{\partial \phi}{\partial r}(\underline{r}\cdot\underline{\gamma})(\underline{r}\cdot\underline{r}') - \phi(\underline{r}'\cdot\gamma)\right\} d\underline{r}\, d\underline{\gamma}$$

$$R^{(11)} = \int e^{-\gamma'^2} \left\{ \frac{1}{r}\frac{\partial \phi}{\partial r} (\underline{r}\cdot\underline{\gamma}')(\underline{r}\cdot\underline{\gamma}) - \phi(\underline{\gamma}\cdot\underline{\gamma}') \right\} d\underline{r}\, d\underline{\gamma}$$

$$R^{(12)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \left(\gamma'^2 - \frac{3}{2}\right) (\underline{r}\cdot\underline{r}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(13)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \left(\gamma'^2 - \frac{3}{2}\right) \gamma^2 (\underline{r}\cdot\underline{r}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(14)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \left(\gamma'^2 - \frac{3}{2}\right) (\underline{r}'\cdot\underline{\gamma})(\underline{r}\cdot\underline{\gamma})\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(15)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \left\{ (\underline{r}\cdot\underline{\gamma}')(\underline{r}'\cdot\underline{\gamma}) + (\underline{r}\cdot\underline{r}')(\underline{\gamma}\cdot\underline{\gamma}') \right\} d\underline{r}\, d\underline{\gamma}$$

$$R^{(16)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} (\underline{r}\cdot\underline{r}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(17)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \left(\frac{5}{2} - \gamma'^2\right) (\underline{r}\cdot\underline{r}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(18)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} (\underline{r}\cdot\underline{\gamma})(\underline{r}'\cdot\underline{\gamma})\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(19)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} (\underline{r}\cdot\underline{\gamma})(\underline{r}'\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(20)} = \int \frac{1}{r}\frac{\partial \phi}{\partial r} e^{-\gamma'^2} \gamma^2 (\underline{r}\cdot\underline{\gamma})(\underline{r}'\cdot\underline{\gamma}')\, d\underline{r}\, d\underline{\gamma}$$

$$R^{(21)} = \int e^{-\gamma'^2} \left\{ \frac{1}{r}\frac{\partial \phi}{\partial r} (\underline{r}\cdot\underline{\gamma}')(\underline{r}'\cdot\underline{r}) - \phi(\underline{r}'\cdot\underline{\gamma}') \right\} d\underline{r}\, d\underline{\gamma}$$

$$R^{(22)} = \int e^{-\gamma'^2}\left(\frac{5}{2}-\gamma'^2\right)\left[\frac{1}{r}\frac{\partial \phi}{\partial r}(\underline{r}\cdot\underline{\gamma})(\underline{r}\cdot\underline{\gamma}') - \phi(\underline{\gamma}\cdot\underline{\gamma}')\right] d\underline{r}\, d\underline{\gamma}$$

Integrals 1 through 5 may be evaluated for mixtures of rigid spheres:

$$R^{(1)}_{\alpha\beta} = \frac{4\pi^2 \sigma_{\alpha\beta}^2}{n}\left[Y_{\alpha\beta(0)}(\sigma) - 1\right]$$

$$R^{(2)}_{\alpha\beta} = \frac{8\pi^2 \sigma_{\alpha\beta}^2}{n}\left[Y_{\alpha\beta(0)}(\sigma) - 1\right]$$

$$R^{(3)}_{\alpha\beta} = R^{(4)}_{\alpha\beta} = -\frac{2\pi^2 \sigma_{\alpha\beta}^2}{n}\left[Y_{\alpha\beta(0)}(\sigma) - 1\right]$$

$$R^{(5)} = \frac{13\pi^2 \sigma_{\alpha\beta}^2}{n}\left[Y_{\alpha\beta(0)}(\sigma) - 1\right]$$

For a binary system, $(Y_{\alpha\beta(0)}(\sigma) - 1)/n$ is given by equation (6.3-11).

For a single component system, the integrals have the following values for rigid spheres:

$$R^{(1)} = \frac{5}{3}\pi^3 \sigma^5$$

$$R^{(2)} = \frac{10}{3}\pi^3 \sigma^5$$

$$R^{(3)} = R^{(4)} = -\frac{5}{6}\pi^3 \sigma^5$$

$$R^{(5)} = 5\left(\frac{13}{12}\right)\pi^3 \sigma^5$$

$$R^{(6)} = -6\pi^{5/2} kT\sigma^{3}$$

$$R^{(7)} = 8\pi^{2} kT\sigma^{4}$$

$$R^{(8)} = \frac{16}{3}\pi^{2} kT\sigma^{4}$$

$$R^{(9)} = R^{(10)} = R^{(11)} = 0.$$

$$R^{(12)} = -4\pi^{5/2} kT\sigma^{3}$$

$$R^{(13)} = -12\pi^{5/2} kT\sigma^{3}$$

$$R^{(14)} = R^{(15)} = R^{(16)} = R^{(17)} = -4\pi^{5/2} kT\sigma^{3}$$

$$R^{(18)} = -2\pi^{5/2} kT\sigma^{3}$$

$$R^{(19)} = R^{(20)} = 0$$

$$R^{(21)} = 8\pi^{2} kT\sigma^{4}$$

$$R^{(22)} = 0$$

For those which are zero, the following values were used:

$$R_{RS}^{(9)} = R_{RS}^{(10)} = -8\pi^{5/2} kT\sigma^{4}$$

$$R_{RS}^{(11)} = R_{RS}^{(19)} = R_{RS}^{(20)} = R_{RS}^{(22)} = -8\pi^{5/2} kT\sigma^{3}$$

to render $R^{(i)*}$ dimensionless.

Appendix B

We list here the various quantities encountered in Chapter V:

$$K_{\alpha 0}^{(2)} = \sum_{\beta} \frac{X_\alpha X_\beta (m_\alpha - m_\beta)}{2\pi^{3/2} m_\alpha M_{\alpha\beta}} R_{\alpha\beta}^{(12)}$$

$$K_{\alpha 1}^{(1)} = \frac{15 X_\alpha kT}{2 m_\alpha}$$

$$K_{\alpha 1}^{(2)} = \frac{15 X_\alpha kT}{2 m_\alpha} \sum_{\beta} B_{\alpha\beta} X_\beta + \sum_{\beta} \frac{4 X_\alpha X_\beta kT \mu_{\alpha\beta}}{m_\alpha M_{\alpha\beta}} \left[\frac{7}{2} T \frac{\partial B_{\alpha\beta}}{\partial T} + T^2 \frac{\partial^2 B_{\alpha\beta}}{\partial T^2}\right]$$

$$+ \sum_{\beta} \frac{5 X_\alpha X_\beta (m_\alpha - m_\beta)}{2\pi^{3/2} M_{\alpha\beta}} R_{\alpha\beta}^{(16)} + \sum_{\beta} \frac{2 X_\alpha X_\beta \mu_{\alpha\beta}}{\pi^{3/2} m_\alpha M_{\alpha\beta}} R_{\alpha\beta}^{(15)}$$

$$+ \sum_{\beta} \frac{X_\alpha X_\beta (m_\alpha - m_\beta)}{\pi^{3/2} m_\alpha M_{\alpha\beta}} \left[\frac{5 m_\beta}{4 M_{\alpha\beta}} R_{\alpha\beta}^{(12)} - \frac{\mu_{\alpha\beta}}{2 m_\alpha} R_{\alpha\beta}^{(13)} - \frac{m_\beta}{M_{\alpha\beta}} R_{\alpha\beta}^{(14)}\right]$$

$$\mathcal{H}_{\alpha\gamma 0}^{(100)} = -\sum_{\beta} 8 \left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}} \left[\frac{m_\beta}{M_{\alpha\beta}} X_\beta \delta_{\alpha\gamma} - \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{\frac{1}{2}} X_\alpha \delta_{\beta\gamma}\right] \Omega_{\alpha\beta}^{(11)}$$

$$\mathcal{H}_{\alpha\gamma 0}^{(101)} = -\sum_{\beta} 8 \left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}} \left[-\frac{m_\beta^2}{M_{\alpha\beta}^2} X_\beta \delta_{\alpha\gamma} + \frac{m_\alpha \mu_{\alpha\beta}^{\frac{1}{2}}}{M_{\alpha\beta}^{3/2}} X_\alpha \delta_{\beta\gamma}\right] \left(\Omega_{\alpha\beta}^{(12)} - \frac{5}{2} \Omega_{\alpha\beta}^{(11)}\right)$$

$$\mathcal{H}_{\alpha\gamma 0}^{(210)} = -\sum_{\beta} 8 \left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}} \left[\frac{m_\beta}{M_{\alpha\beta}} \delta_{\alpha\gamma} - \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{\frac{1}{2}} \delta_{\beta\gamma}\right] X_\alpha X_\beta \Omega_{\alpha\beta}^{(11)}$$

$$\mathcal{H}^{(211)}_{\alpha\gamma 0} = -\sum_{\beta} 8\left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}}\left[-\frac{m_\beta^2}{M_{\alpha\beta}^2}\delta_{\alpha\gamma} + \frac{m_\alpha \mu_{\alpha\beta}^{\frac{1}{2}}}{M_{\alpha\beta}^{3/2}}\delta_{\beta\gamma}\right] X_\alpha X_\beta \left(\Omega^{(12)}_{\alpha\beta} - \frac{5}{2}\Omega^{(11)}_{\alpha\beta}\right)$$

$$\mathcal{H}^{(200)}_{\alpha\gamma 0} = -\sum_{\beta}\frac{2kT}{(\pi^3 \mu_{\alpha\beta} m_\alpha)^{\frac{1}{2}}}\left[\frac{m_\alpha}{M_{\alpha\beta}} X_\beta \delta_{\alpha\gamma} - \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{\frac{1}{2}} X_\alpha \delta_{\beta\gamma}\right] R^{(1)}_{\alpha\beta}$$

$$\mathcal{H}^{(201)}_{\alpha\gamma 0} = -\sum_{\beta}\frac{2kT}{(\pi^3 \mu_{\alpha\beta} m_\alpha)^{\frac{1}{2}}}\left[\frac{m_\beta^2}{M_{\alpha\beta}^2} X_\beta \delta_{\alpha\gamma} - \frac{m_\alpha \mu_{\alpha\beta}^{\frac{1}{2}}}{M_{\alpha\beta}^{3/2}} X_\alpha \delta_{\beta\gamma}\right] R^{(3)}_{\alpha\beta}$$

$$\mathcal{H}^{(100)}_{\alpha\gamma 1} = \mathcal{H}^{(101)}_{\alpha\gamma 0}$$

$$\mathcal{H}^{(210)}_{\alpha\gamma 1} = \mathcal{H}^{(210)}_{\alpha\gamma 0}$$

$$\mathcal{H}^{(101)}_{\alpha\gamma 1} = -\sum_{\beta} 8\left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}}\left\{\left(\frac{m_\beta}{M_{\alpha\beta}}\right)^3\left[\frac{5}{4}\left(\frac{6m_\alpha^2}{m_\beta^2}+5\right)\Omega^{(11)}_{\alpha\beta} - 5\Omega^{(22)}_{\alpha\beta}\right.\right.$$

$$\left. + \Omega^{(13)}_{\alpha\beta} + \frac{2m_\alpha}{m_\beta}\Omega^{(22)}_{\alpha\beta}\right] X_\beta \delta_{\alpha\gamma} + \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{3/2}\left[-\frac{55}{4}\Omega^{(11)}_{\alpha\beta}\right.$$

$$\left.\left. + 5\Omega^{(11)}_{\alpha\beta} - \Omega^{(13)}_{\alpha\beta} + 2\Omega^{(22)}_{\alpha\beta}\right] X_\alpha \delta_{\beta\gamma}\right\}$$

$$\mathcal{H}^{(211)}_{\alpha\gamma 1} = -\sum_{\beta}{}' 8\left(\frac{2kT}{m_\alpha}\right)^{\frac{1}{2}}\left\{\left(\frac{m_\beta}{M_{\alpha\beta}}\right)^3\left[\frac{5}{4}\left(\frac{6m_\alpha^2}{m_\beta^2}+5\right)\Omega^{(11)}_{\alpha\beta} - 5\Omega^{(12)}_{\alpha\beta}\right.\right.$$

$$\left. + \Omega^{(13)}_{\alpha\beta} + 2\frac{m_\alpha}{m_\beta}\Omega^{(22)}_{\alpha\beta}\right]\delta_{\alpha\gamma} + \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{3/2}\left[-\frac{55}{4}\Omega^{(11)}_{\alpha\beta}\right.$$

$$\left.\left. + 5\Omega^{(12)}_{\alpha\beta} - \Omega^{(13)}_{\alpha\beta} + 2\Omega^{(22)}_{\alpha\beta}\right]\delta_{\beta\gamma}\right\} X_\alpha X_\beta$$

$$\mathcal{H}^{(200)}_{\alpha\gamma 1} = -\sum_{\beta}{}' \frac{2kT}{(\pi^3 m_\alpha \mu_{\alpha\beta})^{\frac{1}{2}}}\left[\left(\frac{m_\beta}{M_{\alpha\beta}}\right)^2 X_\beta \delta_{\alpha\gamma} - \frac{m_\beta \mu_{\alpha\beta}^{\frac{1}{2}}}{M_{\alpha\beta}^{3/2}} X_\alpha \delta_{\beta\gamma}\right] R^{(4)}_{\alpha\beta}$$

$$\mathcal{H}^{(201)}_{\alpha\gamma 1} = -\sum_{\beta}{}' \frac{2kT}{(\pi^3 m_\alpha \mu_{\alpha\beta})^{\frac{1}{2}}}\left\{\left[\frac{15\mu_{\alpha\beta}^2}{2m_\alpha M_{\alpha\beta}} R^{(1)}_{\alpha\beta} + \left(\frac{m_\beta}{M_{\alpha\beta}}\right)^3 R^{(5)}_{\alpha\beta}\right.\right.$$

$$\left. + \frac{2\mu_{\alpha\beta}^2}{m_\alpha M_{\alpha\beta}} R^{(2)}_{\alpha\beta}\right] X_\beta \delta_{\alpha\gamma} + \left(\frac{\mu_{\alpha\beta}}{M_{\alpha\beta}}\right)^{3/2}\left[-\frac{15}{2}R^{(1)}_{\alpha\beta} - R^{(5)}_{\alpha\beta}\right.$$

$$\left.\left. + 2R^{(2)}_{\alpha\beta}\right] X_\alpha \delta_{\beta\gamma}\right\}$$

$$L^{(1)}_\alpha = -\frac{10kT}{m_\alpha}$$

$$L_{\alpha\beta}^{(2)} = -\frac{5(m_\alpha - m_\beta)}{6\pi^{3/2} m_\alpha M_{\alpha\beta}} R_{\alpha\beta}^{(16)} - \frac{2\mu_{\alpha\beta}}{\pi^{3/2} m_\alpha^2} R_{\alpha\beta}^{(15)} - \frac{10 kT B_{\alpha\beta}}{m_\alpha}$$

$$+ \frac{8\mu_{\alpha\beta} kT}{3 m_\alpha^2}\left[\frac{7}{2} T \frac{\partial B_{\alpha\beta}}{\partial T} + T^2 \frac{\partial^2 B_{\alpha\beta}}{\partial T^2}\right]$$

$$\mathcal{L}_{\alpha\gamma}^{(0)} = \sum_\beta \frac{32 m_\alpha kT}{3 M_{\alpha\beta}^2}\left\{\left[5\Omega_{\alpha\beta}^{(11)} + \frac{3}{2}\frac{m_\beta}{m_\alpha}\Omega_{\alpha\beta}^{(22)}\right] X_\beta \delta_{\alpha\gamma}\right.$$

$$\left. - \left[5\Omega_{\alpha\beta}^{(11)} - \frac{3}{2}\Omega_{\alpha\beta}^{(22)}\right] X_\alpha \delta_{\beta\gamma}\right\}$$

$$\mathcal{L}_{\alpha\gamma}^{(1)} = \sum_\beta \frac{32 m_\alpha X_\alpha X_\beta kT}{3 M_{\alpha\beta}^2}\left\{\left[5\Omega_{\alpha\beta}^{(11)} + \frac{3}{2}\frac{m_\beta}{m_\alpha}\Omega_{\alpha\beta}^{(22)}\right]\delta_{\alpha\gamma}\right.$$

$$\left. - \left[5\Omega_{\alpha\beta}^{(11)} - \frac{3}{2}\Omega_{\alpha\beta}^{(22)}\right]\delta_{\beta\gamma}\right\}$$

$$\mathcal{L}_{\alpha\gamma}^{(2)} = \sum_\beta \frac{2 m_\alpha kT}{\pi^{3/2} M_{\alpha\beta}^2}\left(\frac{2kT}{\mu_{\alpha\beta}}\right)^{\frac{1}{2}}\left\{\left[\frac{m_\beta}{m_\alpha} R_{\alpha\beta}^{(2)} + \frac{10}{3} R_{\alpha\beta}^{(1)}\right] X_\beta \delta_{\alpha\gamma}\right.$$

$$\left. + \left[R_{\alpha\beta}^{(2)} - \frac{10}{3} R_{\alpha\beta}^{(1)}\right] X_\alpha \delta_{\beta\gamma}\right\}$$

$$M_\alpha^{(1)} = X_\alpha \left\{ \sum_\beta B_{\alpha\beta} X_\beta - B - \frac{7}{3} T \frac{\partial B}{\partial T} - \frac{2}{3} T^2 \frac{\partial^2 B}{\partial T^2} \right\}$$

$$+ \sum_\beta \frac{4 X_\alpha X_\beta \mu_{\alpha\beta}}{3 m_\alpha} \left[\frac{7}{2} T \frac{\partial B_{\alpha\beta}}{\partial T} + T^2 \frac{\partial^2 B_{\alpha\beta}}{\partial T^2} \right]$$

$$+ \sum_\beta \frac{X_\alpha X_\beta (m_\alpha - m_\beta)}{6 \pi^{3/2} M_{\alpha\beta} kT} R_{\alpha\beta}^{(16)}$$

$$M_\alpha^{(2)} = \sum_\beta \frac{10 X_\alpha X_\beta \mu_{\alpha\beta}}{3 m_\alpha} \left[\frac{7}{2} T \frac{\partial B_{\alpha\beta}}{\partial T} + T^2 \frac{\partial^2 B_{\alpha\beta}}{\partial T^2} \right]$$

$$+ \sum_\beta \frac{X_\alpha X_\beta (m_\alpha - m_\beta)}{6 \pi^{3/2} M_{\alpha\beta}^2 kT} \left[R_{\alpha\beta}^{(17)} - 2 R_{\alpha\beta}^{(18)} \right]$$

$$- \sum_\beta \frac{2 X_\alpha X_\beta \mu_{\alpha\beta}}{3 \pi^{3/2} M_{\alpha\beta} kT} \left[\frac{5}{2} R_{\alpha\beta}^{(19)} + \frac{m_\beta}{m_\alpha} R_{\alpha\beta}^{(20)} \right]$$

APPENDIX C

CDC 3600 COMPUTER PROGRAM

```
      PROGRAM TPMDMCGM
      DIMENSION GINT(25), XIINT(25), XIINT1(25), XIINT2(25), RINT(25),
     1F(25),HPT(100),HWT(100),PTGAUS(100),WTGAUS(100),PTCHEBX(100),PTCHE
     2B(100),PTCHEBR(100),PTGAUS2(100),WTGAUS2(100),GINC(25),GINF(25),
     3CON(25),BSUB(15)
      EXTERNAL RF
      COMMON T
 1001 FORMAT (6F12.8)
 1002 FORMAT (6I4)
 1003 FORMAT (4H1T =,F8.3,3X,3HB =,F13.8,3X,4HB1 =,F12.7,3X,4HB2 =,F12.7
     1,3X,7HOMG11 =,F12.7,3X,7HOMG22 =,F12.7)
 1004 FORMAT(6HOGNOT=,I4,3X,7HXIGAUS=,I4,3X,7HXICHEB=,I4,3X,
     18HRHOCHEB=,I4,3X,6HRCHEB=,I4,3X,8HRHOGAUS=,I4)
 1005 FORMAT (/,(5(1X,I2,E18.10,2X)))
 1049 FORMAT(1H0,I2,2X,5HGNOT=,F16.10,2X,5HALMT=,F14.10)
 1050 FORMAT(1H0,I2,2X,5HGNOT=,F16.10,2X,5HALMT=,F14.10,2X,5HBLMT=,F14.
     110,2X,5HCLMT=,F14.10,2X,6HBSTAR=,F14.10)
 3001 FORMAT (/,12H0(B ETA)SC =,E18.10/12H0(B ETA)Y  =,E18.10/12H0(B ETA
     1)   =,E18.10//12H0(B D)SC   =,E18.10/12H0(B D)Y    =,E18.10/12H0(B
     2 D)     =,E18.10//12H0(B L)SC   =,E18.10/12H0(B L)Y    =,E18.10/12
     3H0(B L)     =,E18.10)
      PI = 3.1415926536
      SQPI = SQRTF(PI)
      EPS = 1.E-8
      EPSL=1.E-9
C     USE NEGATIVE TEMPERATURE TO STOP PROGRAM
   50 READ 1001,T,BST,BSTP,BSTPP,OMG11,OMG22
      IF(T.LT.0.) 51,52
   51 STOP
C     NHERM = NUMBER OF HERMITE POINTS IN GNOT INTEGRATION
C     NGAUS = NUMBER OF POINTS BETWEEN A AND B IN XI INTEGRATION
C     NXI=NUMBER OF POINTS BETWEEN CLIMIT AND INFINITY IN XI INTEGRATION
C     NCHEB = NEMBER OF POINTS BETWEEN XI AND INFINITY IN RHO INTEGRATION
C      NCHEBR = NUMBER OF POINTS IN R INTEGRATION
C     NGAUS2=NUMBER OF POINTS BETWEEN R(I-1) AND R(I) IN RHO INTEGRATION
   52 READ 1002, NHERM, NGAUS, NXI , NCHEB,NCHEBR, NGAUS2
```

```
      PRINT 1003,T,BST,BSTP,BSTPP,OMG11,OMG22
      PRINT 1004, NHERM, NGAUS, NXI , NCHEB,NCHEBR, NGAUS2
      L = 0
      CALL QUAD (3HINF, 3HINF, RF, 2 *NHERM, HPT, HWT, L)
      DO 81 I=1,NHERM
      HPT(I) = HPT(NHERM+I)
      HWT(I) = HWT(NHERM+I)
   81 CONTINUE
      L = 0
      CALL QUAD (-1., +1., RF, NGAUS, PTGAUS, WTGAUS, L)
      L = 0
      CALL QUAD (-1., +1., RF, NGAUS2, PTGAUS2, WTGAUS2, L)
      FNCHEB = 4*NCHEB
      FNCHEBR = 4*NCHEBR
      FNXI = 4*NXI
      DO 82 I=1,NCHEB
      FI = I
      PTCHEB(I) = COSF(PI*(2.*FI-1.)/FNCHEB)
   82 CONTINUE
      DO 83 I = 1,NCHEBR
      FI = I
      PTCHEBR(I) = COSF(PI*(2.*FI-1.)/FNCHEBR)
   83 CONTINUE
      DO 84 I = 1,NXI
      FI = I
      PTCHEBX(I) = COSF(PI*(2.*FI-1.)/FNXI)
   84 CONTINUE
      TSQ = T*T
      SQT = SQRTF(T)
C CON(I)-CONSTANTS TO NORMALIZE INTEGRALS TO 0 OR 1 FOR RIGID SPHERES
      CON(1) = 12./(5.*PI*TSQ*T)
      CON(2) = CON(1)/T
      CON(3) = CON(4) = -2.*CON(1)
      CON(5) = 48./(65.*PI*TSQ*T)
      CON(11) = CON(19) = CON(22) = -1./(SQPI*TSQ*T*SQT)
      CON(7) = CON(21) = 1./(TSQ*T)
```

```
      CON(8) = 1.5*CON(7)
      CON(9) = CON(10) = -1./(SQPI*TSQ*T)
      CON(12) = -2./(SQPI*TSQ*SQT)
      CON(14) = CON(15) = 2.*CON(19)
      CON(13) = CON(14)/3.
      CON(6) = 2.*CON(13)
      CON(16) = CON(17) = -2./(SQPI*TSQ*SQT)
      CON(18) = 4.*CON(19)
      CON(20) = CON(19)/T
      DO 101 I=1,22
      GINT(I) = 0.
  101 CONTINUE
C   G INTEGRATION           HERMITE
      DO 499 J=1,NHERM
      GNOT = HPT(J)*SQRTF(T)
      IF(HPT(J).GT.6.)GO TO 500
      GSQ = GNOT*GNOT
C  DETERMINE A
      NG = NGAUS  $  JUMP = 2
      TERM = 0.5*(1.+SQRTF(1.+GSQ))
      ALIMIT = 1./CUBERTF(SQRTF(TERM))
      BLIMIT = CLIMIT = 2.*ALIMIT
C  DETERMINE C
      IF (GSQ.GT.0.8)  115, 104
  115 PRINT 1049,J,GNOT,ALIMIT
      GO TO 120
  104 TERM = 0.2-0.1*SQRTF(4.-5.*GSQ)
      CLIMIT = 1./CUBERTF(TERM)
      BSTAR = CLIMIT*(1.-4.*TERM*(TERM-1.)/GSQ)
      DUMMY=SQRTF(BSTAR)
      CLIMIT = SQRTF(CLIMIT)
C  DETERMINE B
      ZINC = .01 $ Z = 1.15 $ SAVE = 1.
   71 Y = 1./(Z*Z)
      TERM = Y*Y*Y
      TERM = GSQ*(1.-BSTAR*Y)-4.*TERM*(TERM-1.)
```

```
      IF(ZINC.GT.EPSL)70,73
   73 IF((ABSF(TERM)).GT.EPS )70,110
   70 IF( TERM.GT.0.) 74,72
   72 IF(SAVE.GT.0.) 76,75
   75 Z = Z+ZINC
   69 SAVE = TERM
      GO TO 71
   76 Z = Z+ZINC
      ZINC = .1*ZINC
      Z = Z-ZINC
      GO TO 69
   74 IF(SAVE.GT.0.) 78,77
   78 Z = Z-ZINC
      GO TO 69
   77 Z = Z-ZINC
      ZINC = .1*ZINC
      Z = Z+ZINC
      GO TO 69
  110 BLIMIT = Z
      PRINT 1050,J,GNOT,ALIMIT,BLIMIT,CLIMIT,DUMMY
  120 NSUM = NG + NXI
      DO 121 I=1,22
      XIINT(I) = XIINT1(I) = XIINT2(I) = 0.
  121 CONTINUE
C        XI INTEGRATION              GAUSS AND CHEBYSHEV
      DO 399 L=1,NSUM
      GO TO (124,122), JUMP
  122 XI = ALIMIT + (PTGAUS(L) + 1.) * (BLIMIT-ALIMIT)*0.5
      GO TO 126
  124 K = L - NG
      XI = CLIMIT/PTCHEBX(K)
  126 XISQ = XI*XI
      TEMP = 1./XISQ**3
      FXI = 4. * TEMP * (TEMP - 1.)
      XIFP = 24. * TEMP * (1.-2.*TEMP)
      XITERM = XISQ * (GSQ - FXI)
```

```
      SQXI = SQRTF(XITERM)
      CHI = DW = ALPHA = WXI = 0.
C   RHO INTEGRATION      FROM XI TO INFINITY        CHEBYSHEV
      DO 140 MRO=1,NCHEB
      RHO = XI/PTCHEB(MRO)
      ROSQ = RHO*RHO
      TEMP = 1./ROSQ**3
      FRHO = 4. * TEMP * (TEMP - 1.)
      ROTERM = ROSQ * (GSQ - FRHO)
      DCOM = SQRTF(ROTERM - XITERM)
      TEMP = SQRTF(1.-PTCHEB(MRO)*PTCHEB(MRO))
      ALPHA = ALPHA + RHO*TEMP/DCOM
      DW = DW + (RHO*GNOT/DCOM-1.)*ROSQ*TEMP
  140 CONTINUE
      TEMP = 2*NCHEB
      ALPHA = PI*SQXI*ALPHA/(XI*TEMP)
      CHI = PI - 2.*ALPHA
      DW = DW*PI/(TEMP*XI) - XI
      SAVE = XI
      DO 150 I = 1,22
      RINT(I) = 0.
  150 CONTINUE
C    R INTEGRATION        CHEBYSHEV
      DO 299 M = 1,NCHEBR
      R = XI/PTCHEBR(M)
      RSQ = R * R
      TEMP = 1./RSQ**3
      FR = 4. * TEMP * (TEMP-1.)
      RTERM = RSQ*(GSQ-FR)
      SQR = SQRTF(RTERM)
      FPR = 24.*TEMP*(1.-2.*TEMP)/R
      ATERM = WXITERM = 0.
C    RHO INTEGRATION, R LIMITS       GAUSS
      DO 220 MRO = 1, NGAUS2
      RHO = SAVE + (PTGAUS2(MRO)+1.)*0.5*(R-SAVE)
      ROSQ = RHO*RHO
```

```
      TEMP = 1./ROSQ**3
      FRHO = 4. * TEMP * (TEMP - 1.)
      ROTERM = ROSQ * (GSQ - FRHO)
      DCOM = SQRTF(ROTERM - XITERM)
      ATERM = ATERM + WTGAUS2(MRO)/(RHO*DCOM)
      WXITERM = WXITERM + RHO*WTGAUS2(MRO)/DCOM
  220 CONTINUE
      ATERM = SQXI*0.5*(R-SAVE)*ATERM
      WXITERM = .5*GNOT*(R-SAVE)*WXITERM
      ALPHA = ALPHA - ATERM
      WXI = WXI + WXITERM
      DCOM = SQRTF(RTERM - XITERM)
      SINTH = SQXI/SQR
      COSTH = DCOM/SQR
      YACOB = R * GNOT * (XITERM - 0.5*XISQ*XIFP)/(XI*SQR*SQXI*DCOM)
C    INCOMING DEFINITIONS
  225 GORI = -COSF(ALPHA)
      BRI = SINF(ALPHA)
      RPGOI = DW - WXI
      GOGI = -GORI * COSTH + BRI * SINTH
      BGI = -GORI*SINTH - BRI*COSTH
      RRPI = RPGOI*GORI + SQXI*BRI/GNOT
      GRPI = RPGOI*GOGI + SQXI*BGI/GNOT
C    OUTGOING DEFINITIONS
  230 GOR = COSF(ALPHA + CHI)
      BR = SINF(ALPHA + CHI)
      RPGO = DW + WXI
      GOG =  GOR*COSTH + BR*SINTH
      BG = -GOR*SINTH + BR*COSTH
      RRP = RPGO*GOR + SQXI*BR/GNOT
      GRP = RPGO*GOG + SQXI*BG/GNOT
  235 TCON = GSQ/T - 1.5
      GOT = GNOT/T
      GTCON = 1. - TCON
      FCON = RADF(R)*FPR*GNOT
      F(1) = FCON*(GORI+GOR)
```

```
      F(2) = FCON*SQR/R*GNOT*(GORI*GOGI+GOR*GOG)
      F(3) = F(1)*GTCON
      F(4) = FCON* 2.*COSTH*(GSQ-FR)/T*(GOGI-GOG) + F(3)
      F(5) = F(4)*GTCON
      F(6) = GSQ*R  *FPR*(GORI*GORI + GOR*GOR)
      F(7) = GNOT*R*FPR*(DW+DW)
      F(8) = GNOT*R*FPR*(GORI*RRPI + GOR*RRP - 0.33333333333*(DW+DW))
      F(9) = FPR*SQR*COSTH*(RRP - RRPI) - FR*(SQR/R)*(GRPI+GRP)
      F(10) = -F(9) * TCON
      F(11) = GNOT*FPR*SQR*COSTH*(GOR-GORI) - FR*GNOT*SQR/R*(GOGI+GOG)
      F(12) = FPR*TCON*(RRPI + RRP)
      F(13) = (GSQ-FR)*F(12)
      F(14) = FPR * (GSQ-FR) * TCON * COSTH * (GRP-GRPI)
      F(15) = GNOT*FPR*(SQR/R )*(GORI*GRPI + GOR*GRP+RRPI*GOGI+RRP*GOG)
      F(16) = FPR * (RRPI + RRP)
      F(17) = F(16) * GTCON
      F(18) = FPR *(GSQ-FR)*COSTH*(GRP-GRPI)
      F(19) = F(18)*GNOT*R/SQR
      F(20) = F(19) * (GSQ-FR)
      F(21) = GNOT*(R*FPR*(RRPI*GORI+RRP*GOR)-FR*(DW+DW))
      F(22) = GTCON*F(11)
      TEMP = 2*NCHEBR
      FFACT = RTERM*SINTH*YACOB*RSQ*SQRTF(1.-PTCHEBR(M)*PTCHEBR(M))*PI/(
     1XI*TEMP)
      DO 270 I=1,22
      RINT(I) = RINT(I) + FFACT*F(I)
  270 CONTINUE
      SAVE = R
  299 CONTINUE
      GO TO (308, 304), JUMP
  304 DO 306 I=1,22
      XIINT1(I)= XIINT1(I) + WTGAUS(L)*RINT(I)
  306 CONTINUE
      IF (L.EQ.NG) JUMP = 1
      GO TO 399
  308 TERM = PI*SQRTF(1.-PTCHEBX(K)*PTCHEBX(K))
```

```
      DO 310 I = 1,22
      XIINT2(I) = XIINT2(I) + RINT(I)*XISQ*TERM
  310 CONTINUE
  399 CONTINUE
      EGO = EXPF(-GSQ/T)
      TEMP = 2*NXI
      DO 402 I=1,22
      XIINT(I) = XIINT1(I)*(BLIMIT-ALIMIT)*0.5 + XIINT2(I)/(CLIMIT*TEMP)
      GINC(I) = XIINT(I)*SQT*CON(I)
      GINF(I) = GINC(I)*EGO
      GINT(I) = GINT(I) + GINF(I)*HWT(J)
  402 CONTINUE
      PRINT 1005,((I,GINC(I)),I=1,22)
      PRINT 1005,((I,GINF(I)),I=1,22)
  499 CONTINUE
  500 PRINT 1003,T,BST,BSTP,BSTPP,OMG11,OMG22
      PRINT 1005,((I,GINT(I)),I=1,22)
      BSUB(1) = (2.*PI/3.)*(.5*BST-2.*BSTP/3.-2.*BSTPP/15.-.6*GINT(15)
     1+.9*GINT(6))
      BSUB(2) = BSUB(8) = 5.*PI*GINT(2)/(12.*OMG22)
      BSUB(3) = BSUB(1) - BSUB(2)
      BSUB(4) = 2.*PI*(BST - GINT(16))/3.
      BSUB(5)= 5.*PI*GINT(1)/(12.*OMG11)
      BSUB(6) = BSUB(4) - BSUB(5)
      BSUB(7) = (2.*PI/3.)*(BST-.2*BSTPP-.4*GINT(15)+.6*GINT(6))
      BSUB(9) = BSUB(7) - BSUB(8)
      PRINT 3001,(BSUB(I),I=1,9)
      GO TO 50
      END
      FUNCTION RADF(R)
      COMMON T
100   FORMAT(26H RADF NOT DEFINED FOR T = ,F14.8)
      IF(T.EQ.1.)11,20
11    IF(R.GT.2.0)GO TO 12
      RADF = 11.657-R*(17.603-R*(8.1347-1.0122*R))
      RETURN
```

```
12    IF (R.GT.2.6) GO TO 14
      RADF = -129.75+R*(164.-R*(67.872-9.2667*R))
      RETURN
14    RADF=190.64*EXPF(-2.1594*R)
      RETURN
20    IF(T.EQ.2.0)21,30
21    IF(R.GT.2.0)GO TO 22
      RADF = 5.1084-R*(7.5927-R*(2.9521-.22929*R))
      RETURN
22    RT=1./(R-1.8)
      RADF=(11.864+RT*(8.2291-RT*(6.2996-.7972*RT)))*EXPF(-1.9241*R)
      RETURN
30    IF(T.EQ.8.)31,40
31    IF (R.GT.1.8) GO TO 32
      RADF = 3.3345-R*(3.5777-R*(.66075+.14427*R))
      RETURN
32    IF(R.GT.2.0) GO TO 34
      RADF=-.59320+.26120*R
      RETURN
34    RADF = -248.43*EXPF(-4.0816*R)
      RETURN
40    IF(T.EQ.30.) 41,50
41    IF (R.GT.1.6) GO TO 42
      RADF = 2.5863-R*(2.4615-R*(.14083+.23685*R))
      RETURN
42    IF (R.GT.1.8) GO TO 44
      RADF=.64644-R*(.93865-.32867*R)
      RETURN
44    RADF = -7.5857*EXPF(-3.0859*R)
      RETURN
50    IF(T.EQ.100.)51,60
51    IF (R.GT.1.5) GO TO 52
      RADF = 2.0038+R*(-1.9013+R*(-.019016+.26942*R))
      RETURN
52    IF(R.GT.1.8) GO TO 54
      RADF= 1.0899+R*(-1.2932+.37987*R)
```

```
      RETURN
54    RADF=-1.5087*EXPF(-2.9777*R)
      RETURN
60    PRINT 100,T
      STOP
      END
      FUNCTION RF(R)
      RF = 1.
      END

1.0         -2.5380814  4.4282616   -11.53985   1.439       1.587
  20  24  24  48  48  20

2.0         -.62762535  1.6297207   -3.79972    1.075       1.175
  20  24  24  48  48  20

8.0         .41343396   .2524801    -0.639879   .7712       .8538
  20  24  24  48  48  20

30.0        .52692546   -.0174929   -.072012    .6232       .7005
  20  24  24  48  48  20

100.0       .4640695    -.0725244   .036441     .5170       .5882
  20  24  24  48  48  20

-1.0
```

FOOTNOTES

1. All of Boltzmann's papers are contained in: L. Boltzmann, Lectures on Gas Theory (University of California Press, Berkeley, 1964).
2. Maxwell, Collected Papers, 2, 1; quoted in S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge University Press, London, 1961), pp. 173-7.
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13. (a). D. K. Hoffman and C. F. Curtiss, Phys. Fluids 7, 1887 (1964); (b). 8, 667 (1965); (c). 8, 890 (1965).

14. (a). R. F. Snider and C. F. Curtiss, Phys. Fluids 1, 122 (1958); 3, 903 (1960); (b). H. B. Hollinger and C. F. Curtiss, J. Chem. Phys. 33, 1386 (1960).

15. Reference 6, p. 449; reference 13a.

16. Reference 6, section 9.4.

17. J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950).

18. C. F. Curtiss, Symmetric Gaseous Diffusion Coefficients, University of Wisconsin Theoretical Chemistry Institute publication No. 294 (1968).

19. Reference 6, p. 475.

20. Reference 6, section 7.3e.

21. The last term in equation (6.2 - 10) results from the inclusion of three body collision effects. This term is identical with that obtained by Hoffman and Curtiss. The remaining terms in this equation representing collisional transfer effects are identical

with those obtained by Snider and Curtiss.[14a] The full expression used by Hoffman and Curtiss for computational purpose is based upon simplifications of the expressions as developed by Snider and McCourt (Phys. Fluids 6, 1020, 1963). Apparently a typographical error was introduced in the expression which they give for their quantity T_λ (equation 30) in that an overall minus sign is omitted.

22. Reference 6, sections 3.4, 3.5, and 8.2a; H. L. Firsch, Advances in Chemical Physics (Interscience, London, 1964), Vol. VI, pp. 268-270.

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25. F. J. Smith and R. J. Munn, J. Chem. Phys. 41, 3560 (1964); Abramowitz and Stegun, Handbook of Mathematical Functions (National Bureau of Standards, Applied Mathematics Series 55), section 25.4.38.

26. The sign error pointed out in footnote 21 leads to an error in the numerical results of Hoffman and Curtiss. Their results may be corrected by adding:

$$-\frac{4}{15}\left[\frac{7}{2}T^*\frac{\partial B}{\partial T^*} + T^{*2}\frac{\partial^2 B}{\partial T^{*2}}\right]$$

to the tabulated values of B_λ. After this correction is applied their results and the present calculations are in satisfactory agreement.

27. T. S. Lee, G. F. Kuether, R. C. Robinson and W. E. Stewart, Diffusion and Principles of Corresponding States, American Petroleum Institute, Refining Division, Houston, May 1966.