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Thermal diffusion in polyatomic gases

by

Maurice Keith Matzen

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CHAPTER 1. INTRODUCTION

Diffusion is said to occur in a mixture when there is a relative motion of its components. Such a motion is often attributed solely to the diffusion force, the dominant factor of which is a gradient in the chemical potential (modified, of course, to remove that part of the chemical potential gradient which produces macroscopic flow). Diffusion arising from these diffusion forces is commonly termed ordinary diffusion. Diffusive flow may also arise from other inhomogeneities within the mixture. In the case of a nonuniformity of the temperature this phenomenon is called thermal diffusion.

Thermal diffusion is then the relative motion of the components of a mixture due to temperature differences within the mixture. When a temperature gradient is imposed upon a mixture thermal diffusion will result in the creation of concentration gradients which in turn cause ordinary diffusion. The balancing of these two effects leads to a net mass flux of zero.

Thermal diffusion in mixtures of gases belongs to a small class of physical phenomena which were predicted theoretically before being observed experimentally. In liquids the existence of thermal diffusion was first discovered experimentally by Ludwig (1) in 1856 and investigated more fully by Soret (2-5) in 1879-81. Thermal diffusion

in liquids is still commonly referred to as the Soret Effect. As early as 1873 Fedderson (6) suspected the existence of thermal diffusion in gases and in fact, the effect was observed in several phenomena without being recognized. The most notable example in this latter category was the observation by Tyndall (7) in 1870 of the dust free region in the gas space about a hot body, which shows the effect of a temperature gradient on the motion of small particles suspended in a gas. A common example of this effect is the dust patterns which are often seen on walls near hot pipes and radiators.

Despite such observations, thermal diffusion in gases escaped identification until 1917 when the kinetic theory of gases in nonequilibrium states was developed independently by Chapman (8-11) and Enskog (12-15). These theories predict that diffusion due to a temperature gradient should exist; the experimental verification by Chapman (16) soon followed.

The phenomenological diffusion equations illustrate the basic principles involved in diffusion. If for simplicity we consider a binary mixture, the phenomenological flux equation for component α can be written (17) as

$$\mathbf{J}_\alpha = \frac{n^2}{\rho} m_\alpha m_\beta D_{\alpha\beta} \mathbf{c}_\beta - D_\alpha^T \nabla \ln T \quad (1.1)$$

where \underline{J}_α is the flux density, n is the total number density, ρ is the mass density, m_α and m_β are the masses of components α and β , respectively, $D_{\alpha\beta}$ is the ordinary diffusion coefficient, and D_α^T is the coefficient of thermal diffusion. The diffusion force vector, \underline{d}_β , includes the gradients in concentration and pressure as well as the effects of the external forces. A similar equation may be written for \underline{J}_β . To study the counter balancing effects of thermal diffusion and ordinary diffusion, it is convenient to use the thermal diffusion ratio k_T , where

$$k_T \propto D_\alpha^T / D_{\alpha\beta} \quad (1.2)$$

Both kinetic theory and experiment (18) show that k_T is approximately proportional to the mole fraction product $x_\alpha x_\beta$. Thus it is convenient to define the thermal diffusion factor, α_T , by

$$\alpha_T = k_T / x_\alpha x_\beta. \quad (1.3)$$

It is this quantity which is usually chosen for study.

Clusius and Dickel (19) in 1938 showed how thermal diffusion could be utilized to effect the nearly complete separation of the components of a gas mixture. This discovery revived both a theoretical and experimental interest in thermal diffusion. An excellent review of thermal diffusion by Mason, Munn, and Smith (20) summarizes the resulting

developments in these areas.

Since the phenomenon itself depends strongly and sensitively on the forces between the unlike molecules in a mixture, we will utilize thermal diffusion as an experimental tool to study intermolecular forces. This sensitivity on the detailed manner in which molecules exchange linear and angular momentum upon collision leads to severe difficulties when attempting to give a simple physical description of thermal diffusion. This is in sharp contrast to other transport properties such as thermal conductivity, viscosity, and ordinary diffusion which are adequately described by simple mean-free-path theories. These properties primarily depend upon the probability of a molecular collision and only to a very small extent upon the detailed nature of the collision. The elementary theories which have been proposed for thermal diffusion in binary mixtures, such as those of Furth (21), Frankel (22), or Furry (23), seem either to be incorrect in basic essential points or else almost as complicated as the rigorous Chapman-Enskog kinetic theory itself. Recent work by Whalley and Winter (24) and Laranjeira (25) has extended the elementary theories to include multicomponent mixtures.

The transport phenomena in a linear phenomenology are characterized by the transport coefficients, which relate the relevant fluxes to diffusion forces and the gradients

in the streaming velocity and temperature. Thus these transport coefficients arise naturally in the computation of the fluxes of the appropriate mechanical properties (mass, momentum, or energy). The distortions from the Maxwell-Boltzmann equilibrium distribution which give rise to these fluxes are obtained by using the Chapman-Enskog theory to solve the Boltzmann equation. The resulting set of integral equations is commonly expressed in algebraic form, utilizing a matrix representation of the collision operator. The matrix elements of this representation are sometimes called collision integrals since they involve integration over the orientation and momentum variables of a pair of interacting molecules. The evaluation of the transport coefficients thus involves assuming a molecular model for which the dynamics of a collision may be determined. This allows the calculation of the appropriate collision integrals.

The transport coefficients were first calculated for the rigid sphere model. These efforts were followed by calculations for numerous spherical potential functions. Hirschfelder et al. (17) shows the comparison between experiment and theory for several of these models. In general, the spherical collision models give good comparison with experiment for those transport properties which depend mainly on the probability of the occurrence of a collision,

such as thermal conductivity, viscosity and ordinary diffusion. The spherical collision models give poorer results for the thermal diffusion ratio for polyatomic gases, particularly in mixtures of isotopes. This indicates the need for a molecular model with internal structure.

The theory of transport phenomena in polyatomic gases is greatly complicated by the existence of inelastic molecular collisions. Inelastic in this sense implies the possibility that the interacting molecules may exchange rotational energy as well as translational energy. It is assumed that collisions have little effect on the vibrational states of the interacting molecules, since the vibrational energy spacing is large compared to kT . This results in vibrational relaxation times which are of the order of the time required for several molecular encounters. Recently, classical dynamics has been applied to the treatment of the internal degrees of freedom and the thermal diffusion factor has been calculated for rough spheres by Trübenbacher (26) and for loaded spheres by Sandler and Dahler (27). Matzen et al. (28) have extended the calculations to ellipsoids of revolution. In the strictest sense these internal degrees of freedom should, of course, be treated quantum mechanically, but classical mechanics gives reliable results when the rotational energy spacings are small compared to kT . For CO and N₂ (molecules of interest in this

work), the average value of the rotational angular momentum quantum number J is about 10 at room temperature. In comparison the average of J for H_2 is 1 and the rotational collision dynamics for this molecule must be treated by quantum mechanics.

The purpose of the present work is to develop the expressions for the transport properties of a multicomponent mixture of polyatomic gases in both a field-free space and in a constant, static magnetic or electric field. We also wish to examine these expressions for physical insights into the phenomena of thermal diffusion.

The following study of thermal diffusion begins with a brief development of the Boltzmann equation for a polyatomic gas mixture. The method of solution of these equations is then presented in general and the kinetic equations developed in detail for multicomponent gas mixtures. In addition we develop the generalized Onsager force-flux relationships in tensorial form. The perturbation theory for matrices is given in a general form and applied specifically to the kinetic equations of interest for both the field-free and constant magnetic field cases to derive an analytic expression for the thermal diffusion coefficient. In order to perform the matrix inversions required in the perturbation theory for an externally applied field, we develop the theory for the reduction of a general Cartesian tensor into

a linear combination of basis tensors of one dimensional irreducible representations of the group of rotations about the field direction. Finally, we use the ellipsoid of revolution collision model to compare our theory with experimental results for several isotopic binary mixtures. Our major emphasis is on isotopic CO mixtures.

CHAPTER 2. DERIVATION OF THE BOLTZMANN EQUATION

A general classical mechanical treatment of the Boltzmann equation for polyatomic gases has recently been given by Hoffman and Dahler (29). The development given here will closely follow their outline.

The state of a single-component gas consisting of N molecules is described by the distribution function $F^{(N)}(\underline{X}_1, \underline{X}_2, \dots, \underline{X}_N, t)$, where \underline{X}_i is a multidimensional Cartesian vector whose components are the conjugate coordinate (q_i) and momenta (p_i) variables of molecule i . Both q_i and p_i have as many components as the molecule has degrees of freedom. This distribution function is defined such that $F^{(N)} d\underline{X}_1 d\underline{X}_2 \dots d\underline{X}_N$ is the number of N -molecule systems which have one molecule in the range $d\underline{X}_1$ about \underline{X}_1 , one molecule in the range $d\underline{X}_2$ about \underline{X}_2 , and so on for all \underline{X}_i and $d\underline{X}_i$. Here $d\underline{X}_i$ implies the Cartesian volume element $\prod_{\beta} dq_{i\beta} dp_{i\beta}$, where $q_{i\beta}$ and $p_{i\beta}$ are the conjugate coordinate and momentum associated with the β degree of freedom of molecule i . The function $F^{(N)}$ is normalized to $N!$. The lower order distribution function $F^{(n)}$ for an N -molecule system ($1 \leq n \leq N$) is defined to be the probability of finding n molecules in respective ranges $d\underline{X}_1, d\underline{X}_2, \dots, d\underline{X}_n$ about $\underline{X}_1, \underline{X}_2, \dots, \underline{X}_n$ without regard to the positions and momenta of the remaining $(N-n)$ molecules. To obtain $F^{(n)}$ we can integrate the N -molecule distribution function over all the

coordinates and momenta of the $(N-n)$ molecules, that is,

$$F^{(n)} = \left[\frac{1}{(N-n)!} \right] \int d\underline{x}_{n+1} \int d\underline{x}_{n+2} \cdots \int d\underline{x}_N F^{(N)}. \quad (2.1)$$

The equation of motion for the N -molecule system is the Liouville equation

$$\frac{dF^{(N)}}{dt} + \sum_{i=1}^N \sum_{\beta=1}^{\infty} \left\{ \frac{dF^{(N)}}{dq_{i\beta}} \frac{dH^{(N)}}{dp_{i\beta}} - \frac{dF^{(N)}}{dp_{i\beta}} \frac{dH^{(N)}}{dq_{i\beta}} \right\} = 0, \quad (2.2)$$

where $H^{(N)}$ is the Hamiltonian for the system. If we assume that $H^{(N)}$ can be written in the form

$$H^{(N)} = \sum_i H_i^{(1)} + \sum_i \sum_{j>i} V_{ij}, \quad (2.3)$$

where $H_i^{(1)}$ is the single-particle Hamiltonian for molecule i and V_{ij} is the pair interaction potential for the interaction between molecules i and j , and if we integrate Equation 2.2 over $d\underline{x}_{n+1}, d\underline{x}_{n+2}, \cdots, d\underline{x}_N$, then we obtain the BBGKY hierarchy of coupled equations

$$\begin{aligned} & \frac{dF^{(n)}}{dt} + \sum_{i=1}^n \sum_{\beta=1}^{\infty} \left\{ \frac{dF^{(n)}}{dq_{i\beta}} (\dot{q}_{i\beta}) + \frac{dF^{(n)}}{dp_{i\beta}} (\dot{p}_{i\beta}) \right. \\ & \left. = \sum_{i=1}^n \sum_{\beta=1}^{\infty} \int d\underline{x}_{n+1} \left\{ \frac{d}{dp_{i\beta}} \left(F^{(n+1)} \frac{dV_{i,n+1}}{dq_{i\beta}} \right) - \frac{d}{dq_{i\beta}} \left(F^{(n+1)} \frac{dV_{i,n+1}}{dp_{i\beta}} \right) \right\} \right\} \end{aligned} \quad (2.4)$$

which govern the lower order distribution functions $F^{(n)}$.

For systems to which the Hamiltonian in Equation 2.3 is

applicable, the macroscopic properties may be calculated from a knowledge of $F^{(1)}$ and $F^{(2)}$, the singlet and pair distribution functions. These functions are needed to compute the kinetic and potential contributions, respectively, to the macroscopic properties. The distribution functions $F^{(1)}$ and $F^{(2)}$ are proportional, respectively, to the density and the square of the density. Thus for low densities the kinetic effect will be the dominant contribution and $F^{(1)}$ will be sufficient to describe the macroscopic properties of interest. Hence the remainder of this chapter will be concentrated on the singlet distribution function.

We wish now to define a distribution function, $\tilde{F}^{(1)}$, for molecules which are not in the midst of collisional encounters as

$$\tilde{F}_1^{(1)} = N \int d\underline{x}_2 \cdots \int d\underline{x}_N \left(\prod_{j=2}^N \xi_{j,1} \right) F^{(N)}, \quad (2.5)$$

where the subscript indicates that $\tilde{F}^{(1)}$ is a function of the position and momentum variables of molecule 1. Let us define σ_i to be a body fixed, convex region enveloping molecule i . The dimensions of σ_i are arbitrarily chosen but in practice the shape is dictated by the molecular geometry. A convex region $\sigma_{i,j}$, which is a function of the orientation of bodies i and j , is defined to be the volume enclosed by the center of mass of j as it is moved about molecule i in such a way

that the orientations of both bodies is held fixed and the regions σ_i and σ_j are just in contact. The function $f_{j,1}$ of Equation 2.5 is then defined to be zero whenever regions σ_j and σ_i are in contact (or equivalently, when the center of mass of molecule j is inside $\sigma_{i,j}$), and is equal to one otherwise. Thus $\tilde{F}_i^{(1)}$ is the distribution of molecules which are "isolated" in the sense that no other molecule j is in the $\sigma_{i,j}$ region around molecule i . If we write $f_{j,1} = 1 - \delta_{j,1}$, where $\delta_{j,1}$ is defined to be zero when $f_{j,1}$ is one and one when $f_{j,1}$ is zero, then the product $\prod_{j=2}^N f_{j,1}$ can be written as the expansion

$$\prod_{j=2}^N f_{j,1} = 1 - \sum_{j=2}^N \delta_{j,1} + \sum_{j=2}^N \sum_{k=j}^N \delta_{j,1} \delta_{k,1} - \dots \quad (2.6)$$

Putting Equation 2.6 into Equation 2.5 and integrating we obtain this new distribution function in terms of the usual distribution functions $F^{(n)}$ as

$$\tilde{F}_1^{(1)} = F_1^{(1)} - \int_{\sigma_{1,2}} d\underline{X}_2 F_{12}^{(2)} + \frac{1}{2} \int_{\sigma_{1,2}} d\underline{X}_2 \int_{\sigma_{1,3}} d\underline{X}_3 F_{123}^{(3)} - \dots \quad (2.7)$$

or,

$$\tilde{F}_1^{(1)} = \sum_{n \geq 0} [(-1)^n / n!] \int_{\sigma_{1,2}} d\underline{X}_2 \dots \int_{\sigma_{1,n+1}} d\underline{X}_{n+1} F^{(n+1)}. \quad (2.8)$$

The first term on the right hand side just represents the

molecule density, the second term subtracts from this the number of paired molecules (paired in the sense that molecule 2 is in the $\sigma_{1,2}$ region about molecule 1), the third corrects for the counting of pairs which are embedded within molecular trios, and so on.

For any realistic choice of an intermolecular potential, only a finite number of molecules can be confined to a small region about molecule 1. This causes the truncation of the above series after a finite number of terms. In fact, for the rigid collision models which will be of concern in this work, $\sigma_{i,j}$ can always be chosen so that $\tilde{F}^{(i)} = F^{(i)}$ by letting $\sigma_{i,j}$ be only infinitesimally larger than the volume excluded to molecule j by the presence of molecule 1.

To obtain the equation of change for $\tilde{F}^{(i)}$, we multiply the N -particle Liouville equation by $N\Xi_1$, where

$\Xi_1 = \pi \int_{\sigma_{1,2}} f_{2,1}$, and integrate, to obtain

$$\begin{aligned} \frac{d\tilde{F}_1^{(i)}}{dt} + N \int d\underline{x}_2 \cdots \int d\underline{x}_N \Xi_1 [F^{(N)}, \sum_{i=1}^N H_i^{(i)}]^{(N)} \\ = -N \int d\underline{x}_2 \cdots \int d\underline{x}_N \Xi_1 [F^{(N)}, \sum_i \sum_{j>i} V_{ij}]^{(N)} \end{aligned} \quad (2.9)$$

where the brackets represent Poisson brackets for the N -molecule system and are of the form

$$[\Phi, \Psi]^{(N)} = \sum_{i=1}^N \sum_{\beta=1}^N \left\{ \frac{\partial \Phi}{\partial q_{i\beta}} \frac{\partial \Psi}{\partial p_{i\beta}} - \frac{\partial \Phi}{\partial p_{i\beta}} \frac{\partial \Psi}{\partial q_{i\beta}} \right\}. \quad (2.10)$$

This in turn reduces to

$$\begin{aligned} \frac{d\tilde{F}_1^{(1)}}{dt} + [\tilde{F}_1^{(1)}, H_1^{(1)}]^{(1)} - \int d\underline{x}_2 \tilde{F}_{12}^{(2)} [\mathcal{F}_{2,1}, H_1^{(1)} + H_2^{(2)}]^{(2)} \\ = -N \int d\underline{x}_2 \cdots \int d\underline{x}_N \Xi [F^{(N)}, V]^{(N)} \end{aligned} \quad (2.11)$$

with $V = \sum_i \sum_{j>i} V_{ij}$ and where

$$\tilde{F}_{12}^{(2)} = [1/(N-2)!] \int d\underline{x}_3 \cdots \int d\underline{x}_N \left(\prod_{j=3}^N \mathcal{F}_{j,1} \right) F^{(N)} \quad (2.12)$$

is the distribution function for isolated molecule pairs.

If we assume that the linear dimensions of the region $\sigma_{i,j}$ exceed the range of the intermolecule forces, or equivalently, that the intermolecular potential V_{ij} is zero for all states of the two molecules 1 and j when the center of mass of j is outside $\sigma_{1,j}$, then the right hand side of Equation 2.11 vanishes and we have

$$\frac{d\tilde{F}_1^{(1)}}{dt} + [\tilde{F}_1^{(1)}, H_1^{(1)}]^{(1)} = \mathcal{L}_c \tilde{F}_1^{(1)} \quad (2.13)$$

with

$$\mathcal{L}_c \tilde{F}_1^{(1)} = \int d\underline{x}_2 \tilde{F}_{12}^{(2)} [\mathcal{F}_{2,1}, H_1^{(1)} + H_2^{(2)}]^{(2)} \quad (2.14)$$

The space of the center of mass variable of one molecule can be spanned by a sequence of surfaces which are similar in a geometric sense to the surface of the convex region and scaled by a parameter ρ . Thus, the location of the center of mass of molecule 2 can be given in terms of ρ , which specifies the convex surface on which the mass center lies, and \hat{k} , which is the surface normal at the position of the mass center. When $\rho=1$, the center of mass of 2 lies on $\sigma_{1,2}$ and therefore $\xi_{2,1} = \eta(\rho-1)$, where η is the unit step function. We can then replace the Poisson bracket in Equation 2.14 by

$$\mathcal{L}(\rho-1)\dot{P} = \mathcal{L}(\rho-1)[P, H_1^{(1)} + H_2^{(1)}]^{(2)}, \quad (2.15)$$

where $\mathcal{L}(\rho-1)$ is a delta function and $\dot{P} = [P, H_1^{(1)} + H_2^{(1)}]^{(2)}$. The Poisson bracket of a function with the Hamiltonian is the implicit time derivative of the function through the position and momenta coordinates.

The variables of molecule 2 may be written in the separated form $d\underline{X}_2 = d\underline{x}_2 d\underline{\beta}_2 d\underline{2}$, where $\underline{2}$ is the collection of all linear and angular momentum variables, $\underline{\beta}_2$ is the set of molecular orientation variables, and \underline{x}_2 is the position vector of the center of mass. It is convenient to use the three Eulerian angles and the angular momentum, \underline{L} , for the molecular rotation variables even though they do not form a

conjugate set of coordinate and momentum variables. If we let $d\beta_2 = \sin\theta d\theta d\phi d\psi$, where θ and ϕ are the polar angles describing the orientation of an arbitrary body fixed vector and ψ gives the orientation of a second body fixed vector which is perpendicular to the first, then it is easy to show that the Jacobian of the transformation from a conjugate set of rotation variables to these variables is unity (29). The differential position vector $d\underline{x}_2$ may be written as

$d\underline{x}_2 = \rho^2 h d\rho d^2S$ where d^2S is the differential surface element of $\sigma_{1,2}$ and $h \equiv (\underline{s}_1 - \underline{s}_2) \cdot \hat{\underline{k}}$ is the supporting function for the convex region, $\sigma_{1,2}$. Here the symbol \underline{s}_i ($i=1$ or 2) represents a vector extending from the center of mass of molecule i to the point of contact of σ_1 and σ_2 when $\rho=1$. It can be shown (29) that $\dot{\rho} h$ at $\rho=1$ is the relative velocity of the points of contact of σ_1 and σ_2 projected onto $\hat{\underline{k}}$, the surface normal at the point of contact on σ_1 (which, as previously defined, is also the surface normal to $\sigma_{1,2}$ at the position of the center of mass of 2). Therefore we can write $\dot{\rho} h = \underline{g} \cdot \hat{\underline{k}}$, where \underline{g} is the relative velocity of the points of contact and is given by

$$\underline{g} = \underline{c}_2 + (\underline{I}_2^{-1} \cdot \underline{L}_2) \times \underline{s}_2 - (\underline{I}_1^{-1} \cdot \underline{L}_1) \times \underline{s}_1. \quad (2.16)$$

Here $\underline{I}_i = \underline{I}(\beta_i)$ is the inertial tensor (where β_i indicates that the inertial tensors must be referenced to the space

frame), \underline{L}_i the angular momentum of molecule i , and \underline{c}_{21} is the relative velocity of the centers of mass of molecules 2 and 1. The quantity $(\underline{I}_j^{-1} \cdot \underline{L}_j)$ is the angular velocity of molecule j .

We can now write Equation 2.14 as

$$d_c \tilde{F}_1^{(1)} = \int d^2 \int d\beta_2 \int d^2 S (\hat{\lambda} \cdot \underline{g}) \tilde{F}_{12}^{(2)}. \quad (2.17)$$

Since the quantity $\hat{\lambda} \cdot \underline{g}$ is the normal component of the relative velocity of the points of contact of σ_1 and σ_2 , the quantity $d^2 d\beta_2 d^2 S (\hat{\lambda} \cdot \underline{g}) \tilde{F}_{12}^{(2)}$ represents the differential rate at which molecules become paired ($\hat{\lambda} \cdot \underline{g} < 0$) or unpaired ($\hat{\lambda} \cdot \underline{g} > 0$). The entire integral is called the collision operator, since in a physical sense it is the net rate of encounters of molecule 1 with all other molecules j .

In this work we will evaluate the collision operator by assuming that the colliding molecules are rigid, non-deformable convex bodies. This model allows us to consider the entire collision event as a single impulsive encounter (if we ignore the possibility of chattering, that is, a two body collision which consists of a sequence of correlated impulses resulting from the nonspherical nature of the bodies). These rigid collision models are certainly not entirely realistic approximations of the interaction potential. However, they should be reasonably accurate for

fluids composed of relatively small, weakly polar molecules, particularly when the thermal energy is large compared to the van der Waals attractions between the molecules. As mentioned earlier, for rigid collision models we can make $\tilde{F}^{(n)} = F^{(n)}$ by taking $\sigma_{i,j}$ to be differentially larger than the excluded volume. At the point of contact,

$$\tilde{F}^{(2)} = F^{(2)}(x_1, \beta_1, 1; x_1 + \xi_1 - \xi_2, \beta_2, 2; t) .$$

The collisional impulses of rigid bodies are of infinitesimal duration and thus the possibility of a third body affecting the position and momentum states of the two interacting bodies is negligible. Therefore each precollision state of the two colliding molecules which have positions and momenta such that a collision is about to occur can be uniquely connected through the two particle dynamics to a postcollisional state. The probability of observing a pair of molecules in this precollisional state at a given time is exactly equal to the probability of observing the molecules in the associated postcollisional state a short time later. That is, $F_{pre}^{(2)}(t - \tau_c) = F_{post}^{(2)}(t)$, where τ_c is the duration of the collision (which is infinitesimal for rigid bodies). If the surfaces are smooth it can be shown from conservation of energy and linear and angular momentum that the collision reverses the algebraic sign of \hat{A}_{ij} . On the precollisional surface, $\hat{A}_{ij} < 0$; whereas $\hat{A}_{ij} > 0$ for the postcollisional surface. We can now write

Equation 2.17 in the form

$$\begin{aligned} \mathcal{L}_c F_1^{(1)} = & \int d^2 \int d\beta_2 \int d^2 S \hat{\mathcal{L}} \cdot \mathcal{F} F^{(2)}(\underline{x}, \beta_1^*, \beta_1^*; \underline{x} + \underline{s}_1, -\underline{s}_2, \beta_2^*, \beta_2^*; \tau - 0+) \\ & + \int d^2 \int d\beta_2 \int d^2 S \hat{\mathcal{L}} \cdot \mathcal{F} F^{(2)}(\underline{x}, \beta_1, 1; \underline{x} + \underline{s}_1, -\underline{s}_2, \beta_2, 2; \tau). \end{aligned} \quad (2.18)$$

The asterisks denote the state on the precollisional surface which is uniquely connected to a state on the postcollisional surface by the collision dynamics.

The next approximation we make is that of molecular chaos, which is to say that in precollision regions there is no statistical correlation between the probable distributions of molecule 1 and molecule 2. Under this assumption the pair distribution function for a precollisional state factors into a product of the singlet distribution functions as $F^{(2)}(\underline{x}, \beta_1, 1; \underline{x} + \underline{s}_1, -\underline{s}_2, \beta_2, 2) = F^{(1)}(\underline{x}, \beta_1, 1) F^{(1)}(\underline{x} + \underline{s}_1, -\underline{s}_2, \beta_2, 2)$. The difference in position of the centers of mass of molecules 1 and 2 in the singlet distribution functions is negligible to lowest order in the density. Thus we assume the position variables of the two molecules to be identical and will hereafter indicate only the momentum and orientation variables explicitly. Equation 2.18 now becomes

$$\begin{aligned} \mathcal{L}_c F_1^{(1)} = & \int d^2 \int d\beta_2 \int d^2 S [(\hat{\mathcal{L}} \cdot \mathcal{F}) F^{(1)}(1, \beta_1^*) F^{(1)}(2, \beta_2^*) \\ & - (\hat{\mathcal{L}} \cdot \mathcal{F}) F^{(1)}(1, \beta_1) F^{(1)}(2, \beta_2)] \end{aligned} \quad (2.19)$$

$$= \iiint d1' d2' d2 [w(1\beta, 2\beta_2 | 1'\beta', 2'\beta_2') F^{(1)}(1', \beta_1') F^{(1)}(2', \beta_2') \\ - w(1'\beta', 2'\beta_2' | 1\beta, 2\beta_2) F^{(1)}(1, \beta_1) F^{(1)}(2, \beta_2)],$$

where $w(1\beta, 2\beta_2 | 1'\beta', 2'\beta_2')$ is the transition rate of the momentum variables from the $1'2'$ to the 12 states and is seen to be

$$w(1\beta, 2\beta_2 | 1'\beta', 2'\beta_2') = \int_{\hat{k} \cdot \hat{q} > 0} d^2s \hat{k} \cdot \hat{q} \delta(1'-1^*) \delta(2'-2^*). \quad (2.20)$$

The asterisks again refer to precollisional states which are correlated to the 12 states through the binary collision dynamics. In reference (29), the property of bilateral normalization,

$$\iint d1' d2' w(1\beta, 2\beta_2 | 1'\beta', 2'\beta_2') = \iint d1' d2' w(1'\beta', 2'\beta_2' | 1\beta, 2\beta_2) \quad (2.21)$$

is established. This is sufficient to reduce Equation 2.19 to the usual form of the collision operator

$$d_c F_i^{(1)} = \iiint d1' d2' d2 w(1\beta, 2\beta_2 | 1'\beta', 2'\beta_2') \mathcal{X} \\ [F^{(1)}(1', \beta_1') F^{(1)}(2', \beta_2') - F^{(1)}(1, \beta_1) F^{(1)}(2, \beta_2)]. \quad (2.22)$$

The derivation presented for Equation 2.22 is specific to the rigid convex body model. However the same form is obtained for a general model if we utilize slightly more general assumptions. First we consider systems of low

density, so that $\tilde{F}^{(1)} \approx F^{(1)}$. Next we assume that the collisional interactions are isolated binary events, which allows us to replace $F_{post}^{(2)}(1, \beta_1, 2, \beta_2, t)$ with $F_{pre}^{(2)}(1, \beta_1^*, 2, \beta_2^*, t - \tau_c)$, where τ_c is the duration of the interaction and where again the asterisks denote a state on the precollision surface. We then assume molecular chaos and factor the pair distribution function in precollision regions into a product of the corresponding singlet distribution functions,

$F_{pre}^{(2)}(1, \beta_1, 2, \beta_2) = F^{(1)}(1, \beta_1) F^{(1)}(2, \beta_2)$. We assume in these expressions for $F^{(2)}$ that variations in $F^{(1)}$ are negligible over time intervals, τ_c , of the order of the duration and distances of the order of the spatial extension, $\sim \tau_c$, of a collision event. Taking into account these small variations in the position and time dependence of the singlet distribution functions leads to density corrections in the theory.

We are now in position to reduce Equation 2.13 to the usual form of the Boltzmann equation. Since the orientations of the molecules vary on a time scale which is very short compared to the collision frequency, the distribution function must be nearly independent of those orientation variables which are rapidly changing. The Boltzmann distribution function, $f^{(1)}$, is then conveniently defined as an average over an interval of time which is long compared to the duration of a collision but less than the interval

between successive collisions. Thus the distribution function $f(i)$ is a function only of the linear and angular momentum variables and the orientation variables which are free flight invariants. In practice we ignore all the orientation variables and hence define $f(i)$ by

$$f(i) = \int d\beta, F(i, \beta). \quad (2.23)$$

The case of the rigid rotor model (used to represent linear molecules) deserves special attention since this model has only two active rotational degrees of freedom. Since such molecules are cylindrically symmetric about the internuclear axis the distribution function is independent of the angle specifying the orientation about this axis and at the same time the component of angular momentum along this axis is collisionally conserved. For molecules in a Σ state (which represents most of the cases of interest) this component of angular momentum is zero whereas for molecules such as NO there is a nonzero component of angular momentum due to the electrons. The distribution function in the full phase space (that is, with three Eulerian angles and three components of angular momentum), which for present purposes we denote by $f_{(3)}$, can be written

$$f_{(3)} = \frac{1}{2\pi} \int_0^{2\pi} d\phi_1 f_{(2)}, \quad (2.24)$$

where $h(L_1)$ is the normalized distribution of L_1 , the component of angular momentum along the molecular axis, the factor $1/2\pi$ is a normalization constant arising from the trivial Eulerian angle, and $f_{(2)}$ is the distribution function which includes the two active rotational degrees of freedom. The rotational variables in this case can be taken to be either the vector \hat{e}_1 along the internuclear axis (which is described by 2 angles) and the two components of angular momentum L_2 and L_3 in the plane perpendicular to \hat{e}_1 , or can be described by \underline{L} in a space fixed frame (3 components) and the phase angle, ϕ , of the internuclear axis in the plane perpendicular to the angular momentum. The relationship between these variables is such that

$$\frac{1}{L} d\underline{L} d\phi = d\hat{e}_1 dL_2 dL_3. \quad (2.25)$$

The choice of independent variables will be dictated by convenience.

Under these considerations, we can substitute Equation 2.22 into Equation 2.13 and perform the integrations as indicated in Equation 2.23 to obtain

$$\left[\frac{\partial}{\partial t} + \underline{e} \cdot \underline{\nabla} + \underline{F}^{(e)} \cdot \frac{\partial}{\partial \underline{e}} + \underline{N} \cdot \frac{\partial}{\partial \underline{L}} \right] f(\underline{l}) = \underline{J}_c f(\underline{l}), \quad (2.26)$$

which is the standard form of Boltzmann's equation for a single species system. Here $\underline{\nabla} = \nabla_{\underline{x}}$, and $\underline{N} = \underline{L} \times \underline{\nabla}$ is the

torque and $F^{(e)}$ the external body forces which act on the particles during their free-flight motion. The quantity $\underline{\mu}$ is the dipole moment (electric or magnetic) and \underline{F} is the external field (electric or magnetic). For diamagnetic molecules in the magnetic field case (which is the case of interest in the present work), $\underline{\mu}$ is proportional to $g\underline{L}$, where g is the gyromagnetic ratio. Collisional forces are assumed to be much larger than external forces and hence N and $F^{(e)}$ do not affect the transition rates.

The generalization to multicomponent mixtures is straightforward. The rate of change in the distribution function of any one species due to collisions is just the sum of contributions from collisions of that species with itself and with all other species. That is,

$$\left[\frac{\partial}{\partial t} + \underline{c}_1 \cdot \nabla + F_{\alpha 1}^{(e)} \cdot \frac{\partial}{\partial \underline{c}_1} \right] f_{\alpha}(1) = -N_{\alpha} \cdot \frac{\partial}{\partial \underline{c}_1} f_{\alpha}(1) \quad (2.27)$$

$$+ \sum_{\beta} \iiint d1' d2' d2 w_{\alpha\beta}(121'2') [f_{\alpha}(1') f_{\beta}(2') - f_{\alpha}(1) f_{\beta}(2)]$$

where the subscripts α and β represent species and \sum_{β} is a summation over all species in the mixture.

CHAPTER 3. LINEAR TRANSPORT THEORY FOR A
DILUTE POLYATOMIC GAS MIXTURE

Our objective is to obtain numerical estimates of the linear transport coefficients, particularly those associated with concentration and thermal diffusion. This information can be extracted from the "normal" solutions of the Boltzmann equation which are generated by the method of Chapman and Enskog. Since the status and interpretation of these solutions have been considered thoroughly elsewhere (30), the only concern here is with the mechanics of the solution procedure. We assume the external forces, $\underline{F}_\alpha^{(e)}$, to be so weak that they do not significantly alter the states of the molecules during the brief intervals between their successive collisions. Also, if we adopt as our unit interval the free-path transit time, the three terms on the left hand side of Equation 2.27 all are of the same order of magnitude and each is smaller by a factor of approximately λ_{fp}/ℓ than the right hand side (29). Here λ_{fp} is the free-path length and $\ell \gg \lambda_{fp}$, the scale of the spatial inhomogeneities of temperature, velocity and concentration.

To construct the normal solution of Equation 2.27 we multiply its entire left hand side by a dimensionless marker $\epsilon (\approx \lambda_{fp}/\ell)$ and assume that there is a solution of this modified equation of the form $\sum \epsilon^k f_\alpha^{(k)}$. Furthermore, we assume

(see reference (30) for a thorough discussion of the internal consistency of these various assumptions) that the time and position dependence of each function $f_{\alpha}^{(k)}$ is implicit and governed by the variations with t and \underline{x} of the macroscopic variables \underline{f} ($\equiv n_{\alpha}(t, \underline{x}), T(t, \underline{x}),$ and $\underline{u}(t, \underline{x})$).

Finally, we expand the time derivatives of these macroscopic variables in series $\frac{d}{dt} \underline{f} = \sum \epsilon^k \left(\frac{d}{dt} \right)_k \underline{f}$. After these expansions are substituted into the modified Boltzmann equation of Equation 2.27, we assume that the resulting expressions are satisfied order-by-order in the perturbation parameter ϵ . The first of the equations obtained by this procedure are satisfied by the Maxwell-Boltzmann distributions

$$f_{\alpha}^{(0)} = n_{\alpha} (m_{\alpha} / 2\pi kT)^{3/2} z_{\alpha}^{-1} \exp \left\{ -\frac{1}{kT} \left(\frac{1}{2} m_{\alpha} C_{\alpha}^2 + \epsilon_{\alpha} \right) \right\} \quad (3.1)$$

where $\underline{C} = \underline{c} - \underline{u}$, ϵ_{α} is the rotational energy of an α -species molecule and z_{α} is the rotational partition function determined by classical mechanics. Finally, n_{α} , \underline{u} , and T , respectively, are chosen equal to the local, instantaneous values of the number density of species α , the mass average velocity, and temperature. Because of this the higher order terms $f_{\alpha}^{(k)}$, $k > 0$, must conform to the subsidiary conditions

$$\int f_{\alpha}^{(k)}(1) d1 = \sum_{\alpha} \int d1 m_{\alpha} \underline{C}_{\alpha} f_{\alpha}^{(k)}(1) = \sum_{\alpha} \int d1 \left\{ \frac{1}{2} m_{\alpha} C_{\alpha}^2 + \epsilon_{\alpha} \right\} f_{\alpha}^{(k)}(1) = 0. \quad (3.2)$$

We also require the internal angular momentum density of each species to be zero so that $\int d\mathbf{l} \perp f_{\alpha}^{(k)}(1) = 0$, $k > 0$.

The linear phenomenological description of the fluid is completely determined by the functions $f_{\alpha}^{(1)} = f_{\alpha}^{(0)} \phi_{\alpha}$ which satisfy the linear, inhomogeneous integrodifferential equations

$$D_{\alpha}(1) = - \sum_{\beta} \{ n_{\alpha} \hat{\Theta}_{1(\alpha, \beta)}(\phi_{\beta}) + n_{\alpha} n_{\beta} \hat{\Gamma}_{1(\alpha, \beta)}(\phi_{\beta}) \} \quad (3.3)$$

with

$$\begin{aligned} D_{\alpha}(1) &= \left(\frac{\partial}{\partial t} \right)_0 + \mathbf{c}_1 \cdot \nabla + F_{\alpha}^{(e)} \cdot \frac{\partial}{\partial \mathbf{c}_1} \Big) f_{\alpha}^{(0)}(1) \\ &= f_{\alpha}^{(0)}(1) \left[n_{\alpha}^{-1} \left(\frac{\partial}{\partial t} \right)_0 + \mathbf{c}_1 \cdot \nabla \right] n_{\alpha} + T^{-1} \left\{ \frac{m_{\alpha} c_1^2}{2kT} - \frac{3}{2} \right. \\ &\quad \left. + \frac{E_{\alpha}(1) - \bar{E}_{\alpha}}{kT} \right\} \left(\frac{\partial}{\partial t} \right)_0 + \mathbf{c}_1 \cdot \nabla \Big) T + \frac{m_{\alpha}}{kT} \left\{ \left(\frac{\partial}{\partial t} \right)_0 + \mathbf{c}_1 \cdot \nabla \right\} \cdot \mathbf{c}_1 \Big] , \end{aligned} \quad (3.4)$$

$$n_{\alpha} \hat{\Theta}_{1(\alpha, \beta)}(\bar{\Phi}) = \delta_{\alpha\beta} f_{\alpha}^{(0)}(1) \mu_{\alpha}(1) \times \bar{\Phi} \cdot \frac{\partial}{\partial \mathbf{c}_1} \phi_{\alpha}(1) ,$$

and (3.5)

$$n_{\alpha} n_{\beta} \hat{\Gamma}_{1(\alpha, \beta)} = G_{\alpha, \beta}^{(2)} + \delta_{\alpha\beta} \sum_{\gamma} G_{\gamma\alpha}^{(1)} ,$$

where

$$G_{\alpha, \beta}^{(2)} \phi_{\beta} = \iiint d\mathbf{l}' d\mathbf{l}'' d\mathbf{l}''' w_{\alpha\beta}(12|1'2') f_{\alpha}^{(0)}(1) f_{\beta}^{(0)}(2) [\phi_{\beta}(2) - \phi_{\beta}(2')] \quad (3.6)$$

with $\gamma=1$ or 2. If we define θ_α and ϕ_α to be the α th components of the "composition vectors" θ and ϕ , respectively, and interpret $n_\alpha \hat{\theta}_{(\alpha, \beta)}$ and $n_\alpha n_\beta \hat{\Gamma}_{(\alpha, \beta)}$ to be the $\alpha\beta$ -elements of the operators $n\hat{\theta}$ and $n^2\hat{\Gamma}$ in composition space, then Equation 3.3 can be written in the compact form $\theta = -n\hat{\theta}(\phi) - n^2\hat{\Gamma}(\phi) \equiv -\hat{\Lambda}(\phi)$.

For these equations to be soluble it is both necessary and sufficient that θ be orthogonal to all solutions χ of the homogeneous adjoint equations $\hat{\Lambda}^\dagger(\chi) = 0$. These solutions consist of the composition vectors with components $\chi_\alpha^{(1)} = \delta_{\alpha\beta}$ (for all species β), $\chi_\alpha^{(2)} = m_\alpha c$, and $\chi_\alpha^{(3)} = \frac{1}{2} m_\alpha c^2 + \varepsilon_\alpha$ and correspond, respectively, to the summational invariants, namely, the mass for each species, momentum, and energy. The resulting orthogonality conditions,

$$\int dV \theta_\alpha(l) = \sum_\alpha \int dV m_\alpha c, \theta_\alpha(l) = \sum_\alpha \int dV \left\{ \frac{1}{2} m_\alpha c^2 + \varepsilon_\alpha(l) \right\} \theta_\alpha(l) = 0, \quad (3.7)$$

can be rewritten in the forms,

$$\left(\frac{d}{dt} \right)_0 n_\alpha = -\nabla \cdot (n_\alpha \underline{u}) \quad (3.8)$$

$$\left(\frac{d}{dt} \right)_0 \underline{u} = -\underline{u} \cdot \nabla \underline{u} - \rho^{-1} \nabla p + \sum_\alpha (\rho/\rho_\alpha) \underline{F}_\alpha^{(c)}$$

and

$$\left(\frac{d}{dt} \right)_0 T = -\underline{u} \cdot \nabla T - (\rho/c_v) \nabla \cdot \underline{u}$$

with $\underline{v} = \frac{\underline{f}}{2\underline{\lambda}}$, $\rho_\alpha = m_\alpha n_\alpha$, $\rho = \sum \rho_\alpha$, $\rho = n k T$, and $c_v = 3n k/2 + \sum n_\alpha \hat{c}_\alpha$, where \hat{c}_α is the contribution of internal degrees of freedom to the heat capacity (per molecule) of the species α .

Therefore, we must choose for $(\frac{f}{2\underline{\lambda}})_0$, n_α , $(\frac{f}{2\underline{\lambda}})_0 \underline{u}$, and $(\frac{f}{2\underline{\lambda}})_0 T$ the functions defined by Equation 3.8 in order that the integrodifferential equations in Equation 3.3 be soluble. When this is done we find that

$$\begin{aligned} \mathcal{D}_\alpha = f_\alpha^{(0)} \left[\frac{n}{n_\alpha} \underline{c} \cdot \underline{d}_\alpha + (w^2 + \varepsilon_\alpha^* - \frac{3}{2} - \bar{\varepsilon}_\alpha^*) \underline{c} \cdot \frac{\underline{v} T}{T} \right. \\ \left. + \left\{ 2 \underline{w} \underline{w} - \underline{\xi}^{(1)} \left[\frac{\rho}{T c_v} (w^2 + \varepsilon_\alpha^* - \frac{3}{2} - \bar{\varepsilon}_\alpha^*) + 1 \right] \right\} : \underline{v} \underline{u} \right] \end{aligned} \quad (3.9)$$

where $\underline{\xi}^{(1)}$ is the rank 2 unit tensor in 3-dimensional space (see Chapter 6), $\underline{w} = (m_\alpha/2kT)^{1/2} \underline{c}$, $\varepsilon_\alpha^* = \varepsilon_\alpha/kT$, $\bar{\varepsilon}_\alpha^* = \bar{\varepsilon}_\alpha/kT$, and where the generalized diffusion forces

$$\underline{d}_\alpha = \underline{v} (n_\alpha/n) + (n_\alpha/n - \rho_\alpha/\rho) \frac{\underline{v} \rho}{\rho} - \frac{\rho_\alpha}{\rho} \left(\rho \underline{F}_\alpha^{(a)} - \sum_\beta \rho_\beta \underline{F}_\beta^{(a)} \right) \quad (3.10)$$

satisfy the condition $\sum \underline{d}_\alpha = 0$ of linear dependence.

Since the operator $\hat{\mathcal{A}}$ is linear and since \mathcal{D} depends linearly upon the variables \underline{d}_α , $\underline{v} T$, \underline{S} and $\underline{v} \cdot \underline{u}$, the distortion ϕ_α must be of the form,

$$\phi_\alpha = -(2kT)^{1/2} \underline{A}_\alpha \cdot \underline{v} \underline{m} T - \underline{B}_\alpha : \underline{S} - \underline{v}_\alpha \underline{v} \cdot \underline{u} + n \sum_\beta \underline{S}_\alpha^{(B)} \cdot (\underline{d}_\beta / \hat{f}_\beta), \quad (3.11)$$

where $\underline{\xi}$ is the traceless and symmetric portion of the second rank tensor $\nabla \underline{u}$. The most general solution of Equation 3.3 would also include a linear combination, $b_\alpha m_\alpha + \underline{q} \cdot m_\alpha \underline{c} + h(\frac{1}{2} m_\alpha c^2 + \epsilon_\alpha)$, of solutions of the corresponding homogeneous equation (where b_α , \underline{q} , and h are arbitrary constants). However, the subsidiary conditions of Equation 3.2 which arise from our choice of the arbitrary constants in $f_\alpha^{(0)}$ require that $b_\alpha = \underline{q} = h = 0$. It is for this reason and the fact that \mathcal{D} is independent of $\text{curl } \underline{u}$ that we omit from ϕ_α a term proportional to $\text{curl } \underline{u}$. The linear dependence ($\sum \underline{d}_\alpha = 0$) of vectors \underline{d}_α causes an arbitrariness of definition of the coefficients $\underline{\xi}_\alpha^{(\beta)}$ which we resolve by requiring that $\sum_\beta \underline{\xi}_\alpha^{(\beta)} = 0$ for all species α .

The functions \underline{A}_α , \underline{B}_α , D_α , and $\underline{\xi}_\alpha^{(\beta)}$ (which are the α th components, respectively, of the composition vectors \underline{A} , \underline{B} , D , and $\underline{\xi}^{(\beta)}$) are independent of the generalized forces and, in addition, the second rank tensors \underline{B}_α are both symmetric and traceless. The diffusion forces $(\underline{d}_\beta / \rho_\beta - \underline{d}_\mathcal{H} / \rho_\mathcal{H})$ for all $\beta \neq \mathcal{H}$ form a linearly independent set of $N-1$ vectors where N is the number of components. (Here \mathcal{H} is arbitrarily chosen.) We conclude from Equations 3.3, 3.9, and 3.11, the identify $\underline{d}_\alpha / \rho_\alpha = \sum_\beta (\delta_{\alpha\beta} - \rho_\beta / \rho) (\underline{d}_\beta / \rho_\beta - \underline{d}_\mathcal{H} / \rho_\mathcal{H})$, and the independence of the generalized forces, that the unknown tensor functions satisfy the separate linear equations

$$\begin{aligned}
 \theta^{(A)} &= \hat{\Lambda}(\underline{A}) ; & \theta^{(D)} &= \hat{\Lambda}(D) \\
 \theta^{(B)} &= \hat{\Lambda}(\underline{B}) ; & \theta^{(S^{(r)})} &= \hat{\Lambda}(\underline{S}^{(r)})
 \end{aligned}
 \tag{3.12}$$

with

$$\begin{aligned}
 \theta_{\alpha}^{(A)} &= m_{\alpha}^{-1/2} f_{\alpha}^{(0)} [\underline{w} (w^2 + \varepsilon_{\alpha}^* - \frac{\xi}{2} - \bar{\varepsilon}_{\alpha}^*)] \\
 \theta_{\alpha}^{(B)} &= 2 f_{\alpha}^{(0)} [\underline{w}]^{(2)} \\
 \theta_{\alpha}^{(D)} &= f_{\alpha}^{(0)} [(\frac{2}{3} - \rho/\tau c_v) w^2 - \frac{\rho}{\tau c_v} \varepsilon_{\alpha}^* + \{ \frac{\rho}{\tau c_v} (\frac{2}{3} + \bar{\varepsilon}_{\alpha}^*) - 1 \}] \\
 \theta_{\alpha}^{(S^{(r)})} &= f_{\alpha}^{(0)} m_{\alpha} c_{\alpha} [-\delta_{\alpha\gamma} + \beta_{\gamma} / \rho] .
 \end{aligned}
 \tag{3.13}$$

The symbol $[\underline{x}]^{(n)}$ denotes the highest weight irreducible part of the polyad formed from n \underline{x} 's, that is, $\underline{x}\underline{x}\cdots\underline{x}$ (see Chapter 6).

The subsidiary conditions in Equation 3.2 impose the restrictions

$$\int d\underline{l} f_{\alpha}^{(0)} \underline{Q}_{\alpha} \chi_{\alpha}^{(1)} = 0$$

and (3.14)

$$\sum_{\alpha} \int d\underline{l} f_{\alpha}^{(0)} \underline{Q}_{\alpha} \chi_{\alpha}^{(i)} = 0, \quad i = 2 \text{ or } 3$$

upon the tensor-valued functions \underline{Q}_{α} ($\equiv \underline{A}_{\alpha}, \underline{B}_{\alpha}, D_{\alpha}, S_{\alpha}^{(A)}$).

To the linear approximation ($f_{\alpha} \approx f_{\alpha}^{(0)} + f_{\alpha}^{(1)} = f_{\alpha}^{(0)} (1 + \phi_{\alpha})$)

with ϕ_α given by Equation 3.11) the fluxes of mass, momentum and energy are

$$\begin{aligned} \underline{J}_\alpha &= \int dI f_\alpha(I) m_\alpha \underline{c}_1 \approx \int dI f_\alpha^{(0)} \phi_\alpha m_\alpha \underline{c}_1 \\ \underline{\Pi} &= \sum_\alpha \int dI f_\alpha(I) m_\alpha [\underline{c}_1]^2 \approx \sum_\alpha \int dI f_\alpha^{(0)}(I) \phi_\alpha m_\alpha [\underline{c}_1]^{(2)} \\ \Pi &= \frac{1}{3} \sum_\alpha \int dI f_\alpha(I) m_\alpha c_1^2 \approx \frac{1}{3} \sum_\alpha \int dI f_\alpha^{(0)}(I) \phi_\alpha m_\alpha c_1^2 \end{aligned} \quad (3.15)$$

$$\underline{Q} = \sum_\alpha \int dI f_\alpha(I) \underline{c}_1 [\frac{1}{2} m_\alpha c_1^2 + \epsilon_\alpha(I)] \approx \sum_\alpha \underline{J}_\alpha \bar{H}_\alpha + \underline{Q}',$$

where the pressure tensor \underline{p} is given by

$$\underline{p} = p \underline{\underline{\delta}}^{(0)} + \underline{\Pi} + \pi \underline{\underline{\delta}}^{(1)} \quad (3.16)$$

and where

$$\bar{H}_\alpha = m_\alpha^{-1/2} (\frac{\epsilon}{2} kT + \bar{\epsilon}_\alpha)$$

and

$$\underline{Q}' = \sum_\alpha \int dI f_\alpha^{(0)} \phi_\alpha \underline{c}_1 [\frac{1}{2} m_\alpha c_1^2 + \epsilon_\alpha(I) - \frac{\epsilon}{2} kT - \bar{\epsilon}_\alpha].$$

By means of Equations 3.12, 3.13, and the orthogonality conditions in Equation 3.7, it is readily established that

$$\underline{J}_\alpha = - \sum_\gamma \int dI \phi_\gamma \underline{\underline{\delta}}_\gamma^{(S^{(\alpha)})} = - \{ \{ \phi, \underline{\underline{\delta}}^{(\alpha)} \} \}$$

$$\underline{\underline{\Pi}}^0 = \mathcal{L}T \sum_{\alpha} \int d\mathbf{l} \underline{\underline{\Theta}}_{\alpha}^{(B)} \phi_{\alpha} = \mathcal{L}T \{ \{ \phi, \underline{\underline{B}} \} \} \quad (3.17)$$

$$\Pi = \mathcal{L}T \sum_{\alpha} \int d\mathbf{l} \phi_{\alpha} \Theta_{\alpha}^{(D)} = \mathcal{L}T \{ \{ \phi, D \} \}$$

$$\underline{\underline{Q}}' = \mathcal{L}T (2\mathcal{L}T)^{1/2} \sum_{\alpha} \int d\mathbf{l} \phi_{\alpha} \underline{\underline{\Theta}}_{\alpha}^{(A)} = \mathcal{L}T (2\mathcal{L}T)^{1/2} \{ \{ \phi, \underline{\underline{A}} \} \},$$

where we have introduced the (double) bracket integral

$$\{ \{ \underline{\underline{a}}, \underline{\underline{b}} \} \} \equiv (\underline{\underline{a}}, \hat{\Lambda}(\underline{\underline{b}})) \equiv \sum_{\alpha} \int d\mathbf{l} \underline{\underline{a}}_{\alpha}(\mathbf{l}) \sum_{\beta} [n_{\alpha} \hat{\Theta}_{\alpha, \beta}(\underline{\underline{b}}_{\beta}) + n_{\alpha} n_{\beta} \hat{\Gamma}_{\alpha, \beta}(\underline{\underline{b}}_{\beta})]$$

of two tensors $\underline{\underline{a}}$ and $\underline{\underline{b}}$. From Equation 3.11 we establish the general force-flux relationships

$$\underline{\underline{J}}_{\alpha} = \left(\frac{2\mathcal{L}}{T}\right)^{1/2} \nabla T \cdot \{ \{ \underline{\underline{A}}, \underline{\underline{S}}^{(\alpha)} \} \} + \underline{\underline{S}} : \{ \{ \underline{\underline{B}}, \underline{\underline{S}}^{(\alpha)} \} \}$$

$$+ \nabla \cdot \underline{\underline{u}} \{ \{ D, \underline{\underline{S}}^{(\alpha)} \} \} - n \sum_{\beta} (\underline{\underline{d}}_{\beta} / \rho_{\beta}) \cdot \{ \{ \underline{\underline{S}}^{(\alpha)}, \underline{\underline{S}}^{(\beta)} \} \}$$

$$\underline{\underline{\Pi}}^0 = -\mathcal{L}T \left[\left(\frac{2\mathcal{L}}{T}\right)^{1/2} \nabla T \cdot \{ \{ \underline{\underline{A}}, \underline{\underline{B}} \} \} + \underline{\underline{S}} : \{ \{ \underline{\underline{B}}, \underline{\underline{B}} \} \} \right.$$

$$\left. + \nabla \cdot \underline{\underline{u}} \{ \{ D, \underline{\underline{B}} \} \} - n \sum_{\beta} (\underline{\underline{d}}_{\beta} / \rho_{\beta}) \cdot \{ \{ \underline{\underline{S}}^{(\alpha)}, \underline{\underline{B}} \} \} \right]$$

(3.18)

$$\Pi = -\mathcal{L}T \left[\left(\frac{2\mathcal{L}}{T}\right)^{1/2} \nabla T \cdot \{ \{ \underline{\underline{A}}, D \} \} + \underline{\underline{S}} : \{ \{ \underline{\underline{B}}, D \} \} \right.$$

$$\left. + \nabla \cdot \underline{\underline{u}} \{ \{ D, D \} \} - n \sum_{\beta} (\underline{\underline{d}}_{\beta} / \rho_{\beta}) \cdot \{ \{ \underline{\underline{S}}^{(\alpha)}, D \} \} \right]$$

$$\underline{\underline{Q}}' = -\mathcal{L}T (2\mathcal{L}T)^{1/2} \left[\left(\frac{2\mathcal{L}}{T}\right)^{1/2} \nabla T \cdot \{ \{ \underline{\underline{A}}, \underline{\underline{A}} \} \} + \underline{\underline{S}} : \{ \{ \underline{\underline{B}}, \underline{\underline{A}} \} \} \right]$$

$$+ \nabla \cdot \underline{u} \{ \{ D, \underline{A} \} \} - n \sum_{\rho} (d_{\rho} / \rho_{\rho}) \cdot \{ \{ \underline{S}^{(\rho)}, \underline{A} \} \}] .$$

The fluxes are all polar quantities from which it follows that they are eigenfunctions of the parity operator \hat{P} with the properties

$$\begin{aligned} \hat{P} \underline{J}_a &= - \underline{J}_a ; & \hat{P} \underline{\underline{\pi}} &= \underline{\underline{\pi}} \\ \hat{P} Q' &= - Q' ; & \hat{P} \pi &= \pi . \end{aligned} \tag{3.19}$$

In reference (29) it was shown that $\hat{T} \hat{L} = \hat{L}^{\dagger} \hat{T}$, where \hat{T} is the total time-reversal operator and the symbol \dagger indicates the transpose conjugate of the operator. It is readily verified that $\hat{\Theta} = - \hat{\Theta}^{\dagger}$ is antisymmetric, where $\hat{\Theta}$ is a function of the magnetic or the electric field. If we consider the total time-reversal operator, \hat{T} , to be the product $\hat{T}_M \hat{T}_E = \hat{T}_E \hat{T}_M$, where \hat{T}_M and \hat{T}_E operate only on the momentum and external field variables, respectively, then $\hat{T}_M \hat{\Theta} = \pm \hat{\Theta} \hat{T}_M$ and $\hat{T}_E \hat{\Theta} = \mp \hat{\Theta} \hat{T}_E$ (upper sign for magnetic field, lower sign for electric field). Thus $\hat{T} \hat{\Theta} = \hat{\Theta}^{\dagger} \hat{T}$ and hence $\hat{T} \hat{L} = \hat{L}^{\dagger} \hat{T}$.

At this point we diverge a moment to prove a useful operator property. For simplicity, consider a general function of two variables, $F(x, y)$, and an operator \hat{O} . If \hat{O} operates on the integral of $F(x, y)$ over the entire space spanned by x , we can write

$$\hat{O} \int dx F(x, y) \equiv \int dx \hat{O}_y F(x, y) \quad (3.20)$$

where \hat{O}_y indicates that \hat{O} operates only on the variable y . Since the integral is over the entire space spanned by x , we can replace x with $\hat{O}_x^{-1} x$ to obtain

$$\hat{O} \int dx F(x, y) = \int d(\hat{O}_x^{-1} x) \hat{O}_y F(x, y), \quad (3.21)$$

when we have assumed that the Jacobian of the variable change is unity. Now, changing $\hat{O}_x^{-1} x$ to x changes x to $\hat{O}_x x$, so

$$\hat{O} \int dx F(x, y) = \int dx \hat{O}_y F(\hat{O}_x x, y) = \int dx \hat{O}_{x,y} F(x, y), \quad (3.22)$$

where now $\hat{O}_{x,y}$ operates on both x and y . Thus operating on the integral which is a function only of y is equivalent to operating on all the variables in the integrand.

Since \hat{T} is its own inverse, we can write the bracket integrals in the form

$$\{\{ \underline{a}, \underline{b} \}\} = (\underline{a}, \hat{\Lambda}(\underline{b})) = (\underline{a}, \hat{T} \hat{T}^{-1} \Lambda(\underline{b})). \quad (3.23)$$

If $\hat{\Lambda}(\underline{a})$ and $\hat{\Lambda}(\underline{b})$ are assumed to be eigenfunctions of \hat{T} with eigenvalues τ_a and τ_b , respectively, and if we write \hat{T} in its component product form, then

$$\{\{ \underline{a}, \underline{b} \}\} = \tau_b (\underline{a}, \hat{T}_\sigma \hat{T}_M \Lambda(\underline{b})). \quad (3.24)$$

Using the operator property of Equation 3.22, we can write Equation 3.24 as

$$\{\{\underline{a}, \underline{b}\}\} = \tau_b \hat{T}_{\mathcal{F}} (\hat{T}_{\mathcal{F}} \underline{a}, \hat{T}_M \hat{\Lambda}(\underline{b})). \quad (3.25)$$

The operator \hat{T}_M is a function only of the variables of integration, and so by integrating by parts and using the fact that $\hat{T}\hat{\Lambda} = \hat{\Lambda}^T\hat{T}$ we have

$$\{\{\underline{a}, \underline{b}\}\} = \tau_b \hat{T}_{\mathcal{F}} ((\hat{\Lambda}^T \hat{T}_M) \hat{T}_{\mathcal{F}} \underline{a}, \underline{b}) = \tau_b \hat{T}_{\mathcal{F}} (\hat{T}\hat{\Lambda}(\underline{a}), \underline{b}). \quad (3.26)$$

Performing the \hat{T} operation and transposing the indices, we finally obtain the result

$$\{\{\underline{a}, \underline{b}\}\} = \tau_a \tau_b \hat{T}_{\mathcal{F}} (\underline{b}, \hat{\Lambda}(\underline{a}))^T = \tau_a \tau_b \hat{T}_{\mathcal{F}} \{\{\underline{b}, \underline{a}\}\}^T. \quad (3.27)$$

Here \underline{a} and \underline{b} are tensors which may contain a field dependence and the superscript τ indicates bulk transposition of the two sets of indices associated with \underline{a} and \underline{b} .

The expressions for the fluxes as given in Equation 3.18 together with the parity relations (Equation 3.19) and the integral theorem (Equation 3.27) lead immediately to the Onsager-Casimir relationships which may be summarized as follows:

$$(i) \quad \text{Each of } \{\{\underline{A}, \underline{\xi}^{(\alpha)}\}\} = \{\{\underline{\xi}^{(\alpha)}, \underline{A}\}\} \quad , \\ \{\{\underline{\xi}^{(\omega)}, \underline{\xi}^{(\theta)}\}\} = \{\{\underline{\xi}^{(\theta)}, \underline{\xi}^{(\omega)}\}\} \quad , \text{ and } \{\{\underline{A}, \underline{A}\}\}$$

can be expressed in the form

$$\mathcal{L}_\perp(\underline{\underline{\xi}}^{(1)} - \hat{\mathbf{A}} \hat{\mathbf{A}}) + \mathcal{L}_\parallel \hat{\mathbf{A}} \hat{\mathbf{A}} - \mathcal{L}_{\pm r} \hat{\mathbf{A}} \times \underline{\underline{\xi}}^{(1)}$$

where $\mathcal{L}_{\pm r}$ is an odd function of \mathcal{F} for $\mathcal{F} = \mathcal{H}$ and is identically zero for $\mathcal{F} = \mathcal{E}$. Here $\hat{\mathbf{A}}$ is a unit vector in the direction of the field and $\underline{\underline{\xi}}^{(1)}$ is the rank 2 unit tensor in 3-dimensional space.

- (ii) The integrals $\{\{A, D\}\} = -\{\{D, A\}\}$ and $\{\{\underline{\underline{\xi}}^{(1)}, D\}\} = -\{\{D, \underline{\underline{\xi}}^{(1)}\}\}$ are zero for $\mathcal{F} = \mathcal{H}$ and proportional to $\hat{\mathbf{A}}$ for $\mathcal{F} = \mathcal{E}$.
- (iii) In the case of $\mathcal{F} = \mathcal{H}$ the integrals $\{\{A, B\}\} = \{\{B, A\}\}^T$ and $\{\{\underline{\underline{\xi}}^{(1)}, B\}\} = \{\{B, \underline{\underline{\xi}}^{(1)}\}\}^T$ are zero. However, with $\mathcal{F} = \mathcal{E}$, $\{\{A, B\}\} = \{\{B, A\}\}^T$ and $\{\{\underline{\underline{\xi}}^{(1)}, B\}\} = \{\{B, \underline{\underline{\xi}}^{(1)}\}\}^T$ are of the form

$$\mathcal{M}_1 \underline{\underline{F}}^1 + \mathcal{M}_2 \underline{\underline{F}}^2$$

where $\underline{\underline{F}}^1$ and $\underline{\underline{F}}^2$ are the two third rank tensors which are odd in the field and traceless and symmetric on their last pair of indices.

- (iv) $\{\{D, B\}\} = \{\{B, D\}\}$ is proportional to $\hat{\mathbf{A}} \hat{\mathbf{A}} - \frac{1}{3} \underline{\underline{\xi}}^{(1)}$.
- (v) $\{\{B, B\}\}$ can be expressed as a combination of the five linearly independent fourth rank tensors which are traceless and symmetric in their first and last pair of indices. In the

case that $\mathcal{F} = \underline{\xi}$, the coefficients of two of these tensors (those odd in the field) vanish.

The independent tensors for each of the above cases are determined by methods described in Chapter 6. As a further consequence of the integral theorem (Equation 3.27) we note that the rate of entropy production, which is $g_s = k \{ \{ \phi, \phi \} \}$ (k is the Boltzmann constant) in the linear approximation, satisfies the relationship $g_s = \hat{T} g_s$.

The flux vectors of Equation 3.18 can now be written as

$$\begin{aligned} J_\alpha &= \underline{\Omega}'_{\alpha 0} \cdot \nabla \left(\frac{1}{T} \right) - \frac{p}{T} \sum_{\beta} \underline{\Omega}'_{\alpha \beta} \cdot (d_\beta / \rho_\beta) \\ \underline{\Pi} &= -2 \underline{\eta} \theta^2 \underline{\underline{S}} \\ \pi &= -\mathcal{N}_b \nabla \cdot \underline{u} \end{aligned} \tag{3.28}$$

$$\underline{Q}' = \underline{\Omega}'_{00} \cdot \nabla \left(\frac{1}{T} \right) - \frac{p}{T} \sum_{\beta} \underline{\Omega}'_{0\beta} \cdot (d_\beta / \rho_\beta).$$

The $\underline{\Omega}'_{\alpha\beta}$'s used in Equation 3.28 can be defined either in terms of the form of Equation 3.15 or Equation 3.17 as

$$\begin{aligned} \underline{\Omega}'_{\alpha 0} &= \underline{\Omega}'_{0\alpha} = -T^2 \left(\frac{2A}{T} \right)^{1/2} \{ \{ A, \underline{\underline{S}}^{(\alpha)} \} \} \\ &= 2kT^2 m_\alpha^{-1/2} \int dI f_\alpha^{(0)} \underline{A}_\alpha \underline{w} \end{aligned}$$

$$\begin{aligned}\underline{\Omega}'_{\alpha\beta} &= \underline{\Omega}'_{\beta\alpha} = \frac{nT}{\rho} \{ \{ \underline{\xi}^{(\beta)}, \underline{\xi}^{(\alpha)} \} \} \\ &= - \frac{nT}{\rho} (2m_\alpha kT)^{1/2} \int dI f_\alpha^{(0)} \underline{w} \underline{\xi}_\alpha^{(\beta)}\end{aligned}\quad (3.29)$$

$$\underline{\eta} = \frac{kT}{2} \{ \{ \underline{B}, \underline{B} \} \} \quad ; \quad \eta_b = kT \{ \{ D, D \} \}$$

$$\begin{aligned}\underline{\Omega}'_{00} &= 2k^2 T^3 \{ A, A \} \\ &= \sum_\alpha m_\alpha^{-1/2} 2k^2 T^3 \int dI f_\alpha^{(0)} \underline{A}_\alpha \underline{w} \{ w^2 + \epsilon_\alpha^* - \xi_\alpha - \bar{\epsilon}_\alpha^* \}\end{aligned}$$

$$\sum_\alpha \underline{\Omega}'_{\alpha 0} = \sum_\alpha \underline{\Omega}'_{0\alpha} = \sum_\alpha \underline{\Omega}'_{\alpha\beta} = \sum_\alpha \underline{\Omega}'_{\beta\alpha} = 0.$$

In the field-free case all of the force-flux coupling coefficients must be isotropic tensors and thus we find that

$$\begin{aligned}\underline{J}_\alpha &= \underline{\Omega}'_{\alpha 0} \nabla(\frac{1}{T}) - \frac{\rho}{T} \sum_\beta \underline{\Omega}'_{\alpha\beta} (\underline{d}_\beta / \rho_\beta) \\ \underline{\Pi} &= -2\eta \underline{\xi}\end{aligned}\quad (3.30)$$

$$\pi = -\eta_b \nabla \cdot \underline{u}$$

$$\underline{Q}' = \underline{\Omega}'_{00} \nabla(\frac{1}{T}) - \frac{\rho}{T} \sum_\beta \underline{\Omega}'_{0\beta} (\underline{d}_\beta / \rho_\beta)$$

where now

$$\underline{\Omega}'_{\alpha 0} = \underline{\Omega}'_{0\alpha} = \frac{1}{3} \delta_{\alpha 0}^{(1)} \theta^2 \underline{\Omega}'_{\alpha 0}$$

$$\underline{\Omega}'_{\alpha\beta} = \underline{\Omega}'_{\beta\alpha} = \frac{1}{3} \underline{\underline{\underline{\Sigma}}}^{(1)} \odot^2 \underline{\underline{\underline{\Omega}}}'_{\alpha\beta} \quad (3.31)$$

$$\underline{\eta} = \frac{1}{3} \underline{\underline{\underline{\Sigma}}}^{(2)} \odot^4 \underline{\underline{\underline{\eta}}}.$$

In the standard treatment of the kinetic theory of mixtures (17) the final term in Equation 3.11 is written as $n \sum_{\beta} \underline{\underline{\underline{c}}}_\alpha^{(\beta)} \cdot \underline{\underline{\underline{d}}}_\beta$ with the conditions $\underline{\underline{\underline{c}}}_\alpha^{(\alpha)} = 0$ (to account for the linear dependence of the forces $\underline{\underline{\underline{d}}}_\beta$). The coefficients of $\underline{\underline{\underline{d}}}_\beta$ in this convention are related to our previous choice of coefficients by the expressions

$$\underline{\underline{\underline{c}}}_\alpha^{(\beta)} = \underline{\underline{\underline{\Sigma}}}_\alpha^{(\beta)} / \rho_\beta - \underline{\underline{\underline{\Sigma}}}_\alpha^{(\alpha)} / \rho_\alpha \quad (3.32)$$

$$\underline{\underline{\underline{\Sigma}}}_\alpha^{(\beta)} = \rho_\beta \underline{\underline{\underline{c}}}_\alpha^{(\beta)} - \frac{\rho_\beta}{\rho} \sum_{\gamma} \rho_\gamma \underline{\underline{\underline{c}}}_\alpha^{(\gamma)}.$$

Using this form of ϕ_α leads to the following expressions for $\underline{\underline{\underline{J}}}_\alpha$ and $\underline{\underline{\underline{Q}}}'$ in the field free case:

$$\underline{\underline{\underline{J}}}_\alpha = \frac{m_\alpha n^2}{\rho} \sum_{\beta} m_\beta \mathcal{D}_{\alpha\beta} \underline{\underline{\underline{d}}}_\beta - (D_\alpha^T / T) \underline{\underline{\underline{\nabla}}} T \quad (3.33)$$

$$\underline{\underline{\underline{Q}}}' = -P \sum_{\alpha} (D_\alpha^T / \rho_\alpha) \underline{\underline{\underline{d}}}_\alpha - \lambda' \underline{\underline{\underline{\nabla}}} T$$

where

$$\mathcal{D}_{\alpha\beta} = (1/3 n m_\beta) (2kT/m_\alpha)^{1/2} \int d\mathbf{l} f_\alpha^{(0)}(\mathbf{l}) \underline{\underline{\underline{w}}}_1 \cdot \underline{\underline{\underline{c}}}_\alpha^{(\beta)}(\mathbf{l})$$

$$D_\alpha^T = (2kT/3) m_\alpha^{1/2} \int d\mathbf{l} f_\alpha^{(0)}(\mathbf{l}) \underline{\underline{\underline{w}}}_1 \cdot \underline{\underline{\underline{A}}}_\alpha(\mathbf{l}) \quad (3.34)$$

$$\lambda' = (2k^2T/3) \sum_{\alpha} m_{\alpha}^{-1/2} \int d\mathbf{l} f_{\alpha}^{(0)}(\mathbf{l}) [W_{\mathbf{l}}^2 + \epsilon_{\alpha}^*(\mathbf{l}) - \frac{\epsilon}{2} - \bar{\epsilon}_{\alpha}^*] \mathbf{w}_{\mathbf{l}} \cdot \mathbf{A}_{\alpha}(\mathbf{l}).$$

From Equations 3.11, 3.15, 3.32, and 3.34 we then have

$$\theta_{\alpha\beta} = \frac{-\rho\rho}{n^2T} \frac{1}{m_{\alpha}m_{\beta}} \left(\frac{\Omega'_{\alpha\beta}}{\rho_{\beta}} - \frac{\Omega'_{\beta\alpha}}{\rho_{\alpha}} \right) \quad (3.35)$$

or conversely,

$$\Omega'_{\alpha\beta} = (\rho_{\beta} m_{\alpha} n^2 T / \rho \rho^2) [-\rho m_{\beta} \theta_{\alpha\beta} + \sum_{\gamma} \rho_{\gamma} m_{\gamma} \theta_{\alpha\gamma}]$$

and

(3.36)

$$\Omega'_{\alpha 0} = \Omega'_{0\alpha} = T D_{\alpha}^T \quad ; \quad \Omega'_{00} = T^2 \lambda'$$

which establishes the relationships between the transport coefficients in the two treatments.

CHAPTER 4. SOLUTION OF THE KINETIC EQUATIONS

Since our ultimate concern is with a comparison of theory and experimental thermal diffusion, thermal conductivity, and diffusion data, we need only determine the coefficients A_α and $S_\alpha^{(A)}$. To this end we follow the usual procedure of converting the appropriate integral equations into matrix forms by expanding the unknown functions in a complete set of functions which are dependent upon the momentum variables of single molecules. We take these variables to be the reduced linear momentum $\underline{w} = (m/2kT)^{1/2} \underline{c}$ and the reduced angular momentum $\underline{\Omega}$. The i th component of the reduced angular momentum in the principal axis frame is $\Omega_i = (1/2kT)^{1/2} L_i / I_i$, where L_i and I_i are the i th component of rotational angular momentum and the i th principal moment of inertia, respectively.

The functions A_α and $S_\alpha^{(A)}$ can be expressed in terms of a complete set of expansion functions as

$$A_\alpha = \sum_{pqst} S_{p+\frac{1}{2}}^{(s)}(w^2) S_{q-\frac{1}{2}+\frac{1}{2}}^{(t)}(\Omega^2) [w]^{(p)} [\Omega]^{(q)} \Theta^{p+q} A_{\alpha(pqst)}$$

and

(4.1)

$$S_\alpha^{(A)} = \sum_{pqst} S_{p+\frac{1}{2}}^{(s)}(w^2) S_{q-\frac{1}{2}+\frac{1}{2}}^{(t)}(\Omega^2) [w]^{(p)} [\Omega]^{(q)} \Theta^{p+q} S_\alpha^{(A)(pqst)}$$

which was originally proposed by Kagan and Maksimov (31).

Here $S_p^{(i)}$ denotes a Sonine polynomial (17), $[x]^{(y)}$ denotes

the highest weight irreducible part of the polyad formed from γ χ 's (these are discussed in detail in Chapter 6), and the coefficients $\underline{A}_{\alpha}(pqszt)$ and $\underline{\xi}_{\alpha}^{(a)}(pqszt)$ are tensors of rank $p+q+1$. The symbol \odot^{p+q} indicates a $(p+q)$ -fold scalar product of the two tensors between which it is placed and r indicates the number of rotational degrees of freedom of the molecules. The functions \underline{A}_{α} and $\underline{\xi}_{\alpha}^{(a)}$ are themselves the α th components of the "composition" vectors A and $\xi^{(a)}$. We can thus write Equation 4.1 in the more general form

$$A = \sum_{\alpha} \sum_{pqszt} \psi^{\alpha}(pqszt) \odot^{p+q} \underline{A}_{\alpha}(pqszt)$$

and

(4.2)

$$\xi^{(a)} = \sum_{\alpha} \sum_{pqszt} \psi^{\alpha}(pqszt) \odot^{p+q} \underline{\xi}_{\alpha}^{(a)}(pqszt)$$

where $\psi^{\alpha}(pqszt)$ is a basis vector in the composition space and is defined by

$$\psi_{\alpha}^{\alpha}(pqszt) = \int_{\alpha\beta} S_{\rho+\frac{1}{2}}^{(s)}(w^2) S_{q-\frac{1}{2}+\frac{1}{2}}^{(t)}(\Omega^2) [w]^{(p)} [\Omega]^{(q)}. \quad (4.3)$$

The series expansion of Equation 4.1 is convenient due to the orthogonality properties of the Sonine polynomials and of the Cartesian tensors. Thus under the integrations of the form required in the calculation of the fluxes in Equation 3.29, the transport coefficients take the simple tensorial forms

effect).

In the absence of external fields the tensors $\underline{A}_{\alpha(\rho g s t)}$ and $\underline{\xi}_{\alpha(\rho g s t)}^{(\beta)}$ must transform according to the totally symmetric representation of the three-dimensional rotation group. Therefore, as the field strength shrinks to zero the only coefficients which do not vanish identically will be those which reduce to isotropic tensors (see Chapter 6). In this limit each of the pairs of indices s, t and ρ, g , such that $g = \rho$ or $g = \rho \pm 1$, yield a single term with a scalar valued expansion coefficient. These restrictions arise since the direct products such as $[\underline{w}]^{(\rho)} [\underline{\Omega}]^{(g)} \underline{A}_{\alpha(\rho g s t)}$ contain the vector representation ($l=1$) once and only once if ρ and g are so related (see Chapter 6). When the external fields are present the tensor coefficients $\underline{A}_{\alpha(\rho g s t)}$ and $\underline{\xi}_{\alpha(\rho g s t)}^{(\beta)}$ transform only according to the totally symmetric representation of the group C_{∞} of rotations about the direction of the field and hence are not isotropic. The direct products of the form $[\underline{w}]^{(\rho)} [\underline{\Omega}]^{(g)} \underline{A}_{\alpha(\rho g s t)}$ can now in general contain the vector representation more than once, although not all of these will necessarily remain after the contraction of the $\rho+g$ indices. These field considerations greatly expand the dimension of the matrix form of the integral equations, with an associated increase in algebraic complexity.

To illustrate these principles we choose five functions

of the expansion in Equation 4.1:

$$\begin{aligned} \underline{\phi}_\alpha^{(1)} &= \underline{w}_\alpha & ; & \quad \underline{\phi}_\alpha^{(4)} = \underline{w}_\alpha [\underline{\Omega}_\alpha]^{(2)} \\ \underline{\phi}_\alpha^{(2)} &= \underline{w}_\alpha S_{\frac{3}{2}}^{(1)}(w_\alpha^2) = \underline{w}_\alpha \left(\frac{\underline{\xi}}{2} \cdot w_\alpha^2 \right) & ; & \quad \underline{\phi}_\alpha^{(5)} = \underline{w}_\alpha \underline{\Omega}_\alpha \\ \underline{\phi}_\alpha^{(3)} &= \underline{w}_\alpha S_{\frac{5}{3}}^{(1)}(\Omega_\alpha^2) = \underline{w}_\alpha (1 - \Omega_\alpha^2) \end{aligned} \quad (4.7)$$

where the superscripts 1, 2, 3, 4, and 5 are shorthand notation which correspond to the index sets $pgst = 1000, 1010, 1001, 1200,$ and $1100,$ respectively. These particular functions are of interest because they form the truncated basis set which we will ultimately use in our calculations. The trial functions \underline{A}_α and $\underline{\xi}_\alpha^{(A)}$ are formed from linear combinations of these basis elements with tensor coefficients of rank $p+q+1$, that is, rank 2 for $\underline{\phi}_\alpha^{(1)}, \underline{\phi}_\alpha^{(2)}, \underline{\phi}_\alpha^{(3)}$, rank 4 for $\underline{\phi}_\alpha^{(4)}$, and rank 3 for $\underline{\phi}_\alpha^{(5)}$.

In the field-free case each of these terms in the trial functions contain the vector representation once.

Thus we can write the trial solutions in the forms

$\underline{A}_\alpha = \sum_i a_{\alpha(i)} \underline{\phi}'_{\alpha}{}^{(i)}$ and $\underline{\xi}_\alpha^{(A)} = \sum_i c_{\alpha(i)} \underline{\phi}'_{\alpha}{}^{(i)}$, where $a_{\alpha(i)}$ and $c_{\alpha(i)}^{(A)}$ are scalar coefficients and the five vector trial functions corresponding to Equation 4.7 are

$$\begin{aligned} \underline{\phi}'_{\alpha}{}^{(1)} &= \underline{\phi}_\alpha^{(1)} & ; & \quad \underline{\phi}'_{\alpha}{}^{(4)} = \underline{w}_\alpha \cdot [\underline{\Omega}_\alpha]^{(2)} \\ \underline{\phi}'_{\alpha}{}^{(2)} &= \underline{\phi}_\alpha^{(2)} & ; & \quad \underline{\phi}'_{\alpha}{}^{(5)} = \underline{w}_\alpha \times \underline{\Omega}_\alpha \\ \underline{\phi}'_{\alpha}{}^{(3)} &= \underline{\phi}_\alpha^{(3)} \end{aligned} \quad (4.8)$$

The transport coefficients could be computed using these trial functions. However, this is not necessary since Equation 4.5 gives the field-free result when the tensor coefficients $\underline{A}_{\gamma(i)}$ and $\underline{f}_{\gamma(i)}^{(\beta)}$ are isotropic. That is

$$\underline{A}_{\gamma(i)} = a_{\gamma(i)} \underline{f}^{(1)}$$

and

(4.9)

$$\underline{f}_{\gamma(i)}^{(\beta)} = c_{\gamma(i)}^{(\beta)} \underline{f}^{(1)}.$$

The explicit expressions for the field-free transport coefficients are

$$\lambda' = \frac{-\Omega'_{00}}{T^2} = k^2 T \sum_{\gamma} n_{\gamma} m_{\gamma}^{-1/2} [-\frac{1}{2} a_{\gamma(2)} - a_{\gamma(3)}]$$

$$D_{\alpha}^T = \frac{\Omega'_{\alpha 0}}{T^2} = k T n_{\alpha} m_{\alpha}^{-1/2} a_{\alpha(1)}$$

(4.10)

$$D_{\alpha\beta} = (p n_{\alpha} / n m_{\beta}) (k T / 2 m_{\alpha})^{1/2} c_{\alpha(1)}^{(\beta)}.$$

It is convenient to characterize the tensor

$\underline{f}_{\gamma}(\lambda', D_{\alpha}^T, D_{\alpha\beta})$ by the value $\underline{f}_{\gamma}^{(0)} = \underline{f}_{\gamma 0} \underline{f}^{(1)}$ which it assumes in the absence of the external field, and by the field distortion

$$\Delta \underline{f}_{\gamma} = \underline{f}_{\gamma}(\lambda') - \underline{f}_{\gamma}^{(0)} = \Delta f_{\gamma n} \hat{k} \hat{k} + \Delta f_{\gamma \perp} (\underline{f}^{(1)} - \hat{k} \hat{k}) - \Delta f_{\gamma r r} (\hat{k} \chi \underline{f}^{(1)}). \quad (4.11)$$

Thus we associate with each of the tensor \underline{f}_{γ} four transport

coefficients $\mathcal{L}_{\gamma 0}$, $\Delta \mathcal{L}_{\gamma \parallel}$, $\Delta \mathcal{L}_{\gamma \perp}$, and $\Delta \mathcal{L}_{\gamma \pm r}$.

To calculate these transport coefficients, we express the integral equations in a matrix representation. From Equations 3.12, 4.2 and 4.3, we write

$$\mathcal{D}_{\alpha(i)}^{(a)} = \sum_{\beta} \sum_{\gamma} \Lambda_{\alpha\beta(\gamma)} \Theta^{\beta\gamma} Q_{\beta(\gamma)} \quad (4.12)$$

where Q represents A or $\mathcal{S}^{(r)}$ and where

$$\mathcal{D}_{\alpha(i)}^{(a)} = \sum_{\mathcal{H}} \int d\mathcal{H} \hat{T} \psi_{\mathcal{H}}^{\alpha(i)} \mathcal{D}_{\mathcal{H}}^{(a)}$$

and (4.13)

$$\Lambda_{\alpha\beta(\gamma)} = \sum_{\mathcal{H}} \int d\mathcal{H} \hat{T} \psi_{\mathcal{H}}^{\alpha(i)} \Lambda_{\mathcal{H}\beta} \psi_{\mathcal{H}}^{\beta(\gamma)}.$$

Here, as in Equation 4.7, for notational simplicity we use a single index to represent the set of indices $\rho\gamma st$. From this definition of $\Lambda_{\alpha\beta(\gamma)}$ and by following a sequence of steps similar to those in the proof of Equation 3.27, we have

$$\hat{T}_{\mathcal{H}} (\Lambda_{\alpha\beta(\gamma)})^T = \Lambda_{\beta\alpha(\gamma)} \quad (4.14)$$

and thus we say that the matrix representation Λ is self-adjoint in the sense that $\hat{T}\Lambda^T = \Lambda$. This transposed, time-reversal definition of self-adjoint is similar to the usual transposed, complex conjugate definition.

As previously discussed, the presence of an external field expands the number of independent scalar coefficients which must be included in the solution vector \underline{Q}_β . To determine the number of these independent scalar coefficients for each tensor coefficient, we find the number of irreducible bases contained in the direct product representation. Since each of these irreducible bases will contain one and only one element which is invariant to rotations about the field direction, the number of independent coefficients is equal to the number of irreducible bases (see Chapter 6 for a more complete discussion). As an example, consider $\underline{A}_{\alpha(1200)}$, which is a 4th rank tensor which is traceless and symmetric on its first two indices. It is, therefore, a direct product of a weight 2 and two weight 1 irreducible representation bases and thus contains one weight 4, two weight 3, and three weight 2, two weight 1, and one weight 0 irreducible representation bases. There are a total of nine irreducible representation bases and therefore nine independent scalar coefficients in $\underline{A}_{\alpha(1200)}$. Similarly, we find $\underline{A}_{\alpha(1000)}$, $\underline{A}_{\alpha(1010)}$, and $\underline{A}_{\alpha(1001)}$ are the direct product of two weight 1 irreducible representation bases and hence contain three independent scalar coefficients. The coefficient $\underline{A}_{\alpha(1100)}$ is the direct product of three weight 1 irreducible representation bases and contains seven independent scalar coefficients. As previously

discussed, in the absence of external fields, each tensor coefficient has only one independent scalar coefficient.

To illustrate the form of these matrix equations, we consider the field-free case for binary mixtures of species α and β . In keeping with the notation of Equations 4.7-4.9, we can write the column vectors of Equation 4.12 in the partitioned form

$$\underline{D}^{(A)} = \begin{pmatrix} \underline{D}_\alpha^{(A)} \\ \underline{D}_\beta^{(A)} \end{pmatrix}, \quad \underline{a} = \begin{pmatrix} \underline{a}_\alpha \\ \underline{a}_\beta \end{pmatrix}, \quad \underline{D}^{(S^{(A)})} = \begin{pmatrix} \underline{D}_\alpha^{(S^{(A)})} \\ \underline{D}_\beta^{(S^{(A)})} \end{pmatrix}, \quad \underline{S} = \begin{pmatrix} \underline{S}_\alpha \\ \underline{S}_\beta \end{pmatrix},$$

where each of the vectors in the function space are

$$\underline{D}_\gamma^{(A)} = n_\gamma m_\gamma^{-1/2} \begin{pmatrix} 0 \\ -\frac{15}{4} \\ -\frac{3r}{2} \\ 0 \\ 0 \\ \vdots \\ \vdots \end{pmatrix}, \quad \underline{a}_\gamma = \begin{pmatrix} a_{\gamma(1)} \\ a_{\gamma(2)} \\ a_{\gamma(3)} \\ a_{\gamma(4)} \\ a_{\gamma(5)} \\ \vdots \\ \vdots \end{pmatrix}, \quad (4.15)$$

$$\underline{D}_\gamma^{(S^{(A)})} = \frac{p_\alpha p_\beta}{p} (2AT/m_\gamma)^{1/2} \begin{pmatrix} 3/2 \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \\ \vdots \end{pmatrix}, \quad \underline{S}_\gamma = \begin{pmatrix} c_{\gamma(1)}^{(A)} \\ c_{\gamma(2)}^{(A)} \\ c_{\gamma(3)}^{(A)} \\ c_{\gamma(4)}^{(A)} \\ c_{\gamma(5)}^{(A)} \\ \vdots \\ \vdots \end{pmatrix}.$$

Only the coefficients corresponding to Equation 4.7 are explicitly displayed.

The matrix Λ has the partitioned structure

$$\Lambda = \begin{pmatrix} \Lambda_{\alpha\alpha} & \Lambda_{\alpha\beta} \\ \Lambda_{\beta\alpha} & \Lambda_{\beta\beta} \end{pmatrix} \quad (4.16)$$

where each of the explicitly displayed elements is a matrix element in the two species composition space. These composition elements are themselves matrices of elements in the function space defined by the expansion in the complete set of functions of Equation 4.1, and from Equation 3.5 can be written explicitly as

$$\Lambda_{\alpha\alpha}(i_j) = n_\alpha^2 \{ [\underline{\phi}'_{\alpha}^{(i)}, \underline{\phi}'_{\alpha}^{(j)}]_{\alpha\alpha}^{11} + [\underline{\phi}'_{\alpha}^{(i)}, \underline{\phi}'_{\alpha}^{(j)}]_{\alpha\alpha}^{12} \} + n_\alpha n_\beta [\underline{\phi}'_{\alpha}^{(i)}, \underline{\phi}'_{\alpha}^{(j)}]_{\alpha\beta}^{11} \quad (4.17)$$

$$\Lambda_{\alpha\beta}(i_j) = n_\alpha n_\beta [\underline{\phi}'_{\alpha}^{(i)}, \underline{\phi}'_{\beta}^{(j)}]_{\alpha\beta}^{12}$$

and

$$[\underline{\phi}'_{\alpha}^{(i)}, \underline{\phi}'_{\gamma}^{(j)}]_{\alpha\gamma}^{1k} = (n_\alpha n_\gamma)^{-1} \iiint d1 d1' d2' d2 w_{\alpha\gamma}(121'2') \quad (4.18)$$

$$\chi f_\alpha^{(i)}(1) f_\gamma^{(j)}(k) \hat{T} \underline{\phi}'_{\alpha}^{(i)}(1) [\underline{\phi}'_{\gamma}^{(j)}(k) - \underline{\phi}'_{\gamma}^{(j)}(k')]$$

with $\gamma, \delta = \alpha$ or β and $k=1$ or 2 .

The matrix equations $\mathcal{D}^{(\alpha)} = \Lambda A$ and $\mathcal{D}^{(\beta)} = \Lambda \mathcal{S}^{(\beta)}$

as given have indeterminate solutions. This arises from

the fact that ϕ must be arbitrary to within a linear combination of the summational invariants, which are the solutions to the homogeneous equations. This singularity is removed through the use of the auxiliary conditions of Equation 3.2 (in particular, $\sum_{\alpha} \int d\Omega m_{\alpha} \epsilon_{\alpha} f_{\alpha}^{(k)}(1) = 0$). Making use of these conditions, we find unique solutions for the coefficients $a_{\gamma(i)}$ and $\epsilon_{\gamma(i)}^{(\beta)}$.

CHAPTER 5. REDUCTION OF THE KINETIC EQUATIONS
THROUGH PERTURBATION THEORY

Previous attempts (21-23) to explain thermal diffusion in isotopic polyatomic mixtures in terms of a simple physical model are inadequate due to the importance of the contributions of the internal degrees of freedom to the effect itself. Since the present work allows the inclusion of these internal degrees of freedom into the collision model, physical insights into the phenomena of the thermal diffusive process may be gained from an analysis of the effects of the potential and kinematic parameters on the kinetic equations.

The matrix equations which arise in the solution of the kinetic equations are difficult to analyze in an intuitive way, since their exact solution involves matrix inversion of rather large matrices. Thus it is desirable to reduce these expressions to an analytic form through the use of perturbation techniques.

Given a set of linear inhomogeneous equations in matrix form

$$\gamma = J c \quad (5.1)$$

where J is a nonsingular matrix and γ is the inhomogeneity, the solution vector, c , is given by

$$c = J^{-1} y. \quad (5.2)$$

For our kinetic equations, J represents the collision integral matrix Λ defined in Equation 4.13 modified by the subsidiary condition of Equation 3.9 to remove the singularity. If J is assumed to consist entirely of pieces which are zero and first order in the perturbation, that is, $J = J_0 + \epsilon J_1$, then the solution vector may be written in the form

$$c = [1 - \epsilon J_0^{-1} J_1 + \epsilon^2 J_0^{-1} J_1 J_0^{-1} J_1 - \dots] J_0^{-1} y. \quad (5.3)$$

The perturbation solution then is $\sum_i \epsilon^i c_i$; where

$$\begin{aligned} c_0 &= J_0^{-1} y \\ c_1 &= -J_0^{-1} J_1 J_0^{-1} y \\ c_2 &= J_0^{-1} J_1 J_0^{-1} J_1 J_0^{-1} y \\ &\vdots \end{aligned} \quad (5.4)$$

and where the subscript indicates the order of the perturbation.

The inhomogeneities of the last chapter are a function of macroscopic variables and the number of degrees of freedom (Equations 4.13 and 4.15) and therefore it is convenient to take them to be entirely of zeroth order. To obtain the

corresponding solutions c_i ; then requires a consistent definition of the zeroth and first order parts of the matrix, J . To this end we define a matrix transformation which will nearly block diagonalize the collision integral matrix A in a physically meaningful way. The zeroth order matrix will then be determined by the diagonal blocks.

We are concerned with the thermal diffusion of isotopic mixtures, so it seems reasonable to formulate the perturbation expansion in terms of kinematic parameters (that is, parameters relevant to molecular free-flight such as the total molecular mass and internal mass distribution) about what is effectively an average molecule.

Since thermal diffusion is a flux of mass due to a temperature gradient, we propose that the transformation should block diagonalize the collision integral matrix in such a way that the diagonal blocks can be interpreted as the thermal conductivity and self-diffusion integrals in an average molecule limit. The off-diagonal blocks then become the isotopic perturbations.

As a conceptual aid in the discussion which follows it is convenient to write the linear kinetic equations in the form of Equation 3.3 rather than the separated form of Equation 3.12 which utilizes the independence of the generalized forces. If we consider the set of diffusion force vectors, $\{d_{\mu}\}$, and the thermal gradient, ∇T , to be the only

sources of distortions from equilibrium contained in (Equation 3.11), then the inhomogeneity in Equation 3.9 is a linear combination of only these force vectors. For the μ th species,

$$\underline{D}_\mu = n_\mu m_\mu^{-1/2} \begin{pmatrix} 0 \\ -\frac{15}{4} \\ -\frac{3r}{4} \\ 0 \\ 0 \\ \vdots \end{pmatrix} \frac{\nabla T}{T} + \frac{r_\mu}{P} \left(\frac{2\Delta T}{m_\mu} \right)^{1/2} \sum_i \rho_i \left(\frac{d_i}{T_i} - \frac{d_\alpha}{T_\alpha} \right) \begin{pmatrix} \frac{3}{2} \\ 0 \\ 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix} \quad (5.5)$$

where the α th species has been chosen as a reference for removing the linear dependence of the diffusion force vectors (see Chapter 3). Each component \underline{D}_μ of the composition vector will contain as many elements (which in general are tensors) as there are terms in the expansion set of Equation 4.1 and the general inhomogeneity composition vector is of the form

$$\underline{D} = \begin{pmatrix} \underline{D}_\alpha \\ \underline{D}_\beta \\ \underline{D}_\gamma \\ \vdots \\ \underline{D}_N \end{pmatrix} \quad (5.6)$$

for an N -component mixture.

We now define the transformation

$$\mathfrak{A}^{-1} = \begin{vmatrix} \frac{n_A}{\sqrt{m_A}} & -\frac{1}{\sqrt{m_A}} \frac{p_A p_B}{P} & -\frac{1}{\sqrt{m_A}} \frac{p_A p_X}{P} & \dots \\ \frac{n_B}{\sqrt{m_B}} & \frac{1}{\sqrt{m_B}} \frac{p_B (P-p_A)}{P} & -\frac{1}{\sqrt{m_B}} \frac{p_B p_X}{P} & \dots \\ \frac{n_Y}{\sqrt{m_Y}} & -\frac{1}{\sqrt{m_Y}} \frac{p_Y p_A}{P} & \frac{1}{\sqrt{m_Y}} \frac{p_Y (P-p_B)}{P} & \dots \\ \vdots & \vdots & \vdots & \vdots \end{vmatrix} \quad (5.7)$$

where \mathfrak{A} represents a rotation matrix of the composition vector θ . The matrix operation $\mathfrak{A}\theta$ then serves to effect a separation of the independent force vectors in the form

$$\mathfrak{A}\theta \propto \begin{vmatrix} \frac{\nabla T}{T} \\ \frac{d_A}{T_A} - \frac{d_X}{T_X} \\ \frac{d_Y}{T_Y} - \frac{d_X}{T_X} \\ \vdots \\ \frac{d_N}{T_N} - \frac{d_X}{T_X} \end{vmatrix} \cdot \quad (5.8)$$

That is, the inhomogeneity separates into parts corresponding to the temperature gradient for the mixture and the independent diffusion forces.

Having chosen \mathfrak{A} in this manner, we now wish to define a composition transformation matrix θ such that the combination $\mathfrak{A}\theta^{-1}$ yields the self-adjoint (in the sense of Equation 4.14) form

$$\delta \Lambda \rho = \begin{pmatrix} \Lambda_{TT} & \Lambda_{TD_\rho} & \Lambda_{TD_\gamma} & \dots \\ \Lambda_{D_\beta T} & \Lambda_{D_\rho D_\rho} & \Lambda_{D_\rho D_\gamma} & \dots \\ \Lambda_{D_\gamma T} & \Lambda_{D_\gamma D_\rho} & \Lambda_{D_\gamma D_\gamma} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \cdot \quad (5.9)$$

Here Λ_{TT} contains thermal conductivity type integrals, $\Lambda_{D_\mu D_\mu}$ contains self-diffusion type integrals for the μ th species, and Λ_{TD_μ} and $\Lambda_{D_\mu D_\nu}$ type matrices contain the isotopic perturbation integrals. Since Λ is itself self-adjoint and has the structural form

$$\Lambda = \begin{pmatrix} \Lambda_{\alpha\alpha} & \Lambda_{\alpha\beta} & \Lambda_{\alpha\gamma} & \dots \\ \Lambda_{\beta\alpha} & \Lambda_{\beta\beta} & \Lambda_{\beta\gamma} & \dots \\ \Lambda_{\gamma\alpha} & \Lambda_{\gamma\beta} & \Lambda_{\gamma\gamma} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix} \cdot \quad (5.10)$$

Choosing $\rho^{-1} = \delta^T$ yields the self-adjoint matrix product $\delta \Lambda \delta^T$. The total transformation can then be written in the form

$$\delta \theta = (\delta \Lambda \rho^{-1})(\rho \phi) \quad (5.11)$$

Since we have chosen $\rho^{-1} = \delta^T$, we have also that $\rho = (\delta^{-1})^T$. From Equation 5.7 and the distortion ϕ of Equation 3.11, we can write

$$\rho \bar{\Phi} = \begin{pmatrix} (\rho \bar{\Phi})_{Q'} \\ (\rho \bar{\Phi})_{J_x} \\ (\rho \bar{\Phi})_{J_y} \\ \vdots \end{pmatrix} = \begin{pmatrix} \sum_H \frac{\rho_H}{\sqrt{m_H}} \phi_H \\ \frac{\rho_x}{P} \sum_H \frac{(\delta_{xH} P - \rho_H)}{\sqrt{m_H}} \phi_H \\ \frac{\rho_y}{P} \sum_H \frac{(\delta_{yH} P - \rho_H)}{\sqrt{m_H}} \phi_H \\ \vdots \end{pmatrix}. \quad (5.12)$$

If we now use Equation 3.13 to express the mass and heat flux vectors of Equation 3.17 as

$$\underline{Q}' = \Delta T (2\Delta T)^{1/2} \int d\underline{w} \int d\underline{\Omega} e^{-(w^2 + \Omega^2)} \sum_H \frac{\rho_H}{\sqrt{m_H}} \phi_H \underline{w} [-S_{3/2}^{(1)}(w^2) - S_{5/2}^{(1)}(\Omega^2)]$$

and (5.13)

$$\underline{J}_\mu = (\Delta T)^{1/2} \int d\underline{w} \int d\underline{\Omega} e^{-(w^2 + \Omega^2)} \frac{\rho_\mu}{P} \sum_H \frac{(\delta_{\mu H} P - \rho_H)}{\sqrt{m_H}} \phi_H \underline{w},$$

where $S_j^{(i)}(x^2)$ are again Sonine polynomials, the direct correspondence of $\rho \bar{\Phi}$ to the independent flux vectors is seen from

$$\underline{Q}' = \Delta T (2\Delta T)^{1/2} \int d\underline{w} \int d\underline{\Omega} e^{-(w^2 + \Omega^2)} (\rho \bar{\Phi})_{Q'} \underline{w} [-S_{3/2}^{(1)}(w^2) - S_{5/2}^{(1)}(\Omega^2)]$$

and (5.14)

$$\underline{J}_\mu = \sqrt{2\Delta T} \int d\underline{w} \int d\underline{\Omega} e^{-(w^2 + \Omega^2)} (\rho \bar{\Phi})_{J_\mu} \underline{w}.$$

Note that we have chosen \underline{J}_μ as the reference vector to remove the linear dependence $\sum_H \underline{J}_H = 0$.

Lastly, we note that the first row and first column

of $\delta \Lambda \rho^{-1}$ are identically zero. That is, the first row of $\Lambda_{TT}, \Lambda_{TD_\beta}, \Lambda_{TD_\gamma}, \dots$ and the first column of $\Lambda_{TT}, \Lambda_{D_\beta T}, \Lambda_{D_\gamma T}, \dots$ are zero. We choose to remove this singularity by arbitrarily setting the 1,1 element of Λ_{TT} equal to one, and then replacing the first element of the α th composition vector with the relationship between the expansion coefficients derived from the subsidiary conditions in Equation 3.2,

$$\sum_{\mu} n_{\mu} \sqrt{m_{\mu}} \left\{ -(2kT)^{1/2} A_{\mu(1000)} \cdot \frac{\sqrt{T}}{T} + n \sum_{\beta} \frac{g^{(\beta)}}{z_{\mu(1000)}} \cdot \left(\frac{d_{\beta}}{P_{\beta}} - \frac{d_{\alpha}}{P_{\alpha}} \right) \right\} = 0. \quad (5.15)$$

Finally, we emphasize that $\delta \Lambda \rho^{-1}$ becomes a block diagonal matrix in the limit of the average molecule.

We now wish to apply these general perturbation techniques to binary systems. In this case, the matrices assume the forms

$$\Lambda = \begin{vmatrix} \Lambda_{\alpha\alpha} & \Lambda_{\alpha\beta} \\ \Lambda_{\beta\alpha} & \Lambda_{\beta\beta} \end{vmatrix} \quad (5.16)$$

$$\delta = \begin{vmatrix} \sqrt{m_{\alpha}} & \sqrt{m_{\beta}} \\ -\frac{\sqrt{m_{\alpha}} n_{\beta} P}{P_{\alpha} P_{\beta}} & \frac{\sqrt{m_{\beta}} n_{\alpha} P}{P_{\alpha} P_{\beta}} \end{vmatrix}$$

and

$$\rho = \begin{pmatrix} \frac{n_A}{\sqrt{m_A}} & \frac{n_B}{\sqrt{m_B}} \\ -\frac{p_A p_B}{\sqrt{m_A} p} & \frac{p_A p_B}{\sqrt{m_B} p} \end{pmatrix}. \quad (5.17)$$

Here and in all other matrix equations in this section, each of the explicitly displayed elements is a matrix element in the two species composition space. We again emphasize that these composition elements are themselves matrices of elements in the function space defined by the expansion in the complete set of functions of Equation 4.1. The transformed Equation 5.11 is now of the form

$$(\delta D)_A \cdot \frac{\nabla T}{T} + (\delta D)_B \cdot \left(\frac{d\mu}{T} - \frac{d\alpha}{T} \right) = (\delta \Lambda P^{-1})(\rho \bar{\theta})_A \frac{\nabla T}{T} + (\delta \Lambda P^{-1})(\rho \bar{\theta})_B \left(\frac{d\mu}{T} - \frac{d\alpha}{T} \right) \quad (5.18)$$

and since the generalized forces $\frac{\nabla T}{T}$ and $\left(\frac{d\mu}{T} - \frac{d\alpha}{T} \right)$ are independent, this is equivalent to the two matrix equations

$$\begin{pmatrix} \delta T \\ 0 \end{pmatrix} = \begin{pmatrix} \Lambda_{TT} & \Lambda_{TD} \\ \Lambda_{DT} & \Lambda_{DD} \end{pmatrix} \begin{pmatrix} A_T \\ A_D \end{pmatrix}$$

and

(5.19)

$$\begin{pmatrix} 0 \\ \delta D \end{pmatrix} = \begin{pmatrix} \Lambda_{TT} & \Lambda_{TD} \\ \Lambda_{DT} & \Lambda_{DD} \end{pmatrix} \begin{pmatrix} S_T \\ S_D \end{pmatrix}.$$

Here the subscripts T and D on A , S , and D indicate that

these transformed vectors take on forms that we associate with thermal conductivity and self-diffusion, respectively. Furthermore Λ_{TT} represents single species thermal conductivity type integrals, Λ_{DD} the single species self-diffusion type integrals, and Λ_{DT} and Λ_{TD} the isotopic perturbation integrals. Defining the thermal conductivity and the self-diffusion integrals to be the zeroth order elements in the isotopic perturbation parameter ϵ , and the first order elements to be the isotopic perturbation blocks, we find that the solution vectors to zeroth order in ϵ , are:

$${}^0A_T = -\Lambda_{TT}^{-1} B_T \quad ; \quad {}^0A_D = 0 \quad (5.20)$$

$${}^0S_T = 0 \quad ; \quad {}^0S_D = \Lambda_{DD}^{-1} D_D .$$

The first order solution vectors are:

$$\begin{aligned} {}^1A_T &= 0 \\ {}^1A_D &= -\Lambda_{DD}^{-1} \Lambda_{DT} \Lambda_{TT}^{-1} B_T \\ {}^1S_T &= -\Lambda_{TT}^{-1} \Lambda_{TD} \Lambda_{DD}^{-1} D_D \\ {}^1S_D &= 0 . \end{aligned} \quad (5.21)$$

Here the order of the perturbation is denoted by a superscript to the left of the symbol for the solution vector.

From Equations 4.4 and 4.10 it is seen that the

coefficient of interest for thermal diffusion is $\underline{A}_{\tau(1000)}$. The method of removing the singularity of Λ with the subsidiary condition of Equation 5.15 requires that $\underline{A}_{\tau(1000)}$ is identically zero to all orders of the perturbation, and thus we see from Equation 5.20 that the lowest order nonzero perturbation solution vector is $'A_p$. It is easily shown that 2A_p (and in fact all even order perturbations of A_p) is zero. Hence it is likely that $'A_p$ is an adequate approximation to A_p . (This is confirmed by calculations in Chapter 8.)

The expression for $'A_p$ is a matrix product so further simplification is desirable. It is possible to perform yet another perturbation expansion on each of the blocks contained in the transformed collision integral matrices, $\Delta\Lambda P^{-1}$. The rationale for this further perturbation expansion is that there is a dominant elastic contribution to the molecular scattering cross sections. We can in principle construct a spherical collision operator from these elastic cross sections, or equivalently, from the corresponding transition rates. This spherical collision operator, of course, does not affect the molecular angular momentum part of the expansion set terms and hence in the spherical collision integral matrix, all collision integrals corresponding to the coupling of terms which are of different tensor rank in the angular momentum are zero. That is, the

spherical collision integral matrices are diagonal with respect to the angular momentum.

For the true collision operator, these off-diagonal elements are nonzero but small in comparison to the dominant diagonal elements. This suggests we can formulate a perturbation about the spherical limit or alternatively, we can take the total diagonal blocks to be the zeroth order matrix. To simplify the expansion we choose the latter alternative. For example, the zeroth order matrix of in our "nonsphericity" perturbation contains the exact diagonal elements

$${}^0\Lambda_{AB} = \begin{pmatrix} \Lambda_{AB(11)} & \Lambda_{AB(12)} & \Lambda_{AB(13)} & 0 & 0 & \dots \\ \Lambda_{AB(21)} & \Lambda_{AB(22)} & \Lambda_{AB(23)} & 0 & 0 & \dots \\ \Lambda_{AB(31)} & \Lambda_{AB(32)} & \Lambda_{AB(33)} & 0 & 0 & \dots \\ 0 & 0 & 0 & \Lambda_{AB(44)} & 0 & \dots \\ 0 & 0 & 0 & 0 & \Lambda_{AB(55)} & \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{pmatrix} \quad (5.22)$$

where A and B are either Γ or D . This is in general an infinite matrix corresponding to the complete set of functions in Equation 4.1 but only elements contained in Equation 4.7 are explicitly displayed with corresponding subscripts. The first order perturbation nonsphericity matrices contain all the elements not included in zeroth order.

Marking the nonsphericity perturbation expansion by

ϵ_2 , we can write

$$\begin{aligned}
 {}^1 A_D = \epsilon_1 \{ & -\overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} + \epsilon_2 [\overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} + \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DD} \overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \\
 & + \overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \overset{1}{\Lambda}_{TT} \overset{\circ}{\Lambda}_{TT}^{-1}] + \epsilon_2^2 [-\overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DD} \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DD} \overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \\
 & + \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DD} \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} - \overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \overset{1}{\Lambda}_{TT} \overset{\circ}{\Lambda}_{TT}^{-1} \overset{1}{\Lambda}_{TT} \overset{\circ}{\Lambda}_{TT}^{-1} \\
 & - \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DD} \overset{\circ}{\Lambda}_{DD}^{-1} \overset{\circ}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \overset{1}{\Lambda}_{TT} \overset{\circ}{\Lambda}_{TT}^{-1} + \overset{\circ}{\Lambda}_{DD}^{-1} \overset{1}{\Lambda}_{DT} \overset{\circ}{\Lambda}_{TT}^{-1} \overset{1}{\Lambda}_{TT} \overset{\circ}{\Lambda}_{TT}^{-1}] \} \theta_T.
 \end{aligned} \tag{5.23}$$

Our choice of the zeroth order matrices causes the first order contribution in ϵ_2 to go to zero. This behavior is particularly useful if we wish to analyze the specific pieces of the thermal diffusion in terms of single species thermal conductivity and self-diffusion, as is illustrated in the following equations.

If we again display explicitly only those basis functions which appear in Equation 4.7 and emphasize that the form will hold for the general expansion of Equation 4.1, the matrices to zero order which appear in Equation 5.23 are

$$\overset{\circ}{\Lambda}_{AA}^{-1} = \begin{pmatrix} A_D^{-1} \underline{\underline{S}}^{(1)} & 0 & 0 & \dots \\ 0 & [\Lambda_{AA(VV)} \underline{\underline{S}}^{(2)}]^{-1} & 0 & \dots \\ 0 & 0 & [\Lambda_{AA(SS)} \underline{\underline{S}}^{(3)}]^{-1} & \dots \\ \vdots & \vdots & & \ddots \end{pmatrix}$$

and

(5.24)

$${}^0\Lambda_{DT} = \begin{pmatrix} G_0 \underline{\underline{\Sigma}}^{(1)} & 0 & 0 & \dots \\ 0 & \Lambda_{DT(44)} \underline{\underline{\Sigma}}^{(4)} & 0 & \dots \\ 0 & 0 & \Lambda_{DT(55)} \underline{\underline{\Sigma}}^{(5)} & \dots \\ \vdots & \vdots & & \ddots \\ \vdots & \vdots & & \end{pmatrix}$$

where the subscript A represents T or D and correspondingly A_0 represents T_0 or D_0 . Here D_0 , T_0 , and G_0 are the 3×3 zero order matrices of the diffusion, thermal conductivity, and isotopic perturbation. The first order matrices in ϵ_2 are given by

$${}^1\Lambda_{AA} = \begin{pmatrix} 0 & \epsilon_2 \Lambda_{AA(L4)} \underline{\underline{\Sigma}}^{(4)} & \epsilon_2 \Lambda_{AA(L5)} \underline{\underline{\Sigma}}^{(5)} & \dots \\ \epsilon_2 \Lambda_{AA(4j)} \underline{\underline{\Sigma}}^{(4)} & 0 & \epsilon_2 \Lambda_{AA(45)} \underline{\underline{\Sigma}}^{(5)} & \dots \\ \epsilon_2 \Lambda_{AA(5j)} \underline{\underline{\Sigma}}^{(5)} & \epsilon_2 \Lambda_{AA(54)} \underline{\underline{\Sigma}}^{(4)} & 0 & \dots \\ \vdots & \vdots & & \ddots \end{pmatrix}$$

and

(5.25)

$${}^1\Lambda_{DT} = \begin{pmatrix} 0 & \epsilon_2 \Lambda_{DT(L4)} \underline{\underline{\Sigma}}^{(4)} & \epsilon_2 \Lambda_{DT(L5)} \underline{\underline{\Sigma}}^{(5)} & \dots \\ \epsilon_2 \Lambda_{DT(4j)} \underline{\underline{\Sigma}}^{(4)} & 0 & \epsilon_2 \Lambda_{DT(45)} \underline{\underline{\Sigma}}^{(5)} & \dots \\ \epsilon_2 \Lambda_{DT(5j)} \underline{\underline{\Sigma}}^{(5)} & \epsilon_2 \Lambda_{DT(54)} \underline{\underline{\Sigma}}^{(4)} & 0 & \dots \\ \vdots & \vdots & & \ddots \end{pmatrix}$$

where again A is either D or T and where $\Lambda_{TT(ij)}$ and $\Lambda_{TT(is)}$ represent the 1×3 matrices of the thermal conductivity integrals (i and $j = 1, 2,$ or 3), $\underline{\underline{\zeta}}^{(k+l)}$ is a tensor of rank $(k+l)$ which is the matrix element of two basis set terms of rank k and l , respectively, and $\underline{\underline{0}}$ implies a 3×3 null matrix. Substituting Equations 5.24 and 5.25 into Equation 5.23, the solution vector to zero order in becomes

$$\underline{\underline{A}}_D^0 = -D_0^{-1} G_0 T_0^{-1} \mathcal{D}_T \underline{\underline{\zeta}}^{(1)} \quad (5.26)$$

and to second order in ϵ_2 becomes

$$\begin{aligned} \underline{\underline{A}}_D^2(1) &= \sum_{n=4}^{\infty} D_0^{-1} G_0 T_0^{-1} \Lambda_{TT(in)} \underline{\underline{\zeta}}^{(k+l)} \Theta^l [\Lambda_{TT(nn)} \underline{\underline{\zeta}}^{2k}]^{-1} \Theta^l \underline{\underline{\zeta}}^{(k+m)} \Lambda_{TT(jn)} D_0^{-1} \mathcal{D}_T \\ \underline{\underline{A}}_D^2(2) &= \sum_{n=4}^{\infty} D_0^{-1} \Lambda_{DT(in)} \underline{\underline{\zeta}}^{(k+l)} \Theta^l [\Lambda_{TT(nn)} \underline{\underline{\zeta}}^{2k}]^{-1} \Theta^l \underline{\underline{\zeta}}^{(k+m)} \Lambda_{TT(nj)} T_0^{-1} \mathcal{D}_T \\ &\vdots \\ \underline{\underline{A}}_D^2(3) &= \sum_{n=4}^{\infty} D_0^{-1} \Lambda_{DD(in)} \underline{\underline{\zeta}}^{(k+l)} \Theta^l [\Lambda_{DD(nn)} \underline{\underline{\zeta}}^{2k}]^{-1} \Theta^l [\Lambda_{DT(nn)} \underline{\underline{\zeta}}^{2k}] \Theta^l [\Lambda_{TT(mm)} \underline{\underline{\zeta}}^{2m}] \Theta^l \\ &\quad \underline{\underline{\zeta}}^{(k+m)} \Lambda_{TT(nj)} T_0^{-1} \mathcal{D}_T \quad (5.27) \\ \underline{\underline{A}}_D^2(4) &= \sum_{n=4}^{\infty} D_0^{-1} \Lambda_{DD(in)} \underline{\underline{\zeta}}^{(k+l)} \Theta^l [\Lambda_{DD(nn)} \underline{\underline{\zeta}}^{2k}]^{-1} \Theta^l \underline{\underline{\zeta}}^{(k+m)} \Lambda_{DT(nj)} T_0^{-1} \mathcal{D}_T \\ \underline{\underline{A}}_D^2(5) &= \sum_{n=4}^{\infty} D_0^{-1} \Lambda_{DD(in)} \underline{\underline{\zeta}}^{(k+l)} \Theta^l [\Lambda_{DD(nn)} \underline{\underline{\zeta}}^{2k}]^{-1} \Theta^l \underline{\underline{\zeta}}^{(k+m)} \Lambda_{DD(nj)} D_0^{-1} G_0 T_0^{-1} \mathcal{D}_T . \end{aligned}$$

Here the left and right superscripts label the ϵ_1 and ϵ_2 perturbations, respectively, and the number in parentheses

labels the five terms of second order in ϵ_2 .

The thermal conductivity and diffusion type integrals in Equation 5.19 are for a binary mixture of isotopic species. We suspect (and model calculations verify) that these integrals are not sensitive to isotopic changes within the molecules and can therefore replace these isotopic mixture integrals with integrals corresponding to single species thermal conductivity and self-diffusion, where the single species is defined by some average of the isotopic species. The isotopic perturbation blocks Λ_{DT} and Λ_{TD} are identically zero for a single species so if we perform a nonsphericity perturbation for single species thermal conductivity and self-diffusion with the same zero order approximation as was assumed above, we obtain the expressions

$$\overline{A_T^0} = -T_0^{-1} \partial_T \underline{\xi}^{(1)}$$

$$\overline{A_T^2} = -\sum_{n=2}^{\infty} T_0^{-1} \Lambda_{TT(Ln)} \underline{\xi}^{(L+2)} \partial^L [\Lambda_{TT(nn)} \underline{\xi}^{(2L)}]^{-1} \partial^L \underline{\xi}^{(L+m)} \Lambda_{TT(nL)} T_0^{-1} \partial_T \quad (5.28)$$

$$\overline{S_D^0} = -D_0^{-1} \partial_D \underline{\xi}^{(1)}$$

$$\overline{S_D^2} = -\sum_{n=2}^{\infty} D_0^{-1} \Lambda_{DD(Ln)} \underline{\xi}^{(L+2)} \partial^L [\Lambda_{DD(nn)} \underline{\xi}^{(2L)}]^{-1} \partial^L \underline{\xi}^{(L+m)} \Lambda_{DD(nL)} D_0^{-1} \partial_D .$$

The "bar" over the coefficient indicates that the coefficients are for an average molecule. If we substitute these expressions into Equation 5.27 we find the thermal

diffusion coefficients to be

$$\underline{\bar{A}}_D^0 = \underline{S}_D^0 T G_0 \underline{\bar{A}}_T^0 \underline{\zeta}^{(0)} \quad (5.29)$$

in zero order and

$$\begin{aligned} \underline{\bar{A}}_D^2(1) &= \underline{S}_D^0 T G_0 \underline{\bar{A}}_T^2 \\ \underline{\bar{A}}_D^2(2) &= \sum_{n=4}^{\infty} \underline{S}_D^0 T \Lambda_{DT(Ln)} \underline{\zeta}^{(L+2)} \Theta^L [\Lambda_{TT(Ln)} \underline{\zeta}^{(2L)}]^{-1} \Theta^L \Lambda_{TT(n_f)} \underline{\zeta}^{(L+m)} \underline{\bar{A}}_T^0 \\ \underline{\bar{A}}_D^2(3) &= \sum_{n=4}^{\infty} \underline{S}_D^0 T \Lambda_{DB(Ln)} \underline{\zeta}^{(L+2)} \Theta^L [\Lambda_{DB(Ln)} \underline{\zeta}^{(2L)}]^{-1} \Theta [\Lambda_{DT(Ln)} \underline{\zeta}^{(2L)}] \Theta^L \\ &\quad [\Lambda_{TT(Ln)} \underline{\zeta}^{(2L)}]^{-1} \Theta^L \underline{\zeta}^{(L+m)} \Lambda_{TT(n_f)} \underline{\bar{A}}_T^0 \\ \underline{\bar{A}}_D^2(4) &= \sum_{n=4}^{\infty} \underline{S}_D^0 T \Lambda_{DB(Ln)} \underline{\zeta}^{(L+2)} \Theta^L [\Lambda_{DB(Ln)} \underline{\zeta}^{(2L)}]^{-1} \Theta^L \underline{\zeta}^{(L+m)} \Lambda_{DT(n_f)} \underline{\bar{A}}_T^0 \end{aligned} \quad (5.30)$$

$$\underline{\bar{A}}_D^2(5) = \underline{S}_D^2 T G_0 \underline{\bar{A}}_T^0$$

in second order.

The five second order terms above may be split into three sets according to their external field dependence. The coefficients $\underline{\bar{A}}_D^2(1)$ and $\underline{\bar{A}}_D^2(2)$ contain the magnetic field dependence of the single species thermal conductivity coefficients, $\underline{\bar{A}}_D^2(4)$ and $\underline{\bar{A}}_D^2(5)$ contain the field dependence of the diffusion coefficients, and $\underline{\bar{A}}_D^2(3)$ has a hybrid field dependence. For the mixtures we will consider our model calculations show that this hybrid field term is small and thus we can write the second order effect as the sum of a modified thermal conductivity contribution

and a modified self-diffusion contribution. It is this last analytic sum which provides a means to investigate thermal diffusion in terms of the molecular parameters.

CHAPTER 6. CARTESIAN TENSOR REDUCTION

Cartesian tensors may be used to form a basis for a representation of the 3-dimensional rotation group. For example, a 3-dimensional vector, \underline{A} (which is an element of the vector space spanned by the usual unit vectors \hat{i} , \hat{j} , and \hat{k}), is a first rank tensor of weight 1. It forms a basis for a representation of the 3-dimensional rotation group whose elements are second rank tensors. If \underline{R} is the usual rotation matrix, the operation $\underline{R} \cdot \underline{A}$ serves to rotate \underline{A} into a new vector \underline{A}' , that is, $\underline{A}' = \underline{R} \cdot \underline{A}$. Performing a second rotation $\underline{R}' \cdot \underline{A}' = \underline{A}''$ is equivalent to the single rotation $\underline{R}'' \cdot \underline{A} = \underline{A}''$, where $\underline{R}'' = \underline{R}' \cdot \underline{R}$. This defines the group operation. Expressed in matrix form, the vector \underline{A} is a column matrix of three elements whereas the rotation operator \underline{R} is a 3×3 matrix. The identity element for this representation is the symmetric tensor $\underline{\underline{g}}^{(1)} = \hat{i}\hat{i} + \hat{j}\hat{j} + \hat{k}\hat{k}$. The eigenvectors of $\underline{\underline{g}}^{(1)}$ are just the unit vectors \hat{i} , \hat{j} , and \hat{k} with eigenvalues of 1. Of course, they are not unique since any linear combination of these eigenvectors is also an eigenvector. In a similar manner we can extend these ideas to higher rank tensors. For example, a second rank tensor is a basis for a fourth rank representation of the rotation group. Expressed in vector form, the second rank tensor is a column matrix containing nine elements and the fourth rank representation is a 9×9 matrix. In general,

the number of independent elements in a 3-dimensional tensor of n th rank is $(3)^n$. Thus, the dimension of the representation is $(3)^n$.

Let us now consider the subgroup of rotation operations consisting of only rotations about a fixed axis, that is, the 2-dimensional rotation group. Any basis for a representation of the 3-dimensional rotation group is also a basis for the representation of the 2-dimensional group. However, a basis for an irreducible representation of the 3-dimensional rotation group in general is a basis for a reducible representation of the 2-dimensional rotation group.

The collision integrals we calculate are isotropic tensors, that is, tensors which are unchanged by any rotation operation. Likewise, the expansion coefficients of Equation 4.1 in field-free space are isotropic tensors. These isotropic tensors form a basis for the totally symmetric representation of the rotation group. In the presence of an external field, the expansion coefficients are anisotropic in 3-dimensional space but must be invariant to rotations about the field. The formal calculations of the last chapter are greatly facilitated through the consideration of some general group theoretical principles.

From group theory we know that for the 3-dimensional

rotation group the direct product of the bases of two irreducible representations of rank p and q , respectively, forms a basis of rank $(p+q)$ which is in general reducible. It can be resolved into irreducible bases of weights $(p+q), (p+q-1), (p+q-2), \dots, |p-q|$. For a weight l irreducible basis there are $(2l+1)$ independent elements. The quantity $(2l+1)$ is thus the dimension of the irreducible basis. Since Cartesian tensors provide bases for the representation of the rotation group, they conform to these general group properties. For the remainder of this chapter we will consider Cartesian tensors exclusively.

There is, of course, an identity element $\underline{\underline{I}}^{(n)}$ for the direct product representation as well as identity elements $\underline{\underline{I}}_i^{(n)}$ for each of the irreducible representations it contains. Here n is the rank of the direct product basis and $\underline{\underline{I}}^{(n)} = \sum_i \underline{\underline{I}}_i^{(n)}$. The identity elements $\underline{\underline{I}}_i^{(n)}$ are isotropic tensors of rank $2n$ and since they belong to different irreducible representations are orthogonal to each other, that is,

$$\underline{\underline{I}}_i^{(n)} \otimes^n \underline{\underline{I}}_j^{(n)} = \underline{\underline{I}}_i^{(n)} \delta_{ij} \quad (6.1)$$

Thus, they act as projection operators in that they will project out of any given tensor in the direct product basis the part of that tensor which lies in the irreducible representation corresponding to the identity element.

The perturbation expressions for the thermal diffusion coefficients in Equation 5.27 and 5.30 require that we calculate the inverse of the diagonal matrix elements. If we for simplicity, first consider the field-free case, these diagonal elements will be a linear combination of collision integrals of the form given in Equation 4.13 and thus can be expressed as an isotropic tensor $\underline{\underline{T}}^{(n)}$. Here the rank of $\underline{\underline{T}}^{(n)}$ is $2n$, where n is the rank of the associated basis function $[\psi]^{(\rho)}[\Omega]^{(\sigma)}$, that is, $n = (\rho + \sigma)$. By the inverse of $\underline{\underline{T}}^{(n)}$, we imply

$$\underline{\underline{T}}^{(n)} \otimes^n [\underline{\underline{T}}^{(n)}]^{-1} = \underline{\underline{I}}^{(n)} \quad (6.2)$$

We generate the inverse of $\underline{\underline{T}}^{(n)}$ by first projecting $\underline{\underline{T}}^{(n)}$ onto the identity element, $\underline{\underline{I}}_i^{(n)}$, of the i th irreducible representation contained in the direct product basis. This operation gives back the identity element times a scalar coefficient α_i , namely

$$\underline{\underline{T}}^{(n)} \otimes^n \underline{\underline{I}}_i^{(n)} = \alpha_i \underline{\underline{I}}_i^{(n)}. \quad (6.3)$$

Thus projecting $\underline{\underline{T}}^{(n)}$ onto $\underline{\underline{I}}^{(n)}$ transforms the general isotropic tensor into a linear combination of identity elements of the irreducible representations, that is,

$$\underline{\underline{T}}^{(n)} = \underline{\underline{T}}^{(n)} \otimes^n \underline{\underline{I}}^{(n)} = \underline{\underline{T}}^{(n)} \otimes^n \sum_i \underline{\underline{I}}_i^{(n)} = \sum_i \alpha_i \underline{\underline{I}}_i^{(n)}. \quad (6.4)$$

The inverse of $\underline{\Gamma}^{(n)}$ is easily found from Equations 6.1 and 6.4 to be

$$\left[\sum_j \alpha_j \underline{\Gamma}_j^{(n)} \right]^{-1} = \sum_j \frac{1}{\alpha_j} \underline{\Gamma}_j^{(n)}. \quad (6.5)$$

Therefore, the problem of finding the inverse of our diagonal matrix elements has been reduced to finding the identity elements of the irreducible representations of the 3-dimensional rotation group.

An alternate procedure also exists for calculating the inverse of $\underline{\Gamma}^{(n)}$ by assuming a preferred direction. Since $\underline{\Gamma}^{(n)}$ is invariant to any rotation, it is also invariant to rotations about the preferred direction. The identity element for the direct product representation can then be decomposed into a sum of identity elements for the irreducible representations of the 2-dimensional rotation group just as explained above for the 3-dimensional rotation group. Again, projecting $\underline{\Gamma}^{(n)}$ onto any of these identity elements will project out of $\underline{\Gamma}^{(n)}$ that part of $\underline{\Gamma}^{(n)}$ which lies in the irreducible representation corresponding to that identity element. Thus using the 2-dimensional identity elements gives the inverse in a form similar to Equation 6.5.

The irreducible representations for the 2-dimensional rotation group are all one dimensional. Thus, the direct

product representation formed from the direct product of two Cartesian tensors of weight ρ and q will contain $(2\rho+1)(2q+1)$ irreducible one dimensional representations of the 2-dimensional rotation group. In contrast, the direct product will contain $2q+1$ (where $q < \rho$) irreducible representations of the 3-dimensional rotation group.

The identity element for the highest weight irreducible representation of the 3-dimensional rotation group formed from any direct product basis is denoted by $\underline{\underline{f}}^{(n)}$, where n is the rank of the direct product. The tensor $\underline{\underline{f}}^{(n)}$ is of rank $2n$ and is traceless and symmetric on its first n and last n indices. If we denote the orthogonal eigenvectors of $\underline{\underline{f}}^{(n)}$ by the symbol $\hat{\chi}_m^{(n)}$, where n is the tensorial rank and m , $-n \leq m \leq n$, labels the $(2n+1)$ independent eigenvectors, then

$$\underline{\underline{f}}^{(n)} = \sum_{m=-n}^n \hat{\chi}_m^{(n)} \hat{\chi}_m^{\dagger(n)} \quad (6.6)$$

where \dagger denotes the transpose conjugate. If we choose these eigenvectors such that the direct products $\hat{\chi}_m^{(n)} \hat{\chi}_m^{\dagger(n)}$ are the identity elements for the one-dimensional irreducible representations for the 2-dimensional rotation group contained in $\underline{\underline{f}}^{(n)}$, then they form a unique set. We now wish to determine this particular set of eigenvectors, $\hat{\chi}_m^{(n)}$.

Cooper and Hoffman (32) have written the 3-dimensional identity elements, $\underline{\underline{\zeta}}^{(n)}$, in terms of a sum of real tensors $\underline{\underline{\beta}}_m^{(a)}(n)$ which are traceless and symmetric on their first and last n indices, as

$$\underline{\underline{\zeta}}^{(n)} = \sum_{m=0}^n \underline{\underline{\beta}}_m^{(a)}(n). \quad (6.7)$$

To make the connection with the present discussion we note that the quantities $\underline{\underline{\beta}}_m^{(a)}(n)$ which they define are themselves identity elements for mutually orthogonal representations of the group of rotations about the preferred direction in space. The tensor $\underline{\underline{\beta}}_0^{(a)}(n)$ is the identity element for the irreducible totally symmetric, one-dimensional representation of the 2-dimensional rotation group whereas $\underline{\underline{\beta}}_m^{(a)}(n)$, $m > 0$, is the identity element for a two-dimensional reducible representation of the 2-dimensional rotation group. They further define a group of tensors $\underline{\underline{\beta}}_m^{(b)}(n)$ by

$$m \underline{\underline{\beta}}_m^{(b)}(n) \equiv \underline{\underline{\beta}}_m^{(a)}(n) \mathbf{X} \hat{\mathbf{A}} \equiv \hat{\mathbf{A}} \mathbf{X} \underline{\underline{\beta}}_m^{(a)}(n), \quad (6.8)$$

where \mathbf{X} denotes the sum of the terms obtained by crossing $\hat{\mathbf{A}}$ into each of the n right (or left) hand indices of $\underline{\underline{\beta}}_m^{(a)}(n)$. It is shown in reference (32) that these definitions give the following multiplication relationships:

$$\underline{\underline{B}}_m^{(a)}(n) \otimes^n \underline{\underline{B}}_{m'}^{(a)}(n) = \underline{\underline{B}}_m^{(a)}(n) \delta_{mm'}$$

$$\underline{\underline{B}}_m^{(b)}(n) \otimes^n \underline{\underline{B}}_{m'}^{(b)}(n) = -\underline{\underline{B}}_m^{(a)}(n) \delta_{mm'} \quad (6.9)$$

$$\underline{\underline{B}}_m^{(a)}(n) \otimes^n \underline{\underline{B}}_{m'}^{(b)}(n) = \underline{\underline{B}}_{m'}^{(b)}(n) \otimes^n \underline{\underline{B}}_m^{(a)}(n) = \underline{\underline{B}}_m^{(b)}(n) \delta_{mm'}$$

We now construct a set of tensors $\underline{\underline{Q}}_m^{(n)}$ as

$$\underline{\underline{Q}}_m^{(n)} = \frac{1}{2} [\underline{\underline{B}}_m^{(a)}(n) + i \underline{\underline{B}}_m^{(b)}(n)]$$

$$\underline{\underline{Q}}_{-m}^{(n)} = \frac{1}{2} [\underline{\underline{B}}_m^{(a)}(n) - i \underline{\underline{B}}_m^{(b)}(n)] \quad (6.10)$$

$$\underline{\underline{Q}}_0^{(n)} = \underline{\underline{B}}_0^{(a)}(n)$$

where i is the usual imaginary unit, that is, $i^2 = -1$.

From the orthogonality relationships of Equation 6.9, we have immediately that

$$\underline{\underline{Q}}_{\pm m}^{(n)} \otimes^n \underline{\underline{Q}}_{\pm m'}^{(n)} = \underline{\underline{Q}}_{\pm m}^{(n)} \delta_{mm'} \quad (6.11)$$

$$\underline{\underline{Q}}_{\pm m}^{(n)} \otimes^n \underline{\underline{Q}}_{\mp m}^{(n)} = 0.$$

From Equations 6.10 and 6.11 we conclude that the set of $\underline{\underline{Q}}_m^{(n)}$, $-n \leq m \leq n$, contains $(2n+1)$ orthogonal elements labeled by m , each of tensor rank $2n$ and contained entirely in the irreducible representation formed from the direct product basis of weight n . Thus each $\underline{\underline{Q}}_m^{(n)}$ is necessarily an identity element of an irreducible one-dimensional

representation of the 2-dimensional rotation group and we have

$$\underline{\underline{Q}}^{(n)} = \sum_{m=-n}^n \underline{\underline{Q}}_m^{(n)}, \quad (6.12)$$

which also follows directly from Equations 6.7 and 6.10.

From Equation 6.11 and 6.12 we make the correlation

$$\underline{\underline{Q}}_m^{(n)} = \hat{\chi}_m^{(n)} \hat{\chi}_m^{\top (n)}. \quad (6.13)$$

It follows immediately from Equation 6.7 and 6.9 that

$\hat{\chi}_0^{(n)}$, the eigenvector corresponding to $\underline{\underline{Q}}_0^{(n)} = \underline{\underline{B}}_0^{(n)}$, is

$$\hat{\chi}_0^{(n)} = \left[\frac{\underline{\underline{Q}}_0^{(n)} \otimes^n (\hat{k})^n}{[\langle \hat{k} \rangle^n \otimes^n \underline{\underline{Q}}_0^{(n)} \otimes^n (\hat{k})^n]^{1/2}} \right], \quad (6.14)$$

where $(\hat{k})^n$ denotes a polyad of n \hat{k} 's, that is, $\hat{k} \hat{k} \dots \hat{k}$.

The tensor $\hat{\chi}_0^{(n)}$ is obviously an eigenvector of both $\underline{\underline{Q}}_0^{(n)}$ and $\underline{\underline{Q}}^{(n)}$ with eigenvalue of 1.

To generate the explicit expressions for the remaining one-dimensional eigenvectors $\hat{\chi}_m^{(n)}$, we construct the following operator formalism. Let us define the Cartesian operators $\hat{\underline{\underline{H}}}_x^{(n)}$, $\hat{\underline{\underline{H}}}_y^{(n)}$, and $\hat{\underline{\underline{H}}}_z^{(n)}$ by

$$\begin{aligned} \hat{\underline{\underline{H}}}_z^{(n)} &\equiv -i \underline{\underline{Q}}^{(n)} \sum \hat{k} = -i \sum_m m \underline{\underline{B}}_{mz}^{(n)} \\ \hat{\underline{\underline{H}}}_y^{(n)} &\equiv -i \underline{\underline{Q}}^{(n)} \sum \hat{j} = -i \sum_m m \underline{\underline{B}}_{my}^{(n)} \end{aligned} \quad (6.15)$$

$$\hat{\underline{H}}_x^{(n)} = -i \underline{\underline{f}}^{(n)} \underline{\underline{I}} \hat{t} = -i \sum_m m \underline{\underline{B}}_{mx}^{(b)}(n) ,$$

where as in Equation 6.8, the symbol $\underline{\underline{I}}$ indicates the sum of terms obtained by crossing \hat{t} (or \hat{i} or \hat{j}) into each of the n right hand indices of $\underline{\underline{f}}^{(n)}$ and now the subscript x , y , or z corresponds to crossing \hat{t} , \hat{j} , or \hat{i} , respectively. The unit vectors \hat{t} , \hat{j} , and \hat{i} are assumed to form a right-handed coordinate system. We can also define the operators

$$\hat{\underline{H}}_+^{(n)} = \hat{\underline{H}}_x^{(n)} + i \hat{\underline{H}}_y^{(n)}$$

and

(6.16)

$$\hat{\underline{H}}_-^{(n)} = \hat{\underline{H}}_x^{(n)} - i \hat{\underline{H}}_y^{(n)} .$$

If we now define the commutator bracket in general as

$$[\hat{\underline{H}}_A^{(n)}, \hat{\underline{H}}_B^{(n)}] \equiv \hat{\underline{H}}_A^{(n)} \hat{\underline{O}}^n \hat{\underline{H}}_B^{(n)} - \hat{\underline{H}}_B^{(n)} \hat{\underline{O}}^n \hat{\underline{H}}_A^{(n)} \quad (6.17)$$

and consider explicitly the commutation of $\hat{\underline{H}}_x^{(n)}$ and $\hat{\underline{H}}_y^{(n)}$,

we have

$$\begin{aligned} [\hat{\underline{H}}_x^{(n)}, \hat{\underline{H}}_y^{(n)}] &= -(\hat{t} \underline{\underline{I}} \underline{\underline{f}}^{(n)} \hat{\underline{O}}^n \underline{\underline{f}}^{(n)} \underline{\underline{I}} \hat{j} - \hat{j} \underline{\underline{I}} \underline{\underline{f}}^{(n)} \hat{\underline{O}}^n \underline{\underline{f}}^{(n)} \underline{\underline{I}} \hat{t}) \\ &= -(\hat{t} \underline{\underline{I}} \underline{\underline{f}}^{(n)} \underline{\underline{I}} \hat{j} - \hat{j} \underline{\underline{I}} \underline{\underline{f}}^{(n)} \underline{\underline{I}} \hat{t}) . \end{aligned} \quad (6.18)$$

In the Appendix we show in detail that this crossing operation leads to the commutation relationship

$$[\hat{\underline{H}}_x^{(n)}, \hat{\underline{H}}_y^{(n)}] = \hat{\lambda} \underline{\underline{z}}^{(n)} = -i \hat{\underline{H}}_z^{(n)}. \quad (6.19)$$

In a similar manner, we find that

$$\begin{aligned} [\hat{\underline{H}}_y^{(n)}, \hat{\underline{H}}_z^{(n)}] &= -i \hat{\underline{H}}_x^{(n)} \\ [\hat{\underline{H}}_z^{(n)}, \hat{\underline{H}}_x^{(n)}] &= -i \hat{\underline{H}}_y^{(n)} \\ [\hat{\underline{H}}_z^{(n)}, \hat{\underline{H}}_+^{(n)}] &= \hat{\underline{H}}_+^{(n)} \\ [\hat{\underline{H}}_z^{(n)}, \hat{\underline{H}}_-^{(n)}] &= -\hat{\underline{H}}_-^{(n)} \\ [\hat{\underline{H}}_+^{(n)}, \hat{\underline{H}}_-^{(n)}] &= 2 \hat{\underline{H}}_z^{(n)}. \end{aligned} \quad (6.20)$$

If we now define

$$(\hat{\underline{H}}^{(n)})^2 = \hat{\underline{H}}_x^{(n)} \otimes^n \hat{\underline{H}}_x^{(n)} + \hat{\underline{H}}_y^{(n)} \otimes^n \hat{\underline{H}}_y^{(n)} + \hat{\underline{H}}_z^{(n)} \otimes^n \hat{\underline{H}}_z^{(n)} \quad (6.21)$$

then it follows immediately that for $s = x, y, \text{ or } z$,

$$\begin{aligned} [\hat{\underline{H}}_s^{(n)}, \underline{\underline{z}}^{(n)}] &= 0 \quad ; \quad [\hat{\underline{H}}_z^{(n)}, \underline{\underline{Q}}_m^{(n)}] = 0 \\ [(\hat{\underline{H}}^{(n)})^2, \underline{\underline{z}}^{(n)}] &= 0 \quad ; \quad [(\hat{\underline{H}}^{(n)})^2, \underline{\underline{Q}}_m^{(n)}] = 0 \\ [(\hat{\underline{H}}^{(n)})^2, \hat{\underline{H}}_s^{(n)}] &= 0. \end{aligned} \quad (6.22)$$

It is of some interest to note the direct correspondence of the Cartesian tensors to the more familiar spherical case. The eigenvectors, $\hat{\chi}_m^{(n)}$, are analogous

to the spherical harmonics and the \hat{H} operators are analogous to the angular momentum operator, \hat{J} .

From the commutation relationships in Equation 6.22, it is evident that $(\hat{H}_z^{(n)})^2$, $\hat{H}_z^{(n)}$, $\hat{L}^{(n)}$, and $\hat{Q}_m^{(n)}$ can have a set of simultaneous eigenvectors which we denote by $\hat{\chi}_m^{(n)}$, where again m labels the independent eigenvectors of tensor rank n . The following arguments show that in fact the choice of this set of eigenvectors is unique.

It follows immediately from the definitions of $\hat{\chi}_0^{(n)}$ in Equation 6.14 and $\hat{H}_z^{(n)}$ in Equation 6.16 that $\hat{\chi}_0^{(n)}$ must be an eigenvector of $\hat{H}_z^{(n)}$ with an eigenvalue of zero. That is,

$$\hat{H}_z^{(n)} \hat{\chi}_0^{(n)} = (0) \hat{\chi}_0^{(n)}.$$

As in the more familiar case of the angular momentum we can show from Equations 6.16 and 6.21 that $\hat{H}_+^{(n)}$ and $\hat{H}_-^{(n)}$ are the raising and lowering operations with the properties

$$\hat{H}_+^{(n)} \hat{\chi}_m^{(n)} = \sqrt{(n-m)(n+m+1)} \hat{\chi}_{m+1}^{(n)}$$

and

(6.23)

$$\hat{H}_-^{(n)} \hat{\chi}_m^{(n)} = \sqrt{(n+m)(n-m+1)} \hat{\chi}_{m-1}^{(n)}$$

where $\hat{\chi}_m^{(n)}$ are eigenvectors of $\hat{H}_z^{(n)}$ obeying the eigenvalue equation

$$\hat{H}_z^{(n)} \hat{\chi}_m^{(n)} = m \hat{\chi}_m^{(n)} \quad , \quad -n \leq m \leq n . \quad (6.24)$$

All of the $(2n+1)$ one-dimensional eigenvectors of $\hat{H}_z^{(n)}$ generated in this manner span the space of the irreducible representation containing the identity element $\underline{1}^{(n)}$. Furthermore, since the eigenvectors for each of the $(2n+1)$ one-dimensional projection operators $Q_m^{(n)}$ are unique and $Q_m^{(n)}$ and $\hat{H}_z^{(n)}$ commute, it follows that the eigenvectors of $\hat{H}_z^{(n)}$ are identical to the eigenvectors of the one-dimensional projection operators. Hence, determining the $(2n+1)$ eigenvectors of $\hat{H}_z^{(n)}$ by means of Equation 6.23 provides a method for finding all of the desired eigenvectors $\hat{\chi}_m^{(n)}$. We show in the Appendix that $(\hat{H}_z^{(n)})^2$ is given by

$$(\hat{H}_z^{(n)})^2 = n(n+1) \underline{1}^{(n)} . \quad (6.25)$$

Thus it is easily established that the vectors $\hat{\chi}_m^{(n)}$ are also eigenvectors of $(\hat{H}_z^{(n)})^2$ with eigenvalues $n(n+1)$.

To this point we have generated only those eigenvectors which belong to the highest weight $(n = p + q)$ irreducible representation formed from a direct product basis of two irreducible representation bases of weight p and q , respectively. However, the close correspondence of the theories for the Cartesian and spherical harmonic bases suggests that by appropriate formulation of the direct product operations for Cartesian tensors we can obtain a

direct correlation to the more familiar problem of the addition of angular momenta. This correspondence will allow us to express the eigenvectors of the lower weight irreducible representations of any direct product in terms of the eigenvectors of the direct product bases through the use of Clebsch-Gordon coefficients. We now outline this formulation.

Let us consider a tensor $\underline{G}^{(g)}$ of rank $2g$, which is symmetric and its first and last g indices, imbedded in a tensor $\underline{F}^{(p)}$ of rank $2p$ which is symmetric on its first and last p indices, where the indices are ordered as in the direct product $[w]^{(p)} [a]^{(g)} [w]^{(p)} [a]^{(g)}$. The resulting tensor which is of rank $2(p+g)$ we denote by $\underline{F}^{(p)}/\underline{G}^{(g)}$. Then the \hat{H} operators for the direct product representation may be defined as

$$\hat{H}_s^{(p+g)} \equiv \hat{H}_s^{(p)}/\underline{G}^{(g)} + \underline{F}^{(p)}/\hat{H}_s^{(g)} \quad (6.26)$$

where s is either x , y , or z . As shown in the Appendix, we have also that

$$\left(\hat{H}_s^{(p+g)}\right)^2 = \sum_{j=|p-g|}^{p+g} j(j+1) \underline{I}_j^{(p+g)}. \quad (6.27)$$

With these definitions all the commutation relations listed in Equations 6.19, 6.20, and 6.22 hold for the direct product operators, $\hat{H}^{(p+g)}$. The operators $\hat{H}^{(n)}$ of the

preceding discussion are simply that part of $\hat{H}^{(p+q)}$ in the highest weight irreducible representation of the direct product. That is,

$$\hat{H}_s^{(p+q)} = \hat{H}_s^{(p+q)} \otimes \hat{H}_s^{(p+q)} \otimes \hat{H}_s^{(p+q)}. \quad (6.28)$$

Furthermore, the $(2q+1)(2p+1)$ simultaneous eigenvectors of $(\hat{H}_s^{(p+q)})^2$ and $\hat{H}_z^{(p+q)}$ are unique and since these operators commute with the $(2q+1)(2p+1)$ identity elements of the irreducible representations of the 2-dimensional rotation group contained in the direct product, the eigenvectors must in fact be identical to the desired basis vectors of the direct product, which we denote by $\hat{Y}_M^{pq}(j)$. Here M labels the independent basis vectors of the j th weight irreducible representation formed from the irreducible basis vectors of rank p and q .

From our previous discussion, the highest weight eigenvectors ($j = p+q$) are

$$\hat{Y}_M^{pq}(p+q) = \hat{X}_M(p+q), \quad (6.29)$$

but no such simple expression exists for the lower weight eigenvectors. These can, however, be expressed in terms of the direct products $\hat{X}_m(p) \hat{X}_m(q)$ by the use of Clebsch-Gordon coefficients. The construction of these relations will not be given here in detail since the procedure is

exactly that of the familiar angular momentum case. We find that

$$\hat{Y}_M^{p,q}(z) = \sum_{\substack{m, m' \\ \{m+m'=M\}}} C(p, q, j; m, m') \hat{\chi}_m(p) \hat{\chi}_{m'}(q)$$

and

(6.30)

$$\hat{\chi}_m(p) \hat{\chi}_{m'}(q) = \sum_j C(p, q, j; m, m') \hat{Y}_M^{p,q}(z),$$

where $C(p, q, j; m, m')$ are the Clebsch-Gordon coefficients (33). The identity element for the direct product representation can now be written

$$\mathbb{I}^{(p+q)} = \frac{\zeta^{(p)} \zeta^{(q)}}{\zeta^{(p+q)}} = \sum_{j=|p-q|}^{p+q} \mathbb{I}_j^{(p+q)}. \quad (6.31)$$

From this equality we see that

$$\mathbb{I}^{(p+q)} = \sum_{m=-p}^p \sum_{m'=-q}^q \hat{\chi}_m(p) \hat{\chi}_{m'}(q) \hat{\chi}_m^{\dagger}(p) \hat{\chi}_{m'}^{\dagger}(q)$$

or

(6.32)

$$\mathbb{I}^{(p+q)} = \sum_{j=|p-q|}^{p+q} \sum_{M=-j}^j \hat{Y}_M^{p,q}(z) \hat{Y}_M^{p,q\dagger}(z)$$

since

$$\mathbb{I}_j^{(p+q)} = \sum_{M=-j}^j \hat{Y}_M^{p,q}(z) \hat{Y}_M^{p,q\dagger}(z). \quad (6.33)$$

We may also express $\underline{\underline{I}}_j^{(p+q)}$ in terms of the direct product basis as

$$\underline{\underline{I}}_j^{(p+q)} = \sum_{M=-j}^j \left[\sum_m \sum_{m'} \sum_n \sum_{n'} \hat{\chi}_m(p) \hat{\chi}_{m'}(q) \hat{\chi}_n^\dagger(p) \hat{\chi}_{n'}^\dagger(q) \right. \\ \left. \chi C(p, q, j; m, M-m) C(p, q, j; n, M-n) \right], \quad (6.34)$$

where $C(p, q, j; m, m')$ are the Clebsch-Gordon coefficients.

We are now prepared to calculate the inverse of the diagonal elements required in Equation 5.27. From Equation 3.3, 3.5, and 3.6 the form of these elements is seen to be

$$\underline{\underline{\Lambda}}_{AA}(i, i) = \underline{\underline{I}}_j^{(p+q)} + \mathcal{F} \underline{\underline{D}}_j^{(p+q)} \underline{\underline{Y}}_q \hat{\lambda}, \quad (6.35)$$

where $\underline{\underline{I}}_j^{(p+q)}$ is a $2(p+q)$ rank isotropic tensor which is a sum of collision integrals, \mathcal{F} is the scalar coefficient for the field terms, and $\underline{\underline{Y}}_q$ indicates the sum of terms obtained by crossing $\hat{\lambda}$ into the last q indices of $\underline{\underline{D}}_j^{(p+q)}$. From Equations 6.15, 6.24, and 6.31 we have that

$$\underline{\underline{D}}_j^{(p+q)} \underline{\underline{Y}}_q \hat{\lambda} = \underline{\underline{D}}_j^{(p)} / \underline{\underline{D}}_j^{(q)} \underline{\underline{Y}}_q \hat{\lambda} = \underline{\underline{D}}_j^{(p)} / i \underline{\underline{H}}_j^{(q)} \\ = i \sum_{m=-p}^p \sum_{m'=-q}^q m' \hat{\chi}_m(p) \hat{\chi}_{m'}(q) \hat{\chi}_m^\dagger(p) \hat{\chi}_{m'}^\dagger(q). \quad (6.36)$$

We can also write

$$\underline{\underline{I}}_j^{(p+q)} = \sum \alpha_j \underline{\underline{I}}_j^{(p+q)} = \sum_{j=|p-q|}^{p+q} \sum_{M=-j}^j \alpha_j \hat{Y}_M^{p+q}(j) \hat{Y}_M^{p+q}(j). \quad (6.37)$$

If we now interchange the summation order on j and M and then use Equation 6.30 to express $\hat{Y}_M^{P+g}(j)$ in the $\hat{X}_m(\rho)\hat{X}_{M-n}(g)$ basis (and for the sake of definiteness assume that $\rho \geq g$), then

$$\begin{aligned}
 T^{(P+g)} &= \sum_{M=|P-g|+1}^{P+g} \sum_{m,n=M-g}^P B(P,g,M,P+g; m,n,M) \hat{X}_m(\rho) \hat{X}_{M-n}(g) \hat{X}_n^+(\rho) \hat{X}_{M-n}^+(g) \\
 &+ \sum_{M=-|P-g|}^{|P-g|} \sum_{m,n=M-g}^{P+g} B(P,g,|P-g|,P+g; m,n,M) \hat{X}_m(\rho) \hat{X}_{M-n}(g) \hat{X}_n^+(\rho) \hat{X}_{M-n}^+(g) \quad (6.38) \\
 &+ \sum_{M=-P-g}^{-|P-g|-1} \sum_{m,n=-P}^{-M+g} B(P,g,|M|,P+g; m,n,M) \hat{X}_m(\rho) \hat{X}_{M-n}(g) \hat{X}_n^+(\rho) \hat{X}_{M-n}^+(g)
 \end{aligned}$$

where

$$\begin{aligned}
 B(P,g,A,\ell; m,n,M) &= \\
 &\sum_{j=A}^{\ell} \alpha_j C(P,g,j; m, M-m) C(P,g,j; n, M-n). \quad (6.39)
 \end{aligned}$$

By combining Equations 6.36 and 6.38, we see that $\Lambda_{AA}(i)$ is given by

$$\begin{aligned}
 \Lambda_{AA}(i) &= \left[\sum_{M=|P-g|+1}^{P+g} \sum_{m,n=M-g}^P \{ B(P,g,M,P+g; m,n,M) + i \mathcal{F}(M-n) \delta_{mn} \} \right. \\
 &+ \sum_{M=-|P-g|}^{|P-g|} \sum_{m,n=M-g}^{P+g} \{ B(P,g,|P-g|,P+g; m,n,M) + i \mathcal{F}(M-n) \delta_{mn} \} \\
 &\left. + \sum_{M=-P-g}^{-|P-g|-1} \sum_{m,n=-P}^{-M+g} \{ B(P,g,|M|,P+g; m,n,M) + i \mathcal{F}(M-n) \delta_{mn} \} \right] \quad (6.40)
 \end{aligned}$$

$$\times [\hat{\chi}_n(\rho) \hat{\chi}_{M-n}(q) \hat{\chi}_n^\dagger(\rho) \hat{\chi}_{M-n}^\dagger(q)].$$

From Equation 6.40 it is evident that $\underline{\Lambda}_{AA(YY)}$ is a block diagonal matrix where the total number of blocks is determined by the possible values of M and the dimension of the blocks is determined by the m, n summation. Thus to find the inverse of $\underline{\Lambda}_{AA(YY)}$ we must find the inverse of a block diagonal matrix, the largest block of which is of dimension $(2q+1)$.

We note that Equations 6.38 and 6.40 have been written for the case where $\rho \geq q$. For $q > \rho$, we simply interchange the ρ and q indexes in the m, n summation and replace $M-n$ by n in $i(M-n) \delta_{mn}$. We also note that the choice of representation for combining Equations 6.36 and 6.37 is arbitrary. We have chosen the direct product representation for simplicity in the performance of the index contractions which are required in Equation 5.27.

CHAPTER 7. STUDY OF MODEL PARAMETERS AND COMPARISON
WITH EXPERIMENT, NUMERICAL RESULTS

Our goal in the present study of thermal diffusion is two-fold. First we wish to utilize the sensitivity of the effect itself on the detailed nature in which molecules interact as an experimental tool to parameterize the molecular collision model. Secondly, we would like to gain insight into the nature of the physical phenomena involved in the thermal diffusive process. In this chapter we will use the full set of algebraic equations (as given explicitly in Equations 4.12, 4.15 and 4.16 for a binary mixture in field-free space) to study the intermolecular potential parameters and to compare our results with experiment. These calculations then provide the "exact" limit for the perturbation study of the physical phenomena in Chapter 8.

The truncated basis set we choose for our calculations are those five terms which are explicitly displayed in Equation 4.7. There is considerable evidence (34) that this limited basis set yields adequate approximations for the transport coefficients of a single component gas. However, since it is known that the distribution of angular momenta is of little importance for these simple gas transport coefficients but can have a significant effect upon the numerical value of the thermal diffusion coefficient (27), the basis set of Equation 4.7 may be

inadequate for a quantitative comparison of experiment and theory. This basis set does at least include the two lowest order symmetry types (functions which are odd and even in the angular momentum, that is, with time reversal eigenvalues of +1 and -1, respectively) which can contribute to the anisotropy of the angular momentum distribution. Adding more terms to the basis set increases the number of algebraic equations, so the inclusion of more basis functions is best explored in terms of the perturbation techniques of Chapter 5.

In this work we compare experiment and theory for binary mixtures of isotopic diatomic molecules. This choice is occasioned by the availability of good experimental data (35) and the fact that these are the simplest systems which exhibit thermal diffusion influenced by the internal structure of the molecules. To account for this internal structure we choose the rigid ellipsoid of revolution as our interaction model. Previous calculations (36) have shown that the detailed structure of rigid models of the same general shape has little effect on single species thermal conductivity and viscosity. We expect similar behavior for mixtures and for thermal diffusion and thus have chosen the rigid ellipsoid collision model for mathematical convenience in our calculations.

The potential parameters of the rigid ellipsoid model

are $\langle \sigma \rangle$ = average cross sectional area, R = ratio of major to minor axis, and S = separation of the geometric center of the ellipsoid from the center of the bond. The macroscopic parameters are the mole fractions and the temperature. The total molecular mass and the distribution of the atomic masses within the diatomic molecule are fixed by the relative masses of the atoms in the molecular species under consideration. We consider these mass differences to be kinematic parameters which are model independent and thus for present purposes need only consider the potential parameters and the macroscopic parameters.

The thermal diffusion factor, α_T , which is defined as

$$\alpha_T = \frac{p}{n^2 m_\alpha m_\beta x_\alpha x_\beta} \frac{D_\alpha^T}{D_{\alpha\beta}} \quad (7.1)$$

is the property which we will calculate to compare with experiment. We begin our study by using binary mixtures of CO molecules to examine the effect of the potential and macroscopic parameters on α_T in a field-free space. For binary mixtures and the truncated basis set we have chosen, the column matrices in Equation 4.15 contain five elements and the matrix in Equation 4.16 is of dimension 10 x 10. The explicit expressions for the transport coefficients themselves are given in Equation 4.10. We emphasize that from a qualitative viewpoint the results of these parameter

studies are independent of the species chosen. We use CO mixtures only for concreteness and because of our future interest in comparing theoretical and experimental results for these mixtures.

The differential cross section for a rigid model is independent of the energy of the interacting molecules. This fact ultimately leads to a $T^{1/2}$ dependence for both the thermal diffusion, D_{α}^T , and binary diffusion, $D_{\alpha\beta}$, coefficients. Therefore α_T is independent of temperature for the rigid ellipsoid model. We also find that α_T is essentially independent of the mole fraction, x_{α} , and average cross section, $\langle\sigma\rangle$, as illustrated in Tables 1 and 2, respectively. We note here that the perturbation expressions of Chapter 5 predict that $D_{\alpha\beta}$ is nearly independent of mole fraction whereas D_{α}^T should contain an $x_{\alpha}x_{\beta}$ dependence. This leads to the fact that α_T is independent of mole fraction.

The remaining two potential parameters, R and S, have a much larger effect on α_T . In Table 3 we illustrate the effect of varying R from 1.0 to 1.3, which spans the realistic range of molecular shapes for diatomic molecules. By varying S we are in effect moving the center of mass within the ellipsoidal shell. These variations in S may be effected by shifting the atoms along the major axis within the ellipsoid while keeping the bond length fixed.

Two isotopes have the same value of S since the electronic structure is little affected by isotopic differences in the nuclei. The dependence of α_T on S is shown in Table 4. A positive value of S implies that the bond center is displaced in the direction of the heaviest atom from the geometric center of the ellipsoid (e.g., towards ^{16}O in the molecule $^{12}\text{C}^{16}\text{O}$).

In summary, α_T is insensitive to temperature, mole fraction and cross section, but is reasonably sensitive to the parameters R and S . By varying R and S simultaneously at constant mole fraction and cross section, we obtain the contours of α_T shown in Figure 1 for the equimass mixture $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$. It is found experimentally that this mixture has an inversion temperature at 247°K , that is, $\alpha_T > 0$ for $T > 247^\circ\text{K}$ and $\alpha_T < 0$ for $T < 247^\circ\text{K}$. This inversion occurs due to the attractive part of the true molecular interaction potentials (17). Since our rigid model is a purely repulsive potential, we can only hope to calculate the thermal diffusion factor for temperatures greater than the inversion temperature, where the repulsive part of the molecular interaction potential dominates. The contours in Figure 1 are a particularly convenient way to express the results of our calculations, since a vertical linear interpolation of α_T between different contours is quite reliable.

As discussed in detail in Chapter 4, the presence of

an external magnetic field increases the dimension of the matrix expressions of Equations 4.15 and 4.16. For the basis set we have chosen, each column matrix in Equation 4.15 in this case contains 30 elements and correspondingly, Λ is a 60 x 60 matrix. The explicit expressions for these field transport coefficients are given in Equation 4.4 and the coefficients we choose to characterize are given in Equation 4.11. As in Chapter 4, we use the notation $\Delta L_{\gamma i} = L_{\gamma i} - L_{\gamma 0}$, where γ denotes the species of interest and now $i = \parallel, \perp$, or tr corresponds to the parallel, perpendicular, and transverse components, respectively.

The effect of an external field on $\Delta D_{\alpha i}^T$ for a hypothetical binary mixture ($^{15}_A^{15}_A - ^{14}_B^{14}_B$, $\langle \sigma \rangle_{\alpha} = \langle \sigma \rangle_{\beta} = (2.0) 2\pi \text{Å}^2$, $R_{\alpha} = 1.05$, $R_{\beta} = 1.1$, $S_{\alpha} = S_{\beta} = 0$, $X_{\alpha} = 0.5$, $T = 300.0^{\circ}\text{K}$) is shown in Figure 2. This behavior is precisely what we would expect from analogy with the Senftleben-Beenakker effect on thermal conductivity (37), which is given the following physical interpretation.

The presence of a thermal gradient creates an anisotropy in the angular velocity distribution of non-spherical molecules. The rotation of a diamagnetic molecule creates a magnetic moment along the direction of the angular momentum (for paramagnetic molecules we need only consider the component of the magnetic moment along the angular momentum). When an external magnetic field is

imposed upon the system, this magnetic moment precesses about the field. This precession will partially destroy the anisotropy of the angular velocity distribution and cause a corresponding decrease in the transport property of interest. The decrease will be noticeable when the precession frequency is of the order of the collision frequency and will saturate when the precession frequency is much greater than the collision frequency. Since precession frequency is proportional to the field strength H and collision frequency is proportional to the pressure P , the quantities $(H/P)^{1/2}$ and $(\Delta f_{yi})_{sat}$, $i = \parallel$ or \perp , should characterize the effect. The transverse effect reaches a maximum when the precession frequency is of the order of the collision frequency and decreases to zero in the limit where the precession frequency is much greater than the collision frequency. Thus the characteristic values in this case are $(\Delta f_{ytr})_{max}$ and the value of H/P which gives that maximum.

Most mixtures of diatomic molecules will show the behavior as illustrated in Figure 2. However, we find that certain sets of parameters give rise to the type of anomalous behavior that is shown in Figure 3. In general we find that these anomalies occur in the neighborhood of where $\Delta D_{\alpha i}^T = 0$. Furthermore, these null points correspond to a sign inversion of $\Delta D_{\alpha i}^T$. In Figure 4 we show

the locus of points in the $R_{\alpha}-R_{\beta}$ plane where $\Delta D_{\alpha\beta}^T = 0$ for our hypothetical mixture. These curves do, of course, depend also upon the value of the total masses, mass distribution, cross sections, and mole fractions. We can, for example, obtain similar inversion points from a variance of the mass distribution alone, leaving all other parameters fixed. We defer a discussion of these anomalies until the perturbation analysis in Chapter 8 is presented.

We now wish to compare our calculations with experiment for the various binary mixtures of CO isotopes in field-free space. We emphasize again that this choice is based on the availability of good experimental data (35) and the fact that several different isotopic mixtures have been studied. Since the isotopic nature of the nuclei should not affect the electronic structure of the molecules, the R and S values for all species should be the same. The rigid ellipsoid parameters R and $\langle\sigma\rangle$ are selected to give an optimal fit of thermal conductivity data (38, 39) for λ_0 , $(\Delta\lambda/\lambda_0)_{sat}$, and $(H/P)_{1/2}$, where the experimental $\Delta\lambda$ corresponds to $\Delta\lambda = \frac{1}{2}(\Delta\lambda_{||} + \Delta\lambda_{\perp})$. We find $R_{CO} = 1.143$ and $\langle\sigma\rangle_{CO} = (2.17)^2 \pi A^2$. We now use the experimental value of $D_{\alpha\beta}^T$ for the equimass mixture $^{14}C^{16}O-^{12}C^{18}O$ to find $S = -0.027$. Using these parameters we obtain the comparison with experiment as shown in Table 5.

The error for the mixtures other than the equimass

mixture seems to be related to the fact that the rigid sphere is not a good approximation to the spherical part of the interaction potential (17). The relative difference between the values of α_T for the mixtures in which the components differ by two mass units, however, indicates good agreement between experiment and theory, as shown in Table 6. If at this point we assume that the total mass difference and the internal structure give separate, additive contributions to α_T , and also assume that the effect is linear in the mass difference for small mass differences (these assumptions are treated fully in Chapter 8), the calculated numbers are approximately .0073 per mass unit too high. Making this correction we obtain Table 7.

The values of α_T given in Table 5 are calculated using the parameters which give the experimental fit of thermal conductivity in an external magnetic field and field-free thermal diffusion at 300°K. According to the empirical expressions for given by Boersma-Klein and deVries (35), the experimental α_T varies as the $\ln T$. Since the calculated value of α_T is independent of T , we must vary the value of S to fit experimental values of α_T for the equimass mixture at other temperatures (see Figure 1). The mass correction demonstrated in Tables 6 and 7 works about equally well for any value of S .

Since the magnetic field thermal conductivity data is

available only at 300°K, we propose a second, less specific, method of choosing these potential parameters for other temperatures. The field-free thermal conductivity is relatively insensitive to R and S but is very sensitive to $\langle\sigma\rangle$. Since for rigid models, $\lambda = \lambda(T^{1/2})$, we plot $\lambda_{calc}/T^{1/2}$ as a function of $\langle\sigma\rangle$ for our model. Then to find the cross section which fits experiment at any temperature, T_e , we calculate $\lambda_{exp}/T_e^{1/2}$ from experimental data and graphically determine $\langle\sigma\rangle$.

The two sets of contours (of α_T for the equimass mixture $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$) corresponding to the two values of cross section which fit experimental thermal conductivity data for $^{12}\text{C}^{16}\text{O}$ at the temperatures 260 and 420°K are shown in Figure 5. Since the inversion temperature of this mixture is 247°K, these cross sections span a large portion of the temperature range of interest. We note again that a vertical linear interpolation between different contours of constant cross section is quite reliable. It is also possible to perform a linear interpolation between contours of different cross sections.

This method does not provide a unique fit of R and S values. That is, we have an entire contour of corresponding R and S values which will give the experimental value of α_T for the equimass mixture. We also note that the mass correction illustrated in Tables 6 and 7 again works equally

well for any set of R, S values on the constant α_T contour. For both types of parameter fits, we see that a higher temperature requires a positive shift in the value of S. This seems in agreement with the fact that oxygen is more electronegative than carbon.

It is interesting to examine the effect of the ellipsoid parameter R on α_T for the system D_2 -HT, since this mixture has been studied previously by Sandler and Dahler (27) using a loaded sphere model. In Table 8 we show the variation of α_T with R and mole fraction. Because of the symmetry of D_2 , S must necessarily equal 0 for this system. Varying R from 1.0 to 1.3 we obtain the improvement in agreement with experiment (40) as demonstrated in Figure 6. The apparent fit of experiment for $R=1.3$ is rather tenuous, since previous experience has shown that a value of $R=1.3$ is an unrealistic distortion for H_2 . Also, as mentioned earlier, molecules whose rotational levels are so widely spaced cannot be reliably treated using classical mechanics.

We turn now to the study of the effect of an external magnetic field on the thermal diffusion and binary diffusion coefficients of binary mixtures of isotopic diatomic molecules. Since the experimental data available is limited, the most important aspect to these calculations using the exact algebraic equations is to provide a basis for numerical analysis of our perturbation studies. As in the field-free

case, the parameters for CO are fit from experimental thermal conductivity and we find $R_{\text{CO}}=1.143$ and $\langle\sigma\rangle_{\text{CO}}=(2.17)^2\pi\text{\AA}^2$.

For purposes of comparison we also calculate the magnetic field effect on isotopic mixtures of N_2 , for which we find $R_{\text{N}_2}=1.154$ and $\langle\sigma\rangle_{\text{N}_2}=(2.004)^2\pi\text{\AA}^2$. The thermal conductivity in the field is not sensitive to variations in S . The parameters we calculate are $(\Delta f_{r_i})_{\text{sat}}$ and $(H/P)_{1/2}$ (the ratio of the magnetic field strength to pressure at half saturation) for $i = \parallel$ or \perp , and $(\Delta f_{r_{tr}})_{\text{max}}$ and (H/P) of that maximum for the transverse effect.

The field induced effects on the thermal diffusion and binary diffusion coefficients for an equimolar binary mixture $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ are shown in Figure 7. All isotopic binary mixtures of diatoms display similar behavior. In Table 9 and Table 10 we list the appropriate saturation or maximum values together with the field positions of these effects for thermal diffusion and binary diffusion, respectively. In general we find the decrease in the parallel and perpendicular components at saturation to be about 1% for thermal diffusion (except for the equimass CO mixture which shows a larger effect) and $10^{-3}\%$ for binary diffusion. This small effect on diffusion can be seen from Equations 4.4, 4.15, 5.20, 5.21 and 5.22 to arise from the fact that the first field contribution to diffusion is second order in both the ϵ_1 and ϵ_2 expansions.

Again, these results are precisely what we would expect from analogy with the Senftleben-Beenakker effect on thermal conductivity (37). However, experiments performed upon isotopic mixtures containing the paramagnetic triplet O_2 ($^3\Sigma$) have reported no external magnetic field effect on thermal diffusion to within the error limit of the experiments (41, 42). Although our calculations are specific to diamagnetic N_2 and CO, the previous success (36, 43) of the rigid ellipsoid model in calculating related transport coefficients lends credibility to our belief that we have correctly modeled the physical effect itself and suggests that perhaps more experimental effort in these areas is in order.

Table 1. Dependence of α_T on mole fraction
($R=1.1$, $S=0$, $\langle\sigma\rangle=3.25\pi\text{\AA}^2$)

| x_α | Mixture | | | |
|------------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| .01 | .00536 | .01569 | .02474 | .03046 |
| .1 | .00536 | .01567 | .02471 | .03041 |
| .3 | .00534 | .01565 | .02463 | .03030 |
| .5 | .00532 | .01562 | .02455 | .03020 |
| .7 | .00530 | .01559 | .02447 | .03010 |
| .9 | .00528 | .01556 | .02440 | .03000 |
| .99 | .00527 | .01555 | .02436 | .02996 |

Table 2. Dependence of α_T on cross section. Cross section
expressed in units of $\pi\text{\AA}^2$
($R=1.1$, $S=0$, $x_\alpha=.01$)

| $\langle\sigma\rangle$ | Mixture | | | |
|------------------------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| 3.00 | .00526 | .01572 | .02491 | .03053 |
| 3.25 | .00536 | .01569 | .02475 | .03046 |
| 3.50 | .00545 | .01566 | .02460 | .03039 |
| 3.75 | .00553 | .01563 | .02446 | .03032 |
| 4.00 | .00561 | .01560 | .02432 | .03026 |

Table 3. Dependence of α_T on R
 ($\langle\sigma\rangle=3.26\pi\text{\AA}^2$, $S=0$, $\chi_\alpha=.01$)

| R | Mixture | | | |
|------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| 1.00 | .00381 | .01632 | .02762 | .03190 |
| 1.05 | .00426 | .01610 | .02670 | .03139 |
| 1.10 | .00536 | .01569 | .02474 | .03046 |
| 1.15 | .00614 | .01527 | .02315 | .02956 |
| 1.20 | .00613 | .01486 | .02238 | .02874 |
| 1.25 | .00546 | .01437 | .02214 | .02784 |
| 1.30 | .00448 | .01378 | .02199 | .02676 |

Table 4. Dependence of α_T on S. S is expressed in units
 of the length of the minor axis
 (R=1.1, $\langle\sigma\rangle=3.26\pi\text{\AA}^2$, $\chi_\alpha=.01$)

| S | Mixture | | | |
|------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| -.03 | .00177 | .01482 | .02686 | .02878 |
| -.02 | .00290 | .01511 | .02622 | .02935 |
| -.01 | .00410 | .01540 | .02552 | .02990 |
| 0 | .00536 | .01569 | .02474 | .03046 |
| .01 | .00672 | .01599 | .02390 | .03103 |
| .02 | .00816 | .01631 | .02301 | .03162 |
| .03 | .00969 | .01664 | .02207 | .03224 |

Table 5. Comparison of calculated α_T with experiment
 ($\langle\sigma\rangle=(2.17)^2\pi A^2$, $R=1.143$, $S=-0.027$, $X_g=.5$, $T=300^\circ\text{K}$)

| Mixture | Experiment | Calculation |
|---|------------|-------------|
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | .00254 | .00254 |
| $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | .00544 | .0141 |
| $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0100 | .0245 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0132 | .0278 |

Table 6. Comparison of relative α_T values for mixtures
 whose components differ by two mass units

| Mixture | Experiment | Calculation |
|---|------------|-------------|
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0132 | .0278 |
| $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0100 | .0245 |
| difference | .0032 | .0033 |

Table 7. Comparison of mass corrected α_T values with
 experiment

| Mixture | Experiment | Calculation |
|---|------------|-------------|
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | .00254 | .00254 |
| $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | .00544 | .0068 |
| $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0100 | .0099 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | .0132 | .0132 |

Table 8. α_r as a function of R and χ_α for D₂-HT.
 $\langle r \rangle = 1.885\pi A^2$, S=0; a_β is the eccentricity
parameter of Sandler-Dahler (27)

| R | χ_α | | | | | |
|---|---------------|--------|--------|--------|--------|--------|
| | .01 | .2 | .4 | .6 | .8 | .99 |
| Sandler-Dahler Loaded Sphere ($a_\beta = .16667$) | .0579 | .0568 | .0558 | .0548 | .0538 | .0528 |
| 1.0 | .0579 | .0567 | .0560 | .0549 | .0538 | .0528 |
| 1.10 | .0551 | .0546 | .0541 | .0536 | .0531 | .0527 |
| 1.15 | .0494 | .04925 | .04907 | .04890 | .04873 | .04858 |
| 1.20 | .04162 | .04166 | .04171 | .04177 | .04183 | .04189 |
| 1.30 | .02815 | .02839 | .02864 | .02899 | .02916 | .02940 |

Table 9. Characterization of field effects on thermal diffusion for various mixtures (see text). The units of $\Delta D_{\alpha i}^T$ are $\text{gm cm}^{-1} \text{sec}^{-1}$. Here $(H/P)_{1/2}$ is the value of H/P at which a quantity which saturates has half its saturation value, and $(H/P)_{\text{max}}$ is the value of H/P at which a quantity which possesses a maximum has that maximum. The subscript α refers to the first species as the mixture is written

| Mixture | $(\Delta D_{\alpha u}^T)_{\text{sat}}$ | $(H/P)_{1/2}$ | $(\Delta D_{\alpha l}^T)_{\text{sat}}$ | $(H/P)_{1/2}$ | $(\Delta D_{\alpha tr}^T)_{\text{max}}$ | $(H/P)_{\text{max}}$ |
|---|--|-------------------|--|-------------------|---|----------------------|
| $^{14}\text{N}^{15}\text{N}-^{14}\text{N}_2$ | -4.2×10^{-9} | 6.3×10^3 | -6.4×10^{-9} | 4.2×10^3 | 3.1×10^{-9} | 4.1×10^3 |
| $^{15}\text{N}_2-^{14}\text{N}^{15}\text{N}$ | -5.4×10^{-9} | 6.4×10^3 | -8.2×10^{-9} | 4.2×10^3 | 3.9×10^{-9} | 4.2×10^3 |
| $^{15}\text{N}_2-^{14}\text{N}_2$ | -9.6×10^{-9} | 6.4×10^3 | -1.5×10^{-8} | 4.3×10^3 | 6.9×10^{-9} | 4.2×10^3 |
| $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | -9.0×10^{-9} | 7.7×10^3 | -1.4×10^{-8} | 5.2×10^3 | 6.5×10^{-9} | 5.0×10^3 |
| $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | 6.5×10^{-10} | 8.5×10^3 | 9.8×10^{-10} | 5.6×10^3 | -4.7×10^{-10} | 5.4×10^3 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | -1.6×10^{-8} | 7.6×10^3 | -2.4×10^{-8} | 5.0×10^3 | 1.2×10^{-8} | 5.1×10^3 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | -1.8×10^{-8} | 7.7×10^3 | -2.7×10^{-8} | 5.0×10^3 | 1.3×10^{-8} | 5.1×10^3 |

Table 10. Characterization of the field effects on binary diffusion for various mixtures. The units of $\Delta D_{\alpha\beta i}$ are $\text{cm}^3 \text{sec}^{-1}$ and (H/P) is defined as in Table 9

| Mixture | $(\Delta D_{\alpha\beta i})_{sat}$ | $(\text{H/P})_{1/2}$ | $(\Delta D_{\alpha\beta i})_{sat}$ | $(\text{H/P})_{1/2}$ | $(\Delta D_{\alpha\beta i r})_{max}$ | $(\text{H/P})_{max}$ |
|---|------------------------------------|----------------------|------------------------------------|----------------------|--------------------------------------|----------------------|
| $^{14}\text{N}^{15}\text{N}-^{14}\text{N}_2$ | -4.5×10^{-7} | 6.1×10^3 | -6.9×10^{-7} | 4.1×10^3 | 3.3×10^{-7} | 4.0×10^3 |
| $^{15}\text{N}_2-^{14}\text{N}^{15}\text{N}$ | -4.5×10^{-7} | 6.2×10^3 | -6.9×10^{-7} | 4.2×10^3 | 3.3×10^{-7} | 4.1×10^3 |
| $^{15}\text{N}_2-^{14}\text{N}_2$ | -5.2×10^{-7} | 6.2×10^3 | -7.9×10^{-7} | 4.2×10^3 | 3.8×10^{-7} | 4.1×10^3 |
| $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | -7.2×10^{-8} | 7.8×10^3 | -1.1×10^{-7} | 5.2×10^3 | 5.2×10^{-8} | 5.1×10^3 |
| $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | -5.8×10^{-8} | 7.5×10^3 | -8.8×10^{-8} | 5.0×10^3 | 4.2×10^{-8} | 4.9×10^3 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | -2.2×10^{-7} | 7.6×10^3 | -3.4×10^{-7} | 5.0×10^3 | 1.6×10^{-7} | 5.1×10^3 |
| $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | -2.2×10^{-7} | 7.5×10^3 | -3.4×10^{-7} | 5.0×10^3 | 1.6×10^{-7} | 4.9×10^3 |

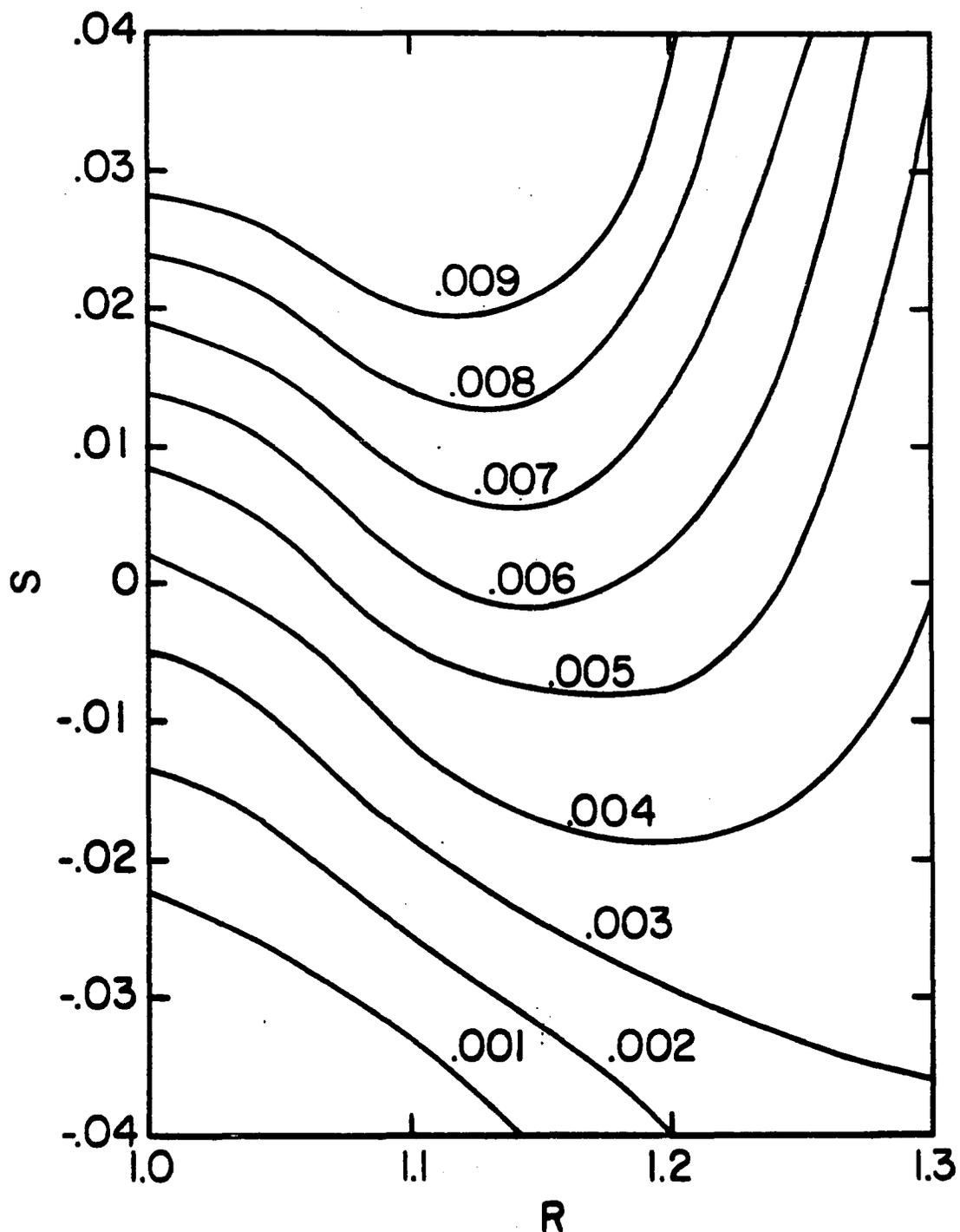


Figure 1. Contours of constant α_T as a function of R and S for an equimolar mixture of $^{14}\text{Cl}^{16}\text{O}$ - $^{12}\text{Cl}^{18}\text{O}$. The value of $\langle\sigma\rangle$ is $(2.17)^2\pi\text{\AA}^2$. The numerical values of α_T are indicated on the contours

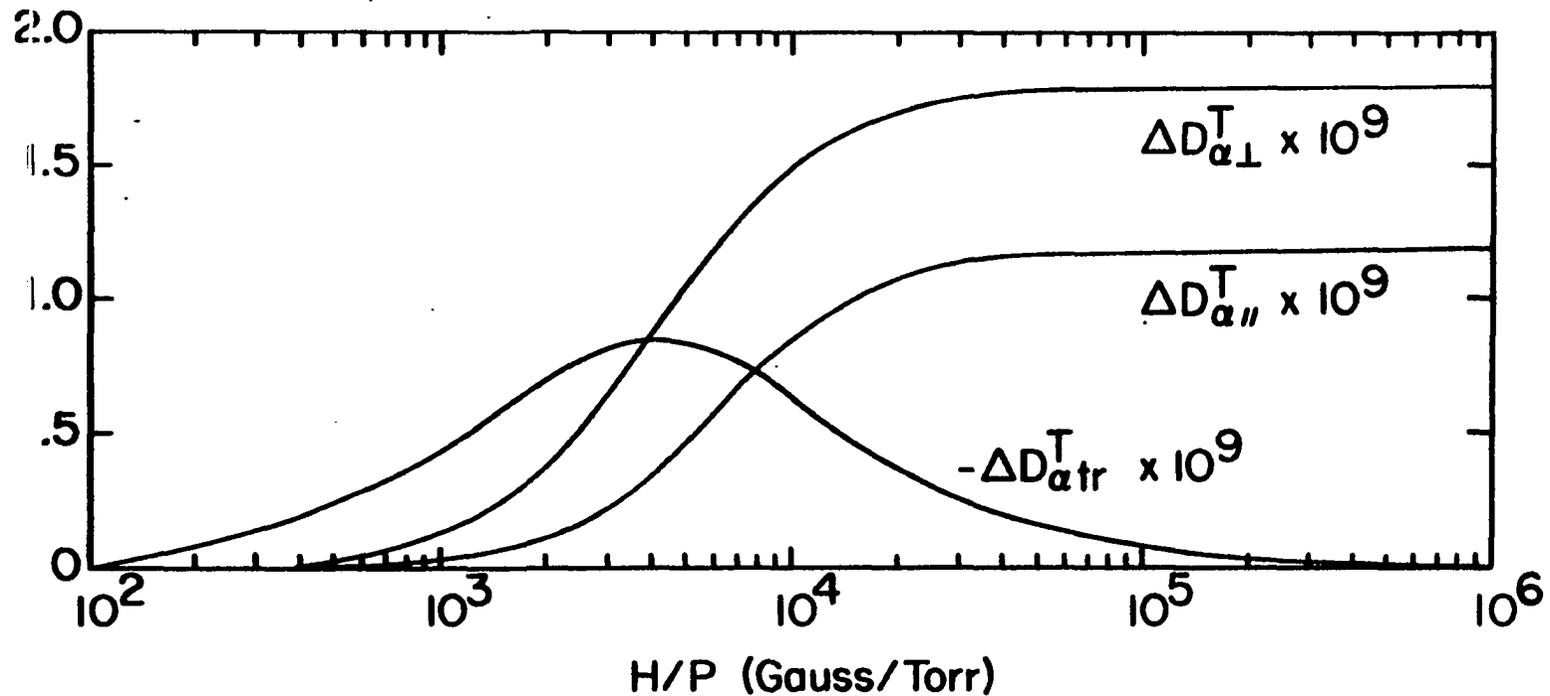


Figure 2. Field-induced effects on the parallel, perpendicular, and transverse thermal diffusion coefficients (in units of g/cm sec) for the mixture defined by: $m_\alpha=30$, $m_\beta=28$, $\langle\sigma\rangle_\alpha=\langle\sigma\rangle_\beta=(2.0)^2\pi\text{\AA}^2$, $R_\alpha=1.05$, $R_\beta=1.1$, $X_\alpha=.5$, $S_\alpha=S_\beta=0$

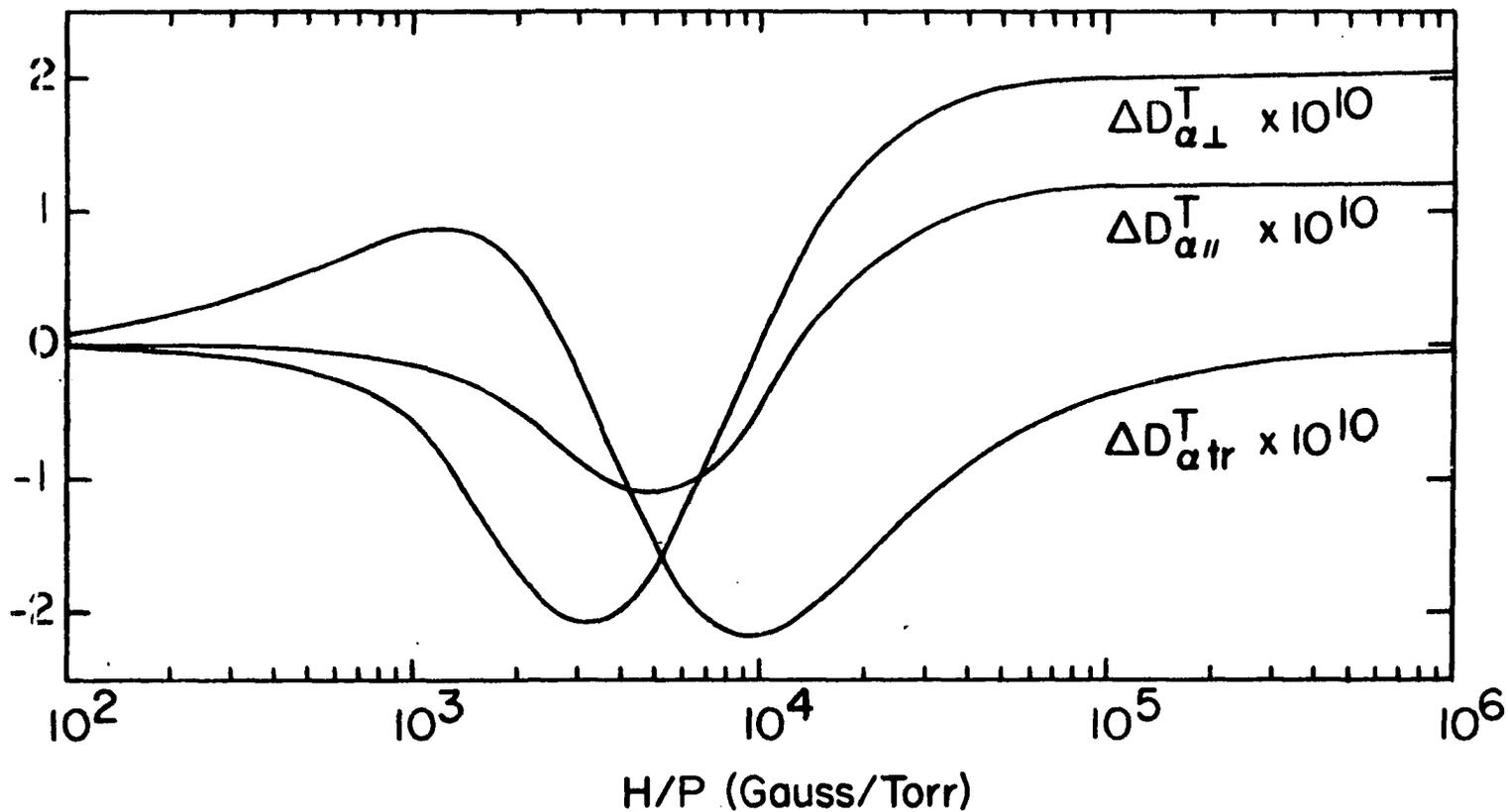


Figure 3. Field-induced effects on the parallel, perpendicular, and transverse thermal diffusion coefficients (in units of g/cm sec) for the mixture defined by: $m_\alpha=30$, $m_\beta=28$, $\langle\sigma\rangle_\alpha=\langle\sigma\rangle_\beta=(2.0)^2\pi A^2$, $R_\alpha=1.091$, $R_\beta=1.1$, $X_\alpha=.5$, $S_\alpha=S_\beta=0$

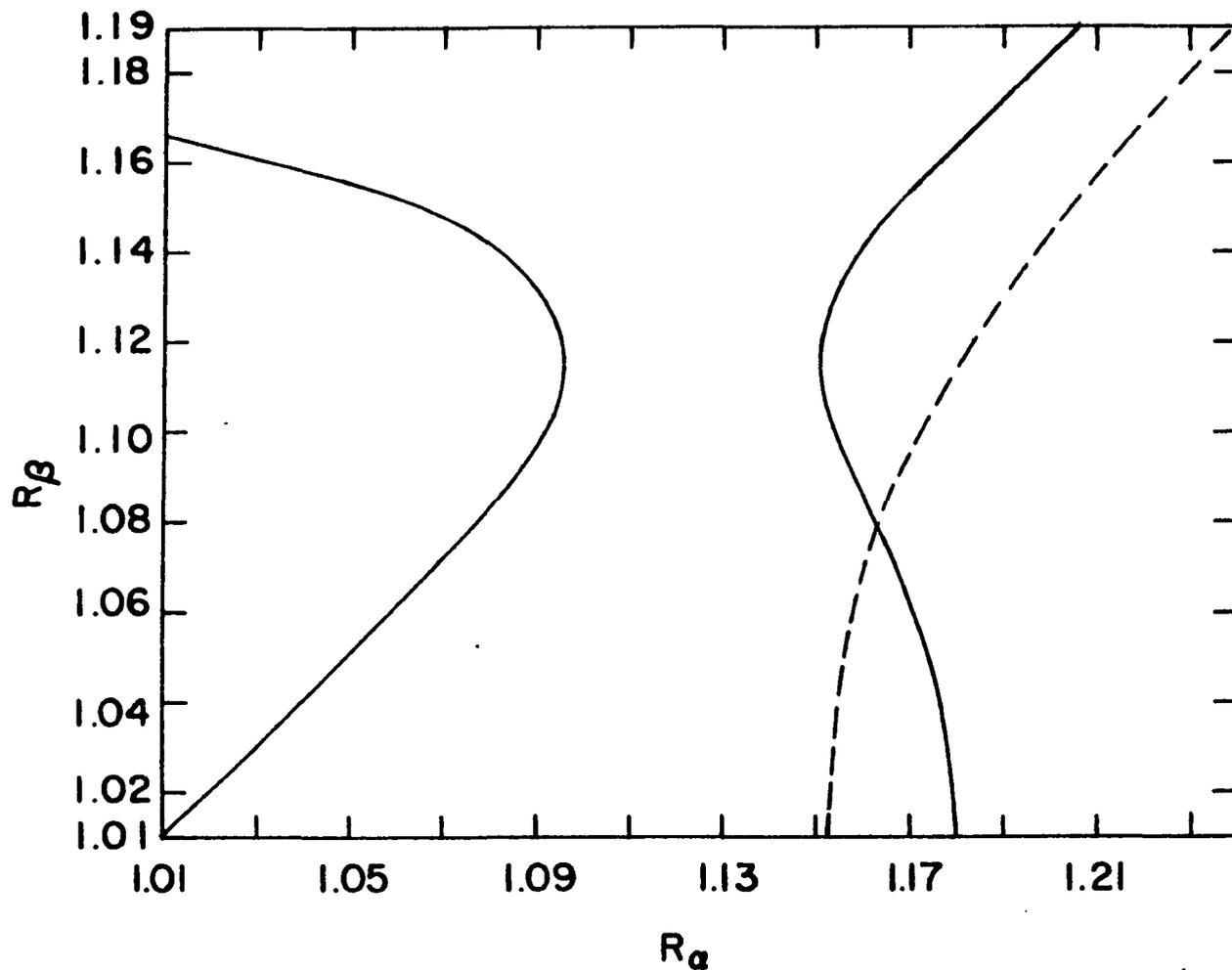


Figure 4. The solid curves represent the locus of points where $(\Delta D_{\alpha}^T)_{sat}$ vanishes and the dashed curve represents the locus of points where $D_{\alpha 0}^T$ vanishes for rigid ellipsoid models; $m_{\alpha}=30$, $m_{\beta}=28$, $\langle \sigma \rangle_{\alpha} = \langle \sigma \rangle_{\beta} = (2.0)^2 \pi \lambda^2$, $x_{\alpha} = .5$, $S_{\alpha} = S_{\beta} = 0$

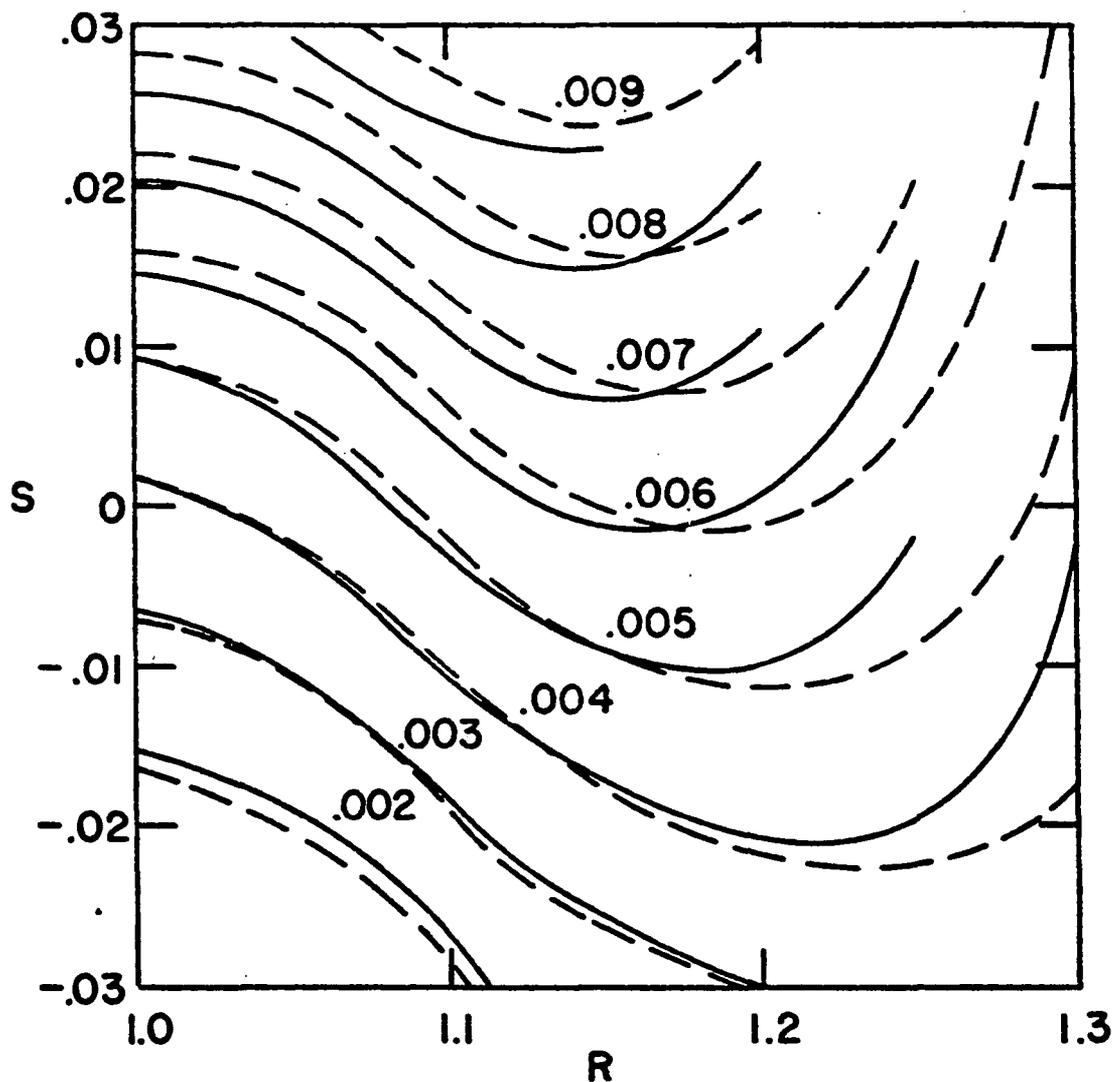


Figure 5. Contours of constant α_T as a function of R and S for the system $^{14}\text{Cl}^{16}\text{O}-^{12}\text{Cl}^{18}\text{O}$. Dashed lines represent $\langle \sigma \rangle_{\text{CO}} = 3.06 \pi \text{ \AA}^2$ and smooth lines represent $\langle \sigma \rangle_{\text{CO}} = 3.75 \pi \text{ \AA}^2$. The numerical values of α_T are indicated on the contours

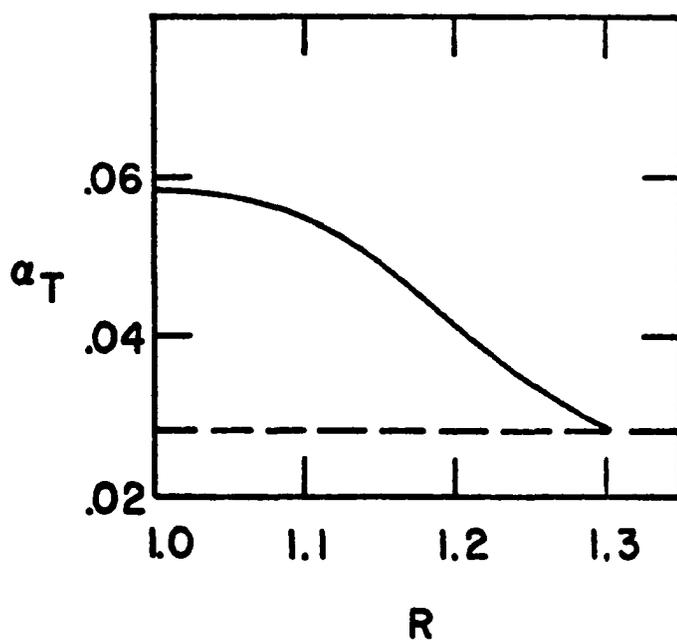


Figure 6. Dependence of α_T on R for D_2 -HT.
 $\langle\sigma\rangle_{H_2} = 1.885\pi\text{\AA}^2$, $S_{H_2} = 0$. Dashed line represents
the experimental value at 338°K

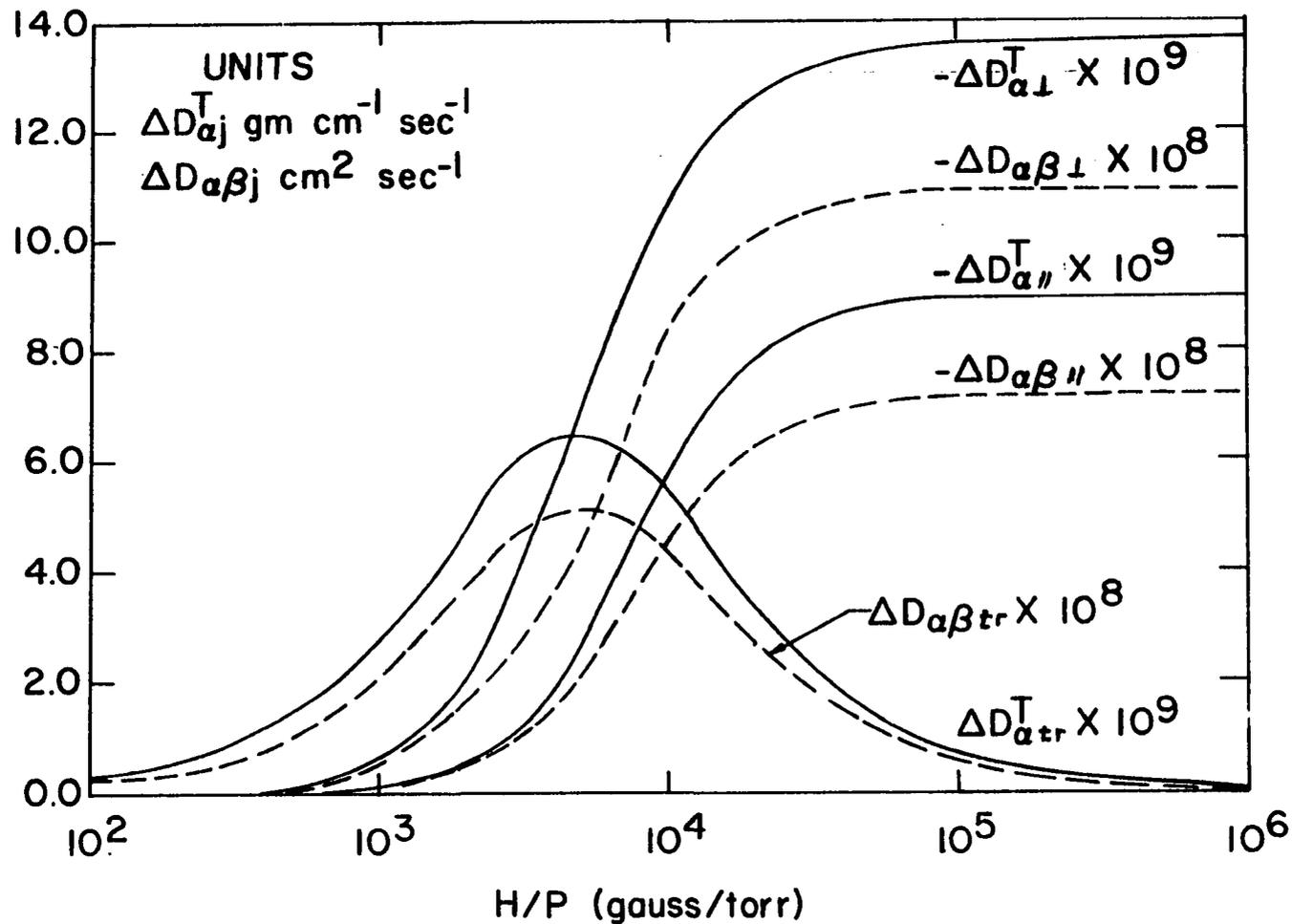


Figure 7. Field-induced effects on thermal diffusion (solid curves) and binary diffusion (dashed curves) coefficients of an equimolar mixture of $^{13}\text{C}^{16}\text{O}$ and $^{12}\text{C}^{16}\text{O}$. $R_{\text{CO}}=1.143$, $\langle\sigma\rangle_{\text{CO}}=(2.17)^2\pi\text{\AA}^2$, $S_{\text{CO}}=0$

CHAPTER 8. CALCULATIONS AND IMPLICATIONS OF THE
PERTURBATION THEORY, NUMERICAL RESULTS

Our objective in this chapter is to examine the analytic expressions given in Equations 5.26 and 5.27, which were derived using perturbation techniques. First we will examine the field-free limit with the aim of gaining some physical insights into the thermal diffusive phenomenon. Next we will investigate the nature of the magnetic field effect and study the anomalies we found in the model studies of Chapter 7. Lastly, we explore how to use these expressions to predict the magnetic field effect on thermal diffusion from the available data on thermal conductivity and field-free thermal diffusion.

For our actual calculations we again choose the truncated basis set displayed in Equation 4.7 and proceed to examine explicitly the associated tensors which appear in Equations 5.24, 5.25, and 5.27. As discussed in Chapter 5, the 3×3 arrays, \underline{T}_0 , \underline{D}_0 , and \underline{G}_0 contain $\underline{\xi}^{(i)}$ as their only tensor element so their inverse is simply $\underline{\xi}^{(i)}$ multiplied by the inverse of the scalar coefficient array. The tensorial nature of the off-diagonal elements is determined by the direct product of the corresponding basis set functions. The element $\underline{\Lambda}_{AB(i\gamma)}$, $i = 1, 2, \text{ or } 3$, is a fourth rank isotropic tensor which is traceless and symmetric on its

first two and last two indices. It must, therefore, be proportional to $\underline{\underline{f}}^{(2)}$. The diagonal element $\underline{\underline{\Lambda}}_{AB(44)}$ is a sixth rank isotropic tensor which is traceless and symmetric on its second and third indices and its fifth and sixth indices. As discussed in Chapter 6, there are three such independent tensors.

It can be shown that for rigid models the matrix elements $\underline{\underline{\Lambda}}_{AB(i5)}$, $i = 1, 2$, or 3 are identically zero. This may be seen from the fact that such integrals are third rank isotropic tensors and hence are proportional to the Levi-Civita density $\underline{\underline{\epsilon}}$, which is the only isotropic third rank tensor. By definition $\epsilon_{ijk} = 1$ for i, j , and k in cyclic order, $\epsilon_{ljk} = -1$ for an anticyclic order, and is zero if any two indices are equal. The rigid model collision integral formulas (44) immediately give that these third rank tensor matrix elements are symmetric on two of their three indices and hence they must be identically zero. The only nonzero, off-diagonal matrix elements with $\underline{\underline{w}}_{\Omega}$ are in fact the elements $\underline{\underline{\Lambda}}_{AB(4,5)}$, and $\underline{\underline{w}}_{\Omega}$ is thus coupled to the 3×3 blocks $\underline{\underline{T}}_0$, $\underline{\underline{D}}_0$, and $\underline{\underline{G}}_0$ only through the term $\underline{\underline{w}}_{\Omega}^{(2)}$. As a consequence, the effect of $\underline{\underline{w}}_{\Omega}$ on diffusion, thermal conductivity, and thermal diffusion is of fourth order in the perturbation. This is evidenced by the fact that in the "exact" calculations of Chapter 7, inclusion of the $\underline{\underline{w}}_{\Omega}$ term is responsible for 1-2% of the field effects which, as we

have seen in Chapter 5, are of second order in the ϵ_1 perturbation.

In the presence of an external field, the diagonal element $\underline{\Lambda}_{AA(44)}$ takes the form of Equation 6.35 and can be expressed in the form of Equation 6.40 in order to perform the required inversion operation. Our choice of representations in Equation 6.40 is now apparent, since if we consider the $\underline{\Lambda}_{AA(44)}$ elements in Equation 5.27, we have the tensor form

$$\underline{\Lambda}_0^2(\underline{f}) \propto \underline{f}^{(2)} \otimes^3 [\underline{T}^{(6)} + \underline{a}^{(6)} \underline{I}_2 \underline{k}] \otimes^3 \underline{f}^{(2)}, \quad (8.1)$$

which can be expressed in terms of the one dimensional unit tensors as

$$\underline{\Lambda}_0^2(\underline{f}) \propto \left(\sum_{j=1}^2 \hat{\chi}_j^{(2)} \hat{\chi}_j^{+(2)} \right) \otimes^3 \left(\sum_{m=1}^2 \sum_{n=1}^2 \hat{\chi}_m^{(1)} \hat{\chi}_{m-n}^{(2)} \hat{\chi}_n^{+(1)} \hat{\chi}_{n-n}^{+(2)} \right) \otimes^3 \left(\sum_{j=1}^2 \hat{\chi}_j^{(2)} \hat{\chi}_j^{+(2)} \right). \quad (8.2)$$

The contraction of the indices of the unit tensors yields the result

$$\underline{\Lambda}_0^2(\underline{f}) \propto [b_1(\underline{f}) \hat{\chi}_1^{(1)} \hat{\chi}_1^{+(1)} + b_2(\underline{f}) \hat{\chi}_2^{(1)} \hat{\chi}_2^{+(1)} + b_{-1}(\underline{f}) \hat{\chi}_{-1}^{(1)} \hat{\chi}_{-1}^{+(1)}]. \quad (8.3)$$

If we express the isotropic sixth rank tensor in terms of a linear combination of the identity elements $\underline{I}_j^{(6)}$, that is,

$$\underline{T}^{(6)} = \sum_{j=1}^2 \alpha_j \underline{I}_j^{(6)}, \quad (8.4)$$

where Δ_j are scalars, then the coefficients b_i are given by

$$b_1 = (u + iv) / (u + i v)$$

$$b_0 = [\Delta_2 \Delta_3 + \frac{2}{5} \mathcal{F}^2] / [\Delta_1 \Delta_2 \Delta_3 + \mathcal{F}^2 (\frac{3}{5} \Delta_3 + \frac{7}{5} \Delta_1)] \quad (8.5)$$

$$b_{-1} = (u - iv) / (u - i v)$$

where

$$u = \Delta_2 \Delta_3 - \frac{1}{5} \mathcal{F}^2$$

$$v = \mathcal{F} (\frac{2}{3} \Delta_2 + \frac{5}{6} \Delta_3)$$

$$u = \Delta_1 \Delta_2 \Delta_3 - \mathcal{F}^2 (\frac{1}{5} \Delta_1 + \Delta_2 + \frac{4}{5} \Delta_3)$$

$$v = \mathcal{F} [\frac{7}{3} \Delta_1 \Delta_2 + \frac{5}{6} \Delta_1 \Delta_3 + \frac{2}{3} \Delta_2 \Delta_3]. \quad (8.6)$$

We can in turn express the coefficients $\underline{A}_0^2(t)$ in terms of real second rank tensors as

$$\underline{A}_0^2(t) \propto [b_{11}(t) \hat{k} \hat{k} + b_{\perp}(t) (\underline{\underline{e}}^{(1)} - \hat{k} \hat{k}) - b_{tr}(t) (\hat{k} \times \underline{\underline{e}}^{(1)})], \quad (8.7)$$

where

$$b_{\perp} = (u u + v v) / (u^2 + v^2)$$

and (8.8)

$$b_{tr} = (u v - v u) / (u^2 + v^2).$$

The expression in Equation 8.7 can be seen to correspond to

property (i) of the Onsager-Casimer relations in Chapter 3.

Before applying these perturbation expressions to the systems of interest, we need to check their convergence against the exact calculations of Chapter 7. Using the potential parameters which fit experimental data (Chapter 7), we find that first order in ϵ_1 compares to the exact inversion to within 5 parts in 3000 for all field-free and magnetic field coefficients. Furthermore, these coefficients to second order in the nonsphericity perturbation, ϵ_2 , compare with the first order ϵ_1 coefficients to within 2%. This excellent convergence assures that our perturbation calculations contain the essence of the exact inversion calculations.

We further proposed in Chapter 5 to make Λ_{TT} and Λ_{DD} correspond to single species thermal conductivity and self-diffusion matrices. For this interpretation they should be insensitive to the isotopic differences. A detailed examination of the elements of Λ_{DD} for the four CO mixtures does indeed reveal a variance of less than 1%. The situation for Λ_{DD} , however, is slightly more complex. In general we find that the variance is less than 3%, however, the elements corresponding to the coupling of the first and third and the second and third basis set terms in Equation 4.5 vary nearly 15% over these four mixtures, and the element corresponding to the coupling of the first and

fourth basis set terms varies over an order of magnitude. These terms which are sensitive to isotopic variations are simply the elements corresponding to angular momentum dependent basis functions. This sensitivity does not affect our binary diffusion calculations since the crucial element for these calculations is $\Lambda_{DD(11)}$. All the off-diagonal elements of Λ_{DD} prove to be small compared to this element.

We are now prepared to use the perturbation expressions of Equation 5.26 and 5.27 to address the problems we have outlined previously. Our first application is the study of the thermal diffusive phenomenon itself, which we approach by examining the isotopic mixtures of CO in field-free space. For this case the coefficient of the transverse effect (b_{tr} of Equation 8.7) is identically zero and the coefficients of the parallel ($b_{||}$) and perpendicular (b_{\perp}) effects are equal, thus yielding D_{α}^T as a single scalar coefficient times the isotropic tensor $\underline{\underline{\zeta}}^{(1)}$. In Chapter 7 we dealt with the effect of the macroscopic and potential parameters on thermal diffusion. We now use the perturbation expressions to examine the kinematic parameters.

Each species in the mixture originally has three independent kinematic variables: the masses of atoms 1 and 2 and the internuclear distance. The masses are, of course, determined by the species under consideration and we assume that the internuclear distance is fixed by spectroscopic

data and is the same for all isotopic species. Consequently, a binary mixture will have four independent kinematic variables which are subject to isotopic variation.

The formulation of the perturbation expressions in Chapter 5 is based on the perturbation of the isotopic differences about the limit of a simple gas of "average" molecules. The utility of this approach lies in the insensitivity we have already noted in the Λ_{TT} and Λ_{DD} matrices. One possible choice of the average molecule is a mole fraction average of the masses of like atoms between the two species, that is,

$$m_1 = X_\alpha m_{\alpha 1} + X_\beta m_{\beta 1}$$

and

(8.9)

$$m_2 = X_\alpha m_{\alpha 2} + X_\beta m_{\beta 2}$$

where $m_{\gamma 1}$ and $m_{\gamma 2}$ are the masses of the atoms 1 and 2, respectively, in the diatomic species γ (α or β) with mole fraction X_γ , and m_1 and m_2 are the average masses of atoms 1 and 2. The four independent variables can be taken to be the average masses m_1 and m_2 , the difference in the total mass, ΔM , where

$$\Delta M = (m_{\alpha 1} + m_{\alpha 2}) - (m_{\beta 1} + m_{\beta 2}) \quad (8.10)$$

and the difference in the mass distribution,

$$\Delta m = (m_{\alpha 1} - m_{\alpha 2}) - (m_{\beta 1} - m_{\beta 2}). \quad 8.11)$$

We can expand each of the elements contained in Equations 5.26 and 5.27 as a power series in ΔM and Δm . With this expansion we find that the elements are effectively linear in the total mass difference but that we must retain terms through second order in Δm to obtain the convergence to within 2%. Furthermore we find that the contributions from $\Delta M \Delta m$ and $(\Delta m)^2$ are of roughly the same order of magnitude and are approximately 1% of the linear mass distribution contribution. Due to the nonlinearity in Δm , we choose to calculate the thermal diffusion coefficient as additive contributions from the mass difference and the moment of inertia difference, as illustrated in the following manner.

The first two rows in Table 11 give the values of ΔM and Δm for the mixtures (in units of the mass of species β , $m_{\beta 1} + m_{\beta 2}$) as calculated from Equations 8.10 and 8.11. The row label "mass" implies that the given thermal diffusion coefficient is calculated for the case where the mass distribution of each of the two species of interest is fixed at the average molecule value and the total mass of each species is set to its exact value. The row label "mass distribution" implies a similar calculation for the case that the total masses of the two species are equal to

the average molecule total mass, but the molecular mass distributions are exact. The row labeled sum is simply the sum of the previously two entries and the row labeled exact contains the result of the perturbation calculation using the actual molecular parameters.

First, we note that the sum of the separate effects compares to the exact effect to within a fraction of a percent. As previously mentioned, we conclude from this that the effects due to Δm and ΔM are not coupled in the lower perturbation orders. Next we note that as assumed in Chapter 7, the contribution due to the total mass difference is very nearly linear. This results from the fact that the percent variation of the mass is small. However, as has already been noted the contribution due to the mass distribution difference is not linear. This can be seen to arise from the fact that the difference in the mass distribution between the two species is of the order of the molecular mass distributions themselves.

As mentioned previously, the quantities m_1 , m_2 , ΔM , and Δm form a set of independent parameters. However, the mass distribution difference Δm is not a physically meaningful parameter, and thus we choose to view the mass distribution in terms of two other parameters, the moment of inertia

$$I_Y = \left[\frac{m_{Y1} m_{Y2}}{m_{Y1} + m_{Y2}} \right] r_e^2 \quad (8.12)$$

and the load,

$$l_Y = \left[\frac{m_{Y1} - m_{Y2}}{m_{Y1} + m_{Y2}} \right] \frac{r_e}{2}, \quad (8.13)$$

which is the distance of the center of mass from the geometric center of the bond. In both expressions r_e is the internuclear distance and is fixed.

By splitting the mass distribution difference into contributions from the load difference and moment of inertia difference, we obtain the results as shown in Table 12. The quantities $\Delta I = (I_\alpha - I_\beta) / m_\beta r_e^2$ and $\Delta l = (l_\alpha - l_\beta) / m_\beta r_e$ are unitless numbers with the masses expressed again in terms of the mass of species β and the distances expressed in units of the internuclear distance, r_e . The row labeled moment of inertia gives the thermal diffusion coefficient calculated with the total masses and loads of each of the two species in the mixture set to the total mass and load of the average molecule respectively and the moments of inertia given by their exact values. The load row results from a similar calculation where only the load differs between the molecules. The mass distribution row is calculated as in Table 11.

We see again the sum of the moment of inertia and the

load effects give the mass distribution value to within a fraction of a percent. This implies lack of coupling between the contributions from ΔI and Δl , and also that the contributions from the total mass difference, load difference, and moment of inertia difference add separately to give the total thermal diffusive effect. We further note that the contribution due to the moment of inertia difference is nearly linear and thus the nonlinearity has been isolated to the contribution from the load difference.

A positive value of D_a^T implies that the α -species migrates down the temperature gradient and concentrates at the cooler end of the system. Throughout this work we have written the mixtures in the form α - β . For example, for the mixture $^{13}\text{C}^{16}\text{O}$ - $^{12}\text{C}^{16}\text{O}$, $^{13}\text{C}^{16}\text{O}$ corresponds to species α and $^{12}\text{C}^{16}\text{O}$ corresponds to species β . From Table 11 we see that for all cases the heavy species migrates to the cold side. Table 12 shows that, other things being equal, the species with the largest moment of inertia migrates down the temperature gradient as does the species with the smallest load.

It is difficult to explain these thermal diffusive results in detail with a simple mechanistic picture, but the general idea is as follows. Simple mean free path arguments establish that there is a flux of thermal energy (translational and rotational) down the temperature gradient.

The thermal conductivity coefficient is proportional to both the average molecular velocity and the mean free path. For an equimolar, isotopic mixture the lighter species gives the largest contribution to thermal conductivity because the average molecular speed is greater for the lighter species. However, the effective mean free path associated with the heavier species slightly larger than for the lighter species. This larger effective mean free path results from the fact that in a collision between the two different species, the velocity of the heavier component is slightly more persistent.

The existence of an energy flux down the temperature gradient tends also to give rise to a mass flux down the gradient. However, since there is no net mass flux (relative to the streaming velocity), the species that actually moves down the gradient is the one for which thermal flux and mass flux are most strongly coupled. This is the species which is the least dynamically affected during a collision between unlike molecules. If there is only a mass difference between the molecules, there is a coupling of mass flux with the flux of both translational and rotational energy and the heavier molecule has the most persistent velocity and consequently moves to the cold end. If there is only a moment of inertia difference between molecules, a coupling only exists between the mass flux

and the rotational energy flux. The molecule with the largest moment of inertia is the least collisionally affected and moves down the temperature gradient. For the case when there is only a load difference between molecules there is again a coupling only between the mass flux and the rotational energy flux. The molecule with the smallest load is least affected by collision and hence moves down the temperature gradient. It should be noted that these arguments basically apply only to impulsive interactions. Attractive molecular interactions can, in fact, lead to an inversion in the direction of separation at lower temperatures.

These conclusions are supported by the perturbation analysis. All of the calculations we report in Tables 11 and 12 are for the full basis set to second order in ϵ_2 . We find, however, that for the field-free case the thermal diffusion coefficient can be obtained to within about 10% of the "exact" coefficient if we consider only the $\underline{\Lambda}_{DD(11)}$ element of Λ_{DD} , $\underline{\Lambda}_{DT(12)}$ and $\underline{\Lambda}_{DT(13)}$ in Λ_{DT} , and $\underline{\Lambda}_{TT(22)}$, $\underline{\Lambda}_{TT(23)}$, $\underline{\Lambda}_{TT(32)}$, and $\underline{\Lambda}_{TT(33)}$ elements in Λ_{TT} . Since these particular elements of Λ_{TT} and Λ_{DD} are insensitive to isotopic variations, the integrals which are important in the calculations of the thermal diffusion coefficient are $\underline{\Lambda}_{DT(12)}$ and $\underline{\Lambda}_{DT(13)}$. These elements, in turn, contain collision integrals which couple the mass flux trial

function w with the translational energy flux function $w(\frac{1}{2}-w^2)$ and the rotational energy flux function $w(1-\Omega^2)$, respectively, for an α - β type collision. In fact, the element $\underline{\Delta}_{DT(12)}$ is essentially the difference between the collision integral coupling w and $w(\frac{1}{2}-w^2)$ for the α th species and the collision integral coupling the same trial functions for the β th species. Similarly, $\underline{\Delta}_{DT(13)}$ is the difference between the collision integrals coupling w and $w(1-\Omega^2)$ for the α th and β th species. Both $\underline{\Delta}_{DT(12)}$ and $\underline{\Delta}_{DT(13)}$ are nonzero for the case when there is a mass difference between the species, but only $\underline{\Delta}_{DT(13)}$ is nonzero when there is only a difference in moment of inertia or load. The sign of the matrix elements $\underline{\Delta}_{DT(12)}$ and $\underline{\Delta}_{DT(13)}$ ultimately determines which species concentrates at the cold end, and this sign difference can be predicted from a consideration of which species is most dynamically affected in collision.

There is no field effect in our calculations unless we include trial terms which are anisotropic in the angular momentum. As previously discussed, for our purposes we need only include the anisotropic term $w[\Omega]^{(2)}$. Since this term is of little consequence in the field-free case the analysis just completed sheds little light on what happens in the field. The inclusion of this term increases the complexity of the analytic expressions to such an extent

that we make no attempt to explain the field effect in physical terms. We examine instead the three distinct types of field contributions (as seen from Equation 5.30 and the discussion in Chapter 5) and the additivity of each contribution.

As is seen in Equation 4.5, the external field induces three separate coefficients $f_{||}$, f_{\perp} , and f_{tr} . In the perturbation expressions the field effect is contained entirely in the five second order contributions to thermal diffusion, $'A_D^2(j)$, $j=1$ to 5 . Each of these five contributions contain the three field coefficients $b_{||}(j)$, $b_{\perp}(j)$, and $b_{tr}(j)$, as indicated in Equation 8.7. The thermal conductive type contributions ($'A_D^2(1)$ and $'A_D^2(2)$) have the same field dependence, that is $b_i(1) = b_i(2)$, $i = ||, \perp, tr$. Similarly the self-diffusion type contributions ($'A_D^2(4)$ and $'A_D^2(5)$) have the same field dependence, that is $b_i(4) = b_i(5)$. Furthermore we find that all coefficients except $b_i(3)$ are only sensitive to about 2% over the range of the isotopic CO mixtures. This last observation is the basis for our association of these field terms with the simple gas thermal conductivity and self-diffusion, respectively.

In this work we will emphasize only calculations for the parallel component, $\Delta D_{\alpha\beta}^T$, and simply note that the perpendicular and transverse components exhibit analogous

behavior. In Table 13 we display the three distinct field contributions to the thermal diffusion coefficient ΔD_{α}^T . Except for the mixture $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$, the thermal conductive type contribution is the dominant factor. An inspection of the two terms $'\underline{A}_D^2(1)$ and $'\underline{A}_D^2(2)$ which comprise the thermal conductive contribution reveals that they are of the same sign and add for all mixtures except $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$. In this exceptional case the two terms are nearly equal but opposite in sign. As we shall later see this results from the fact that $^{12}\text{C}^{18}\text{O}$ has both a larger moment of inertia and a larger load than does $^{12}\text{C}^{16}\text{O}$.

To examine these field contributions more thoroughly, we test their additivity in the kinematic parameters. We find that the thermal conductive contribution does exhibit additivity with respect to mass, moment of inertia, and load, whereas the diffusion and hybrid field contributions do not. This is shown in Table 14 for the mixture $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$. The form of the expressions in Equation 5.27 again indicate the source of this behavior. Our previous investigation of the isotopic sensitivity of the elements in \underline{A}_{DD} indicated that $\underline{A}_{DD(13)}$, $\underline{A}_{DD(23)}$, and $\underline{A}_{DD(14)}$ (and, of course, the corresponding transpose elements) are in fact dependent on isotopic variations. The terms which contain the thermal conductivity type field contribution ($'\underline{A}_D^2(1)$ and $'\underline{A}_D^2(2)$) depend upon the self-diffusion elements

only through \underline{D}_0 , which is effectively insensitive to the isotopic variations. On the other hand, the hybrid field dependence ($\underline{A}_D^2(3)$) and self-diffusion field dependence ($\underline{A}_D^2(4)$ and $\underline{A}_D^2(5)$) contain a sum of products of Λ_{DD} elements, and those products which are sensitive to the isotopic variations are not negligible and may even dominate. Thus only the thermal diffusive type terms exhibit additivity. The additivity can now be used to examine the smallness of the thermal conductive contribution in the mixture $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$. The sign inversion we noted earlier occurs for $\underline{A}_D^2(2)$, and more specifically, for the contribution to $\underline{A}_D^2(2)$ due to the difference in the loads. The sign change due to load contribution is expected since this is the only CO mixture where the α -species has the largest load. However, the fact that the thermal conductive contributions nearly cancel in this case appears to be a fortuitous consequence of the particular kinematic parameters of this mixture.

We now wish to utilize these separations we have obtained for the field effect to investigate the anomalies which appeared in the parameter studies of Chapter 7. Examination of the inversion points of Figure 4 with the perturbation expressions of Equation 5.27 yields the type of results which are illustrated in Figure 8 for the parallel component. We see that the inversion in the sign of

$\Delta D_{\alpha\parallel}^T$ corresponds to a cancellation of the self-diffusion and thermal conductive type field contributions, each of which is much larger than the hybrid field contribution. It is important to note that both the self-diffusion and thermal conductive pieces exhibit the usual field saturation effect; it is their sum which yields the anomalous behavior. This same type of behavior is exhibited for the perpendicular and transverse components, except that for the transverse component we see a cancelling effect on the thermal conductive and diffusive maximum "humps" rather than in the saturation value, as shown in Figure 9.

The perturbation study of single species thermal conductivity (32) shows that the ratio $\Delta\lambda_{\perp}/\Delta\lambda_{\parallel}$ to second order in the nonsphericity expansion is equal to 3/2 in saturation, which agrees with the prediction of Knaap and Beenakker (45). A similar perturbation study on the self-diffusion field terms yields the same ratio. Since our thermal conductive type field terms (1 and 2 of Equation 5.27) and self-diffusion type field terms (4 and 5) contain exactly this same field dependence, our thermal diffusion field results also show this same 3/2 saturation ratio when the hybrid field term is negligible. This effect can be seen in Table 9 of the last chapter.

As a further application of our perturbation expressions we would like to be able to use them to predict the

field effect on thermal diffusion from experimentally obtained data for other effects with minimum reliance on any particular collision model. Since field effects are difficult to measure experimentally, this would be a useful result. To make these characterizations we would use the available experimental data to parameterize the collision integrals (or collections of collision integrals) and field terms needed to evaluate Equation 5.27. As in our potential parameter fitting, we have available experimental data for thermal conductivity in both field and field-free space and field-free thermal diffusion.

As discussed previously, the b_i 's of Equation 8.7 are insensitive to isotopic variations. This insensitivity in combination with the thermal conductivity field data allows us to determine the field dependence

$(\underline{\underline{\epsilon}}^{(2)})^3 \underline{\underline{\Lambda}}_{TT}^{(4)} \underline{\underline{\epsilon}}^{(2)}$ for those mixtures where the thermal conductive type field terms dominate. From Equation 5.27 we see that we now need to determine the field-free factor which multiplies this field term. The field-free factor is identical to the second order ϵ_2 perturbation in field-free space (that is, $\underline{\underline{\Lambda}}_D^2(1)$ and $\underline{\underline{\Lambda}}_D^2(2)$ when $\mathcal{F} = 0$) so to find this factor from experimental data we must separate the zero and second order effects. This separation can in principle be obtained by using the field-free thermal diffusion data to parameterize the collision model. If this

parameterization is sufficiently accurate, we can then use the model to separate the zero order contribution from the total effect. Our rigid model is inadequate for these purposes since we cannot accommodate for the fact that the rigid spherical limit gives the dominant contribution for mixtures in which the species differ in total mass. These separations and the resulting characterization of the thermal diffusion field effect thus require a model with a more realistic spherical limit than that of our rigid models. Some preliminary considerations of this matter are the subject of the next chapter.

Table 11. Additivity of D_a^T for the separate contributions in the total mass difference (ΔM) and mass distribution difference (Δm). The quantities ΔM and Δm are expressed in units of m_0 . The units of D_a^T are g/cm sec. $\langle \sigma \rangle = (2.17)^2 \pi A^2$, $R=1.143$, $S=-.027$, $X_\alpha=.5$, $T=300$

| | Mixture | | | |
|-------------------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| ΔM | 0 | .0358 | .0716 | .0716 |
| Δm | -.1336 | -.0358 | .0716 | -.0716 |
| mass | 0 | .5163x10 ⁻⁶ | 1.0126x10 ⁻⁶ | 1.0236x10 ⁻⁶ |
| mass distribution | .2738x10 ⁻⁶ | .1267x10 ⁻⁶ | -.0337x10 ⁻⁶ | .2236x10 ⁻⁶ |
| sum | .2738x10 ⁻⁶ | .6430x10 ⁻⁶ | .9789x10 ⁻⁶ | 1.2472x10 ⁻⁶ |
| exact | .2738x10 ⁻⁶ | .6438x10 ⁻⁶ | .9780x10 ⁻⁶ | 1.2492x10 ⁻⁶ |

Table 12. Additivity of D_{α}^T for the separate contributions in the load (Δl) and moment of inertia (ΔI) differences. ΔI is expressed in units of $m_{\beta} r_e^2$ and Δl is in units of $m_{\beta} r_e$. The units of D_{α}^T are g/cm sec. $\langle \sigma \rangle = (2.17)^2 \pi A^2$, $R=1.143$, $S=-.027$, $X_{\alpha}=.5$, $T=300$

| | Mixture | | | |
|-------------------|---|---|---|---|
| | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{18}\text{O}$ | $^{13}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{12}\text{C}^{18}\text{O}-^{12}\text{C}^{16}\text{O}$ | $^{14}\text{C}^{16}\text{O}-^{12}\text{C}^{16}\text{O}$ |
| ΔI | .0089 | .0113 | .0123 | .0218 |
| Δl | -.0668 | -.0198 | .0286 | -.0382 |
| moment of inertia | $.0598 \times 10^{-6}$ | $.0705 \times 10^{-6}$ | $.0811 \times 10^{-6}$ | $.1313 \times 10^{-6}$ |
| load | $.2130 \times 10^{-6}$ | $.0560 \times 10^{-6}$ | $-.1148 \times 10^{-6}$ | $.0915 \times 10^{-6}$ |
| sum | $.2728 \times 10^{-6}$ | $.1265 \times 10^{-6}$ | $-.0337 \times 10^{-6}$ | $.2228 \times 10^{-6}$ |
| mass distribution | $.2738 \times 10^{-6}$ | $.1267 \times 10^{-6}$ | $-.0337 \times 10^{-6}$ | $.2236 \times 10^{-6}$ |

Table 13. Values of $\Delta \rho_{\alpha}^r \times 10^8$ for the three types of field contributions (see text). Units of $\Delta \rho_{\alpha}^r$ are g/cm sec. $\langle \sigma \rangle = (2.17)^2 \pi \text{\AA}^2$, $R=1.143$, $S=-.027$, $X_{\alpha}=.5$, $T=300$

| Mixture | Magnetic Field Contributions | | | |
|---------------------------------|------------------------------|-----------------------------|----------------|-----------------------------|
| | ${}^1A_D^2(4)+{}^1A_D^2(5)$ | ${}^1A_D^2(1)+{}^1A_D^2(2)$ | ${}^1A_D^2(3)$ | $\sum_{j=1}^5 {}^1A_D^2(j)$ |
| ${}^{14}C^{16}O-{}^{12}C^{18}O$ | -.0116 | -1.7939 | .0030 | -1.8025 |
| ${}^{13}C^{16}O-{}^{12}C^{16}O$ | .0036 | -.9051 | .0007 | -.9008 |
| ${}^{12}C^{18}O-{}^{12}C^{16}O$ | .0290 | .0518 | -.0163 | .0645 |
| ${}^{14}C^{16}O-{}^{12}C^{16}O$ | .0098 | -1.6126 | .0032 | -1.5986 |

Table 14. Additivity of $\Delta \rho_{\alpha}^r \times 10^9$ for the three types of contribution to the field effect for the mixture ${}^{14}C^{16}O-{}^{12}C^{16}O$. $\langle \sigma \rangle = (2.17)^2 \pi \text{\AA}^2$, $R=1.143$, $S=-.027$, $X_{\alpha}=.5$, $T=300$

| | Magnetic Field Contributions | | |
|-------------------|------------------------------|-----------------------------|----------------|
| | ${}^1A_D^2(4)+{}^1A_D^2(5)$ | ${}^1A_D^2(1)+{}^1A_D^2(2)$ | ${}^1A_D^2(3)$ |
| mass | -.2443 | - 2.645 | .1267 |
| load | .1016 | - 6.174 | -.0260 |
| moment of inertia | .2261 | - 7.021 | -.0493 |
| sum | .0833 | -15.840 | .0514 |
| exact | .09824 | -16.116 | .0316 |

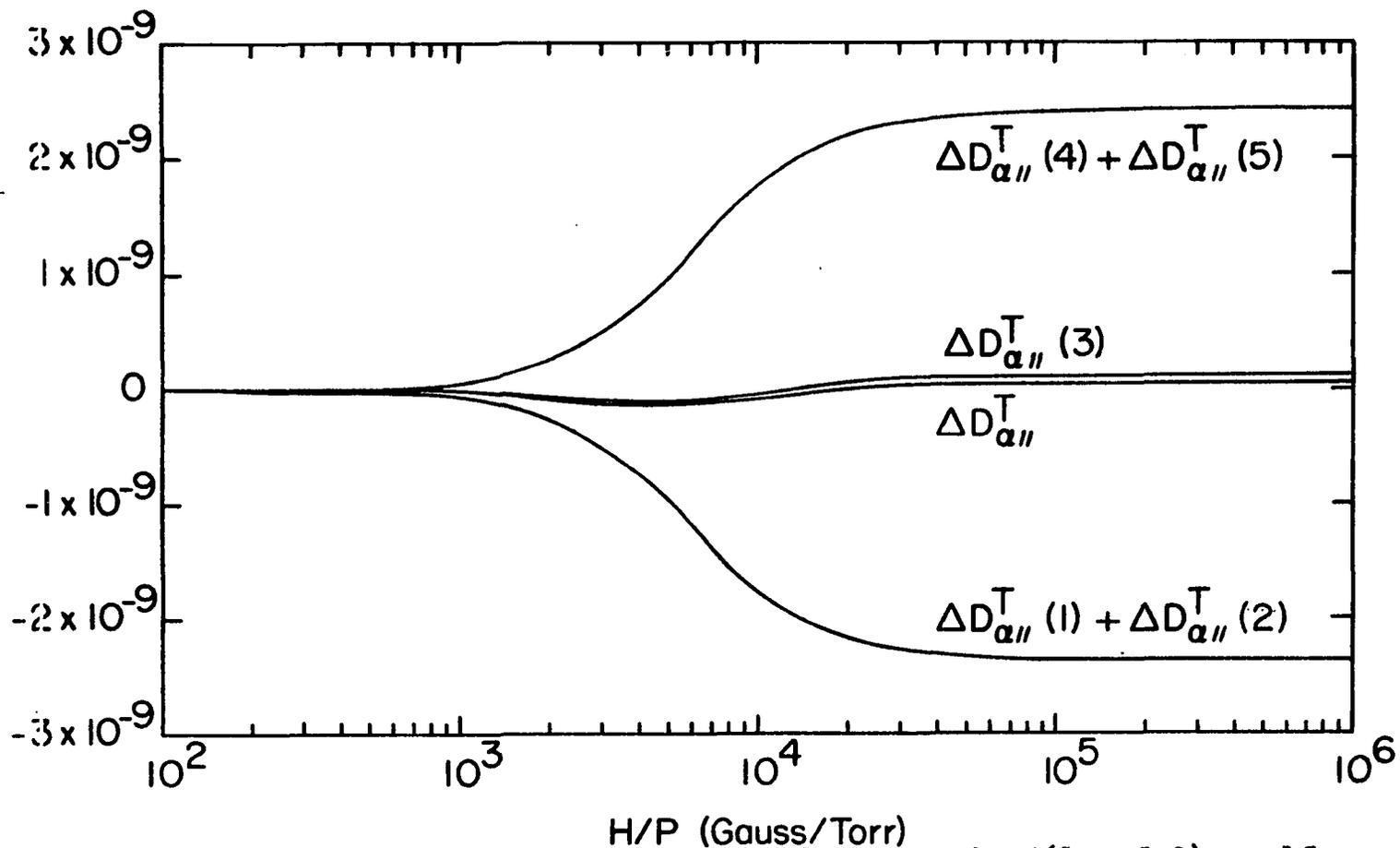


Figure 8. Field-induced effects on the thermal conductive (1 and 2), self-diffusion (4 and 5), and hybrid (3) type contributions to the parallel component of the thermal diffusion coefficient. $\Delta D_{\alpha//}^T = \sum_{i=1}^5 \Delta D_{\alpha//}^T(i)$. The units of $\Delta D_{\alpha//}^T$ are g/cm sec., $m_{\alpha}=30$, $m_{\beta}=28$, $\langle \sigma \rangle_{\alpha} = \langle \sigma \rangle_{\beta} = (2.0) 2\pi \text{\AA}^2$, $R_{\alpha}=1.091$, $R_{\beta}=1.1$, $X_{\alpha}=0.5$, $S_{\alpha}=S_{\beta}=0$

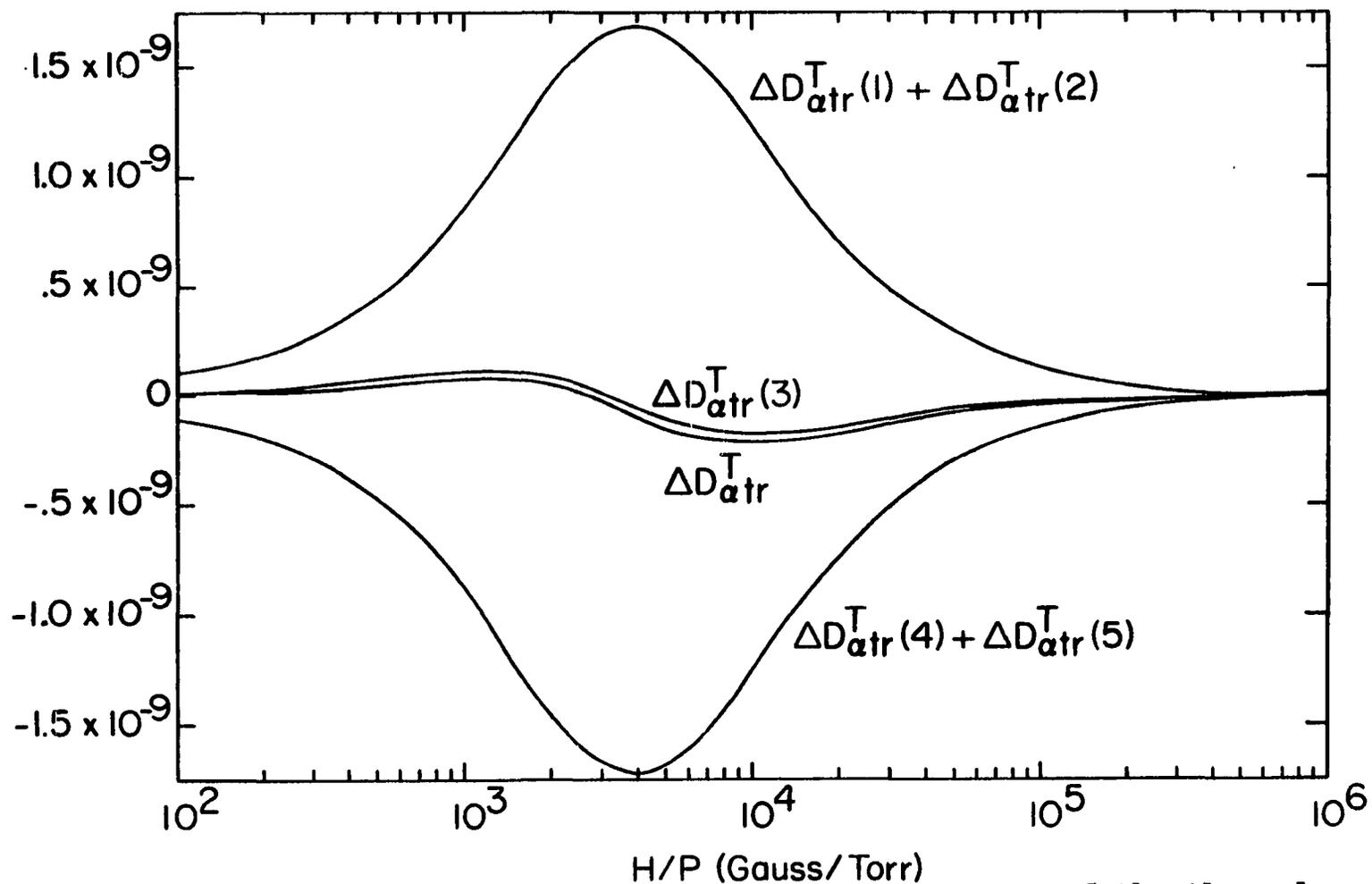


Figure 9. Field-induced effects on the transverse component of the thermal diffusion coefficient, ΔD_{atr}^T . The parameters and the curve identification are the same as those for Figure 8

CHAPTER 9. A PROPOSAL FOR IMPROVED MODEL CALCULATIONS

Throughout this work our calculations have been limited by the failure of the rigid sphere limit of our rigid ellipsoid models to form an adequate basis for computation of the dominant spherical part of the desired collision integrals. We now suggest a scheme to remedy this situation. Since these topics will be the subject of future research work, we present here only a very brief outline of the concepts involved and hopefully the spirit of future work.

We first consider briefly the dynamics of a rigid collision. From the laws of mechanics we have

$$\frac{d\mathbf{p}_i}{dt} = \mathbf{F}_i = -\mathbf{F}_2 = -\frac{d\mathbf{p}_2}{dt} \quad (9.1)$$

and

$$\frac{d\mathbf{L}_i}{dt} = \mathbf{N}_i = \mathbf{s}_i \times \mathbf{F}_i, \quad \frac{d\mathbf{L}_2}{dt} = \mathbf{N}_2 = \mathbf{s}_2 \times \mathbf{F}_2 \quad (9.2)$$

where \mathbf{p}_i and \mathbf{L}_i are the linear and angular momenta of molecule i , \mathbf{s}_i is the vector from the center of mass of body i to the point of collisional contact, and \mathbf{F}_i and \mathbf{N}_i are the force and torque, respectively, on molecule i . To calculate the collisional change resulting from the impulsive interaction we simply integrate Equations 9.1 and 9.2 over the infinitesimal time interval of the collision to obtain

$$\Delta p_2 = -\Delta p_1 = \hat{k}_1 K$$

and (9.3)

$$\Delta L_1 = (\underline{s}_1 \times \hat{k}_1) K, \quad \Delta L_2 = (\underline{s}_2 \times \hat{k}_2) K,$$

where \hat{k}_i is the outward directed unit normal to the surface of body i at the point of collisional contact. The quantity K is found from conservation of energy to be given by

$$K = \frac{2 \mu \hat{k}_1 \cdot \underline{g}}{1 + \mu \left[\underline{I}_1^{-1} : (\underline{s}_1 \times \hat{k}_1)(\underline{s}_1 \times \hat{k}_1) + \underline{I}_2^{-1} : (\underline{s}_2 \times \hat{k}_2)(\underline{s}_2 \times \hat{k}_2) \right]}. \quad (9.4)$$

Here μ is the reduced mass, \underline{g} is the relative velocity of the points of contact (Equation 2.16), and \underline{I}_i is the inertial tensor of molecule i .

The dynamical results of Equation 9.3 can be compactly written (44) in terms of a multidimensional vector

$$\underline{\eta} = (\underline{\Gamma}, \underline{\gamma}, \underline{\Omega}_1, \underline{\Omega}_2) \quad (9.5)$$

where $\underline{\Omega}_1$ and $\underline{\Omega}_2$ are the reduced angular momenta and

$\underline{\Gamma} = (\mu/m_1)^{1/2} \underline{w}_2 + (\mu/m_2)^{1/2} \underline{w}_1$ is the reduced center of mass and

$\underline{\gamma} = (\mu/m_1)^{1/2} \underline{w}_1 - (\mu/m_2)^{1/2} \underline{w}_2$ is the reduced relative momentum.

Here \underline{w}_i and m_i are the reduced linear momentum and the mass of particle i and $\mu = m_1 m_2 / (m_1 + m_2)$. We find that

$$(\mu/2\Delta T)^{1/2} \hat{k}_1 \cdot \underline{g} = D \hat{e}_n \cdot \underline{\eta} \quad \text{and}$$

$$(\underline{\eta} - \underline{\eta}') \cdot \hat{e}_n = 2 \hat{e}_n \cdot \underline{\eta} \quad (9.6)$$

where $\hat{\epsilon}_n = (0, \hat{k}, a_1, a_2)$ and $D = \sqrt{1 + a_1^2 + a_2^2}$. For linear molecules $a_1 = (\mu/I_1)^{1/2}(\underline{s}_1 \times \hat{k}_1)$ and $a_2 = (\mu/I_2)^{1/2}(\underline{s}_2 \times \hat{k}_2)$. From energy conservation it follows that

$$\eta^2 = \eta'^2 \quad (9.7)$$

and from Equation 9.6 it can be shown that

$$\hat{\epsilon}_n \cdot \underline{\eta} = -\hat{\epsilon}_n \cdot \underline{\eta}'$$

and (9.8)

$$\underline{\eta}_\perp = \underline{\eta} - \hat{\epsilon}_n \cdot \underline{\eta} \hat{\epsilon}_n = \underline{\eta}'_\perp .$$

Thus the result of a collision is simply to change the sign of the component of $\underline{\eta}$ along $\hat{\epsilon}_n$, which in a geometric sense corresponds to an improper rotation of $\underline{\eta}$ in the multi-dimensional space.

For the special case of rigid spheres we need only consider the reduced relative velocity \underline{y} and the surface normal, $\hat{\lambda}$, at the point of contact. This unit vector is given by $\hat{\lambda} = \underline{y} - \underline{y}' / (|\underline{y} - \underline{y}'|)$, where the primed quantities denote precollisional and unprimed denote postcollisional relative velocities. Clearly, $y^2 = y'^2$, $\underline{y} \cdot \hat{\lambda} = -\underline{y}' \cdot \hat{\lambda}$, and $\underline{y}_\perp = \underline{y} - (\hat{\lambda} \cdot \underline{y}) \hat{\lambda} = \underline{y}'_\perp$, and the collision serves only to change the sign of the relative velocity component in the direction of $\hat{\lambda}$. The general rigid collision results are thus simply a multidimensional generalization of a rigid sphere

collision in three dimensions.

For a spherical, soft, purely repulsive potential, we can replace every collision by a dynamically equivalent rigid interaction. The unit vector $\hat{\lambda}$ of the equivalent collision is along the apse vector (that is, along $\underline{y} - \underline{y}'$) and the diameters of the equivalent rigid spheres are now, of course, functions of \underline{y} .

For a soft, nonspherical interaction an analogous result in the multidimensional space of $\underline{\eta}$ can be obtained. We define a unit vector $\hat{\epsilon}_n$ (a generalized apse vector) by

$$\hat{\epsilon}_n = \underline{\eta} - \underline{\eta}' / (|\underline{\eta} - \underline{\eta}'|) \quad (9.9)$$

which is the nonspherical analog of $\hat{\lambda}$. As an immediate consequence of this definition, we have that

$$\begin{aligned} \hat{\epsilon}_n \cdot \underline{\eta} &= -\hat{\epsilon}_n \cdot \underline{\eta}' \\ \underline{\eta} - (\hat{\epsilon}_n \cdot \underline{\eta}) \hat{\epsilon}_n &= \underline{\eta}_\perp = \underline{\eta}'_\perp \\ \eta^2 &= \eta'^2. \end{aligned} \quad (9.10)$$

Furthermore the unit vector $\hat{\epsilon}_n$ can be written in the form

$$\hat{\epsilon}_n = (1/\rho) (0, \hat{H}, a_1, a_2), \quad (9.11)$$

where \hat{H} is a unit vector along $\underline{y} - \underline{y}'$ and $\rho^2 = 1 + a_1^2 + a_2^2$. These results are formally the same as those for rigid nonspherical bodies. However, they differ from the true rigid case

in that the shapes of the equivalent interacting rigid bodies (and in particular, a_1 and a_2) now depend upon the components of η .

The collision integral for any interaction model can now be written in the general form

$$[\xi, \psi]_{\mu, \nu}^{i, j} = \left(\frac{2kT}{\mu}\right)^{1/2} B^{(n)} \int d\hat{k} \int d\beta_1 \int d\beta_2 \int d\eta e^{-\eta^2} \quad (9.12)$$

$$\chi \Delta D(\hat{\epsilon}_n \cdot \eta) (\hat{T} \xi_{\mu}^i) [\psi_{\nu}(z) - \psi_{\nu}(z')]$$

where $(2kT/\mu)^{1/2} B^{(n)}$ is a normalization constant, ξ and ψ are basis functions of the expansion of the distortion, β_i is the orientation vector of molecule i , and Δ is a generalized cross section. The differences in the collision models are manifested in the variable dependence of Δ , that is,

$\Delta = \Delta(\beta_1, \beta_2, \hat{k})$ for rigid models (in particular, Δ is a constant for rigid spheres) and $\Delta = \Delta(\gamma, \hat{k})$ for spherical soft potentials, whereas in the general case $\Delta = \Delta(\beta_1, \beta_2, \hat{k}, \eta)$.

Equation 9.12 is, of course, an exact result and amounts to nothing more than a particular choice of integration variables to evaluate the general collision integral of Equation 4.18. The purpose of the foregoing discussion was merely to provide a rationale for this particular choice of variables in terms of a comparison with the rigid interaction model. To proceed we need an expression for Δ which we propose to choose in such a way as to

yield exact results in the limiting cases of a rigid interaction model and for a soft, spherical potential.

One possible method of approach arises from further consideration of the rigid body collision integrals as given in reference (44). The collision dynamics may be simply expressed in a rotated frame by introducing an orthogonal transformation matrix $\underline{\xi}$ defined such that

$$\underline{\xi} = \underline{\xi}^T \cdot \underline{\eta} \quad (9.13)$$

where $\underline{\xi}$ is the generalized momentum vector expressed in a coordinate frame that has \hat{e}_n as its n th unit vector. From the previous discussion it is seen that $\underline{\xi}$ is only a function of \hat{k} , β_1 , and β_2 . In the rotated frame, all $(n-1)$ components of $\underline{\xi}$ normal to \hat{e}_n are constants of the motion and ϵ_n (the component of $\underline{\xi}$ along \hat{e}_n) simply changes sign upon collision. The collision integrals then become

$$[\underline{\xi}, \psi]_{\mu, \nu}^{L, D} = \left(\frac{2\Delta T}{\mu}\right)^{1/2} B^{(n)} \int d\beta_\mu \int d\beta_\nu \int d\hat{k} \frac{d}{d_{r.s.}} \underline{\xi}_i \underline{\xi}_j : \Delta_{r.s.}(\underline{u}, \underline{v}) D \quad (9.14)$$

where

$$\Delta_{r.s.}(\underline{u}, \underline{v}) = \int_{\hat{e}_n > 0} d\underline{\xi} \Delta_{r.s.} d\underline{\xi} \epsilon_n \exp(-\epsilon^2) (\underline{u}' - \underline{u}) \underline{v}'. \quad (9.15)$$

Here $\langle \sigma \rangle_i$ is the average cross sectional area of a molecule i and $\Delta_{r.s.} = \frac{1}{\pi} (\langle \sigma \rangle_i + \langle \sigma \rangle_j + 2\sqrt{\langle \sigma \rangle_i \langle \sigma \rangle_j})$ is the value of Δ for rigid spheres. The tensors \underline{u} and \underline{v} are polyads in the n

dimensional vector space formed from u and v ξ 's, respectively, and the basis functions \underline{f}_i , written as a tensor in the multidimensional space, has the form $\underline{f}_i = \underline{S}_{f_i} \cdot \underline{u}$ where \underline{S}_{f_i} is a projection operator (see reference (44) for details). The primes denote precollision variables while the unprimes denote postcollision variables.

We see by comparison of Equations 9.12 and 9.14 that the valuation of $\mathcal{A}_{r,s}(u, v)$ is equivalent to performing the momentum integrations of the collision integral. This momentum integration is particularly simple since the only change upon collision is a change in the sign of the component along \hat{e}_n . Thus to perform the momentum integration we simply use the fact that $\underline{\xi} = \underline{\xi}_\perp + \epsilon_n \hat{e}_n$ and $\underline{\xi}' = \underline{\xi}_\perp - \epsilon_n \hat{e}_n$ where $\underline{\xi}_\perp$ is the projection of $\underline{\xi}$ on the subspace normal to \hat{e}_n . From Equation 9.15 it is evident that this momentum integral is independent of the shape of the rigid convex model. The shape dependence is instead, contained in D , the cross section δ , and the projection operators \underline{S}_{f_i} and \underline{S}_{ψ_j} . Thus the tensor $\mathcal{A}_{r,s}(u, v)$ is exactly the same for nonspherical molecules as it is for rigid spheres.

To generalize the model, we simply replace $\mathcal{A}_{r,s}(u, v)$ for the rigid sphere interaction by the appropriate corresponding quantity for a spherical soft potential and let the remaining quantities δ , \underline{S}_{f_i} , \underline{S}_{ψ_j} , and D retain their rigid convex body form. The collision integrals obtained

in this approximate manner will be exact in the limit of spherical, soft collisions and in the limit of nonspherical rigid body interactions.

The principles involved in this alteration of the collision integrals are reasonably straightforward but the algebraic details are rather tedious. Thus the actual calculations are left as a future project.

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APPENDIX

We first wish to prove the commutation relationship in Equation 6.19, namely

$$[\hat{H}_x^{(n)}, \hat{H}_y^{(n)}] = -i \hat{H}_z^{(n)}. \quad (\text{A.1})$$

From the definitions in Equations 6.15 and 6.17, we have as in Equation 6.18,

$$[\hat{H}_x^{(n)}, \hat{H}_y^{(n)}] = -(\hat{i} \times \underline{\underline{f}}^{(n)} \times \hat{j} - \hat{j} \times \underline{\underline{f}}^{(n)} \times \hat{i}). \quad (\text{A.2})$$

The identity element $\underline{\underline{f}}^{(n)}$ can always be expressed in terms of combinations of $\underline{\underline{f}}^{(1)}$, the 3-dimensional second rank unit tensor, which explicitly is

$$\underline{\underline{f}}^{(1)} = \hat{i} \hat{i} + \hat{j} \hat{j} + \hat{k} \hat{k} \equiv U. \quad (\text{A.3})$$

By definition, the symbol $\underline{\underline{f}}_{(n)}$ (where the subscript n is usually implied) in Equation A.2 indicates the sum of terms obtained by crossing the unit vector \hat{i} (or \hat{j} or \hat{k}) into each of the n right (or left) hand indices of $\underline{\underline{f}}^{(n)}$. The only terms of Equation A.2 which survive this summation of cross products are those terms which correspond to crossing both indices of a U which bridges the two sets of indices, that is, one index is a member of the left n indices and one index is a member of the right n indices.

We prove the above crossing properties by considering

a single U of the $2n$ rank tensor. If both indices of the U lie in either the left n or right n indices, the crossing operation will give a term with

$$\hat{U} \times U = \hat{U} \times U + (U \times \hat{U}) = 0 \quad (\text{A.4})$$

imbedded in the remaining $n-2$ indices of the left or right set. Hence to get a contribution the U must bridge the two sets of indices. Now consider the crossing into only one index of a bridging U . The commutation definition in Equation A.2 must necessarily give in sum the combination

$$\hat{U} \times U - U \times \hat{U} = 0 \quad (\text{A.5})$$

imbedded in a bridging manner in the resulting tensor. Thus bridging U 's with only one index crossed will not contribute. Finally, for a bridging U with both indices crossed we have from the commutation definition that the tensor

$$\hat{U} \times U \times \hat{U} - \hat{U} \times U \times \hat{U} = \hat{U} \times U = U \times \hat{U} \quad (\text{A.6})$$

will be imbedded in the resulting tensor. It follows immediately that

$$\hat{U} \times \underline{\underline{U}}^{(n)} \times \hat{U} - \hat{U} \times \underline{\underline{U}}^{(n)} \times \hat{U} = \underline{\underline{U}}^{(n)} \times \hat{U} \quad (\text{A.7})$$

From Equation A.2 and 6.15, this can be written as

$$[\hat{U}_x^{(n)}, \hat{U}_y^{(n)}] = -i \hat{U}_z^{(n)} \quad (\text{A.8})$$

and our proof is completed.

Next, we wish to prove the relationship given in Equation 6.25, that is,

$$(\hat{\underline{H}}^{(n)})^2 = n(n+1) \underline{f}^{(n)}. \quad (\text{A.9})$$

By definitions in Equations 6.21 and 6.15 we have that

$$(\hat{\underline{H}}^{(n)})^2 = \hat{\underline{H}}_x^{(n)} \circ^n \hat{\underline{H}}_x^{(n)} + \hat{\underline{H}}_y^{(n)} \circ^n \hat{\underline{H}}_y^{(n)} + \hat{\underline{H}}_z^{(n)} \circ^n \hat{\underline{H}}_z^{(n)} \quad (\text{A.10})$$

can be written in either the form

$$(\hat{\underline{H}}^{(n)})^2 = - \sum_{\hat{\alpha}} (\hat{\alpha} \underline{X} \underline{f}^{(n)} \underline{X} \hat{\alpha}) = - \underline{X} \underline{f}^{(n)} \underline{X} \quad (\text{A.11})$$

or

$$(\hat{\underline{H}}^{(n)})^2 = - \sum_{\hat{\alpha}} (\underline{f}^{(n)} \underline{X} \hat{\alpha} \circ^n \hat{\alpha} \underline{X} \underline{f}^{(n)}) = - \underline{f}^{(n)} \underline{X} (\circ^n) \underline{X} \underline{f}^{(n)} \quad (\text{A.12})$$

where $\hat{\alpha} = \hat{i}, \hat{j},$ or \hat{k} . From Equation A.12 we see that the first n and last n indices of $(\hat{\underline{H}}^{(n)})^2$ are traceless and symmetric. Hence, since $(\hat{\underline{H}}^{(n)})^2$ is isotropic, it must be proportional to $\underline{f}^{(n)}$. Let us now examine a single term of $\underline{f}^{(n)}$ in Equation A.11 which contains all bridging U 's. We first note that a term in $(\hat{\underline{H}}^{(n)})^2$ with all bridging U 's can only come from terms with all bridging U 's. For the term under consideration there are a total of n^2 combinations of crossing into n bridging U 's. Of these combinations, n have crosses into the same U , which results in 2^n bridging

U 's each with a factor of -1 . The remaining $n(n-1)$ combinations have crosses into different U 's and give rise to $n(n-1)$ bridging U 's each with a factor of -1 . Hence the crossing operation in effect multiplies each term of bridging U 's by a factor of $-n(n-1) - 2n$ or $-n(n+1)$ and thus

$$\left(\hat{H}_{\underline{z}}^{(n)}\right)^2 = n(n+1) \underline{z}^{(n)}. \quad (\text{A.13})$$

Finally we extend this last proof to the direct product tensor $\left(\hat{H}_{\underline{z}}^{(p+q)}\right)^2$. From the definitions in Equations 6.26 and 6.15 we have

$$\hat{H}_{\underline{z}}^{(p+q)} = -i \left[\hat{\alpha} X_{(p)} \underline{z}^{(p)} / \underline{z}^{(q)} + \underline{z}^{(p)} / \hat{\alpha} X_{(q)} \underline{z}^{(q)} \right] \quad (\text{A.14})$$

or

$$\hat{H}_{\underline{z}}^{(p+q)} = -i \hat{\alpha} X_{(p+q)} \left(\underline{z}^{(p)} / \underline{z}^{(q)} \right) = -i \hat{\alpha} X_{(p+q)} \underline{z}^{(p+q)}. \quad (\text{A.15})$$

By expressing the identity element for the direct product representation in terms of the identity elements for the irreducible representations, we have that

$$\begin{aligned} \left(\hat{H}_{\underline{z}}^{(p+q)}\right)^2 &= - \left(X \underline{z}^{(p+q)} X \right) = - \left(X \sum_{z=|p-q|}^{p+q} I_z^{(p+q)} X \right) \\ &= - \sum_{z=|p-q|}^{p+q} \left(X I_z^{(p+q)} X \right) \end{aligned} \quad (\text{A.16})$$

or

$$\left(\hat{q}_{\underline{1}}^{(\rho+q)}\right)^2 = -\underline{q}^{(\rho+q)} \sum \left(\underline{0}^{\rho+q}\right) \sum \underline{q}^{(\rho+q)}. \quad (\text{A.17})$$

These relations are established in a manner similar to Equations A.11 and A.12. From Equation A.17 we see that $\left(\hat{q}_{\underline{1}}^{(\rho+q)}\right)^2$ is a linear combination of the identity elements $\underline{I}_{\underline{1}}^{(\rho+q)}$. The last line of Equation A.16 makes use of the fact that the crossing operation does not transfer the identity element of an irreducible representation out of that representation.

If we now determine the number of bridging U 's in each $\underline{I}_{\underline{1}}^{(\rho+q)}$ we can apply the arguments of Equation A.13 to obtain the proportionality factor for each irreducible representation identity element in the linear combination. Consider as an example the irreducible representation of weight $|\rho-q|$. If we assume for discussion purposes that $\rho > q$, and consider a tensor $\underline{S}^{(\rho)} \underline{T}^{(q)}$ in the direct product basis where $\underline{S}^{(\rho)}$ is a traceless and symmetric tensor of weight ρ and $\underline{T}^{(q)}$ is a similar tensor of weight q , then $\underline{S}^{(\rho)} \otimes \underline{T}^{(q)}$ is a basis function for the irreducible representation of weight $|\rho-q|$. Thus the number of bridging U 's in the identity element for this irreducible representation is $(\rho-q)$, and the proportionality constant is then $(\rho-q)[(\rho-q)+1]$. A similar argument holds for every weight representation contained in the direct product basis, and thus we have that

$$\underline{\underline{(\hat{H}^{(p+g)})^2}} = \sum_{j=1}^{p+g} j(j+1) \underline{\underline{I_j^{(p+g)}}}, \quad (\text{A.18})$$

which establishes the desired relation.