1975

Prediction of transport properties of gases using classical nonspherical models

Jerome Daniel Verlin
Iowa State University

Recommended Citation

Verlin, Jerome Daniel, "Prediction of transport properties of gases using classical nonspherical models " (1975). *Retrospective Theses and Dissertations*. 5640.
https://lib.dr.iastate.edu/rtd/5640

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106

76-9609

VERLIN, Jerome Daniel, 1943-
PREDICTION OF TRANSPORT PROPERTIES OF GASES USING CLASSICAL NONSPHERICAL MODELS.

Iowa State University, Ph.D., 1975
Chemistry, physical

Xerox University Microfilms, Ann Arbor, Michigan 48106

Prediction of transport properties of gases using classical nonspherical models

by

Jerome Daniel Verlin

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Physical Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1975

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1. INTRODUCTION

In a fluid, the steady state transport (flux) of mass, linear momentum and kinetic energy is known to be related to gradients in concentration (for mixtures), velocity and temperature if the gradients are not too large. The linear phenomenological coefficients relating the fluxes to the gradients are known as transport coefficients. In general the fluxes act to dissipate the gradients. The elementary mechanism of this drive toward uniformity is that an average particle carries properties determined by the local equilibrium at the beginning of its mean free path to the end. Particle collisions regulate the flux by determining the mean free path length. Hence it is apparent that the transport coefficients are determined by the collision events and, therefore, by the intermolecular potential.

Brush (1), in a survey, points out the hope which existed at one time that an interaction potential derived from transport properties would be of a universal form governing all molecular interactions. This universal potential was envisioned by Newton (2) as a microscopic analog of the gravitational potential. However, experimental evidence from transport and other properties has accrued to demonstrate the impossibility of such a universality at such a relatively simple level. In the modern view intermolecular potentials can be computed from wave mechanics. Since transport properties are of primary concern to us, we do not search for universality but confine ourselves to the study and prediction of only these properties. In the process we use the simplest interaction model which corresponds closely enough to reality to accomplish the task at hand.

An exact analysis of transport phenomena in a gas begins with the fact that any flux J_ρ of a property ρ at a macroscopic point in a dilute gas can be written as

$$J_\rho = \langle \rho (\underset{\sim}{c} - \underset{\sim}{u}) \rangle \tag{1.1}$$

where $\underset{\sim}{c}$ is the velocity of a particle in the system, $\underset{\sim}{u}$ is the streaming velocity at the point, and $\langle a \rangle$ signifies an average of the value of a over all molecules at that point. It is necessary in applying Equation 1.1 to have a functional form for the distribution of molecules with respect to position, linear momentum and internal states. Assuming molecules to interact through a central force potential and using classical mechanics, Boltzmann (3) derived a closed integrodifferential equation for this distribution function. Chapman (4) and Enskog (5) independently obtained a particular (normal) solution to Boltzmann's equation by a judicious expansion of the singlet distribution function in a series whose zeroth order term is the local equilibrium singlet distribution function and whose higher order terms describe distortions from equilibrium which are due to gradients in the macroscopic field.

The significance of this normal solution can be seen by considering a system in some arbitrary distribution. If the environment of the system is uniform, the system relaxes, within a time of the order of the inverse of the collision frequency, to its normal state which is described by the Maxwell-Boltzmann equilibrium distribution function. If the environment is nonuniform, the system relaxes, also within a time of the order of the inverse of the collision frequency, to a normal state which is characterized by molecular migration which tends to dissipate spatial nonuniformity. This dissipation is modulated by collision processes which tend to maintain a local Maxwell-Boltzmann distribution. The normal state is that described by the Chapman-Enskog normal solution.

The Chapman-Enskog method leads to expressions for the transport properties in terms of collision integrals, which are various averages of the collision cross section. They are dependent on the collision interaction model. We will use a modified form of the Boltzmann equation, with the Chapman-Enskog solution, to analyze experiments for which the internal structure of the molecules is important.

The first such phenomenon which we analyze is the alteration of thermal conductivity (relating energy flux to the temperature gradient) and viscosity (relating linear momentum flux to the streaming velocity gradient) of a diamagnetic diatomic or polyatomic gas by the action of an applied magnetic field. These phenomena are referred to as Senftleben-Beenakker effects after Senftleben (6), who discovered the magnetic field effect on the thermal conductivity of a paramagnetic gas (O_2), and Beenakker (7), who initially found this effect in viscosity of diamagnetic diatomic gases (N_2 and CO). For diamagnetic molecules (which is the case we study) there is a small net magnetic moment, due to molecular tumbling, which precesses about the field. This precession causes an increase in the collision cross section and hence a decrease in the transport coefficients. Much of the experimental work on the Senftleben-Beenakker effect has been reviewed in articles by Beenakker (8, 9). The particular Senftleben-Beenakker effect measurements of concern in this work are contained in References 10-13. The reason that internal structure is important in this case is that the field partially destroys an anisotropy in the angular momentum distribution which affects the transport properties. This anisotropy is caused by macroscopic field gradients; it cannot be produced if the molecules do not have internal structure and hence do not suffer nonspherical collisions.

The second phenomena we study is thermal diffusion in isotopic binary mixtures of CO. The thermal diffusion coefficient is the factor of proportionality between the flux of mass and the temperature gradient. There is no simple picture for thermal diffusion because it depends on the mean free path of both the thermal conductivity and the diffusion processes. Cowling (14) has given a lengthy "elementary" interpretation of thermal diffusion. The measurements we use were made by Boersma-Klein and deVries (15) over a temperature range for which this property inverts (i.e., the direction of the mass flux along the gradient is reversed) for all mixtures studied. The reason that internal structure is important in this case is that the effect is observed in mixtures whose components have the same total mass but unequal mass distribution.

The effect of translational degrees of freedom on transport can be dealt within the scope of a classical theory (i.e., the Boltzmann equation). The effect of rotational degrees of freedom on transport is quantum mechanical in origin (for which a new formulation is necessary) but can be treated approximately in the classical limit. The vibrational degrees of freedom are not important in transport at ordinary temperatures because vibrational spacing is large compared to kT (where k is Boltzmann's constant and T is the local temperature). Thus nonspherical models with rotational structure are sufficient to account for the important effects in the cases we study.

The first attempts to formulate a quantum mechanical kinetic equation were made for spherical models (16). In this work a quantum mechanical cross section was substituted for the classical mechanical cross section in the Boltzmann equation. In the same way Wang-Chang and Uhlenbeck (17) extended the Boltzmann equation for molecules with rotational degrees of freedom. In the latter case, the equation is merely an extension beyond the classical limit and does not rigorously follow from quantum mechanics. Waldmann (18) and Snider (19) have derived a rigorous quantum mechanical generalization of the Boltzmann equation which properly takes into account rotational structure. McCourt and Snider (20, 21) have shown how the Waldmann-Snider equation can be applied to the analysis of the Senftleben-Beenakker effects.

Although the quantum mechanical generalization of transport theory has been made, we use a classical theory. The advantage of this latter theory is that it reproduces the major features of the experiments studied and it is still relatively easy to apply. As a starting point for the classical approach, a generalized Boltzmann equation for molecules with internal states is needed. The first modification of the Boltzman equation in this direction was made by Pidduck (22) for the rough sphere model (rough spheres are rigid spheres which collide without slipping). Although this model has collisionally active rotational degrees of freedom, it is unrealistic in that the molecular forces and torques are not determined solely from the molecular configuration. Curtiss (23), in his original attempt to develop a general classical theory to account for orientation dependence of the interaction potential, did not allow for the nonequilibrium distortion of the distribution function to contain any anisotropy in the angular momentum. As a consequence no Senftleben-Beenakker effects are predicted. Kagan and Afanas'ev (24) were the first to correct this restriction of Curtiss. Since then many contributors have improved the derivation of extensions of the Boltzmann equation and have refined their application (see, for instance, the review by Dahler and Hoffman (25)). We use the formulation of one of the more recent of these works by Hoffman and Dahler (26).

Rigid, classical, convex bodies of revolution have been applied as models to the calculation of the Senftleben-Beenakker effect. Klein et al. (27) have used rough spheres as a molecular model and loaded spherocylinders (28) (a cylinder whose flat ends are replaced by hemispherical caps of the same radius as the cylinder) to model linear molecules. The latter model was a substantial improvement for linear molecules. Cooper and Hoffman (29) have found the loaded rigid ellipsoid to be a more versatile model for linear molecules.

The classical model used by Sandler and Dahler (30) to calculate thermal diffusion in a D_2-HD mixture was the loaded rigid sphere. For the same phenomenon in binary mixtures of CO isotopes, Matzen et al. (31) have applied a rigid ellipsoid model. Rigid models were found to fit these data fairly well at a single high temperature but could not correctly predict the temperature dependence.

Though we apply classical, nonspherical collision models to transport analysis, other methods have been used in regard to the same phenomena. Köhler (32) has performed a quantum mechanical model calculation of Senftleben-Beenakker effects using the distorted Born wave approximation. The collision model used was that of two ellipsoids which are repelled by a constant force when they touch or overlap but do not otherwise interact. A second method is that of a classical trajectory calculation in which collisions are simulated for all conditions by computer instead of being solved analytically. In this manner van de Ree and Scholtes (33a) have calculated diffusion and thermal diffusion in HD-D_2 using a loaded soft sphere model for HD and a central soft model for D_2. Malone (in Reference 33b) has also done trajectory calculations on HD.

In Chapter 2 we review the derivation of the nonspherical Boltzmann equation as given in Reference 26. In Chapter 3 we review the Chapman-Enskog solution as given for the case of the Senftleben-Beenakker effect in Reference 29 and for the case of thermal diffusion in isotopic binary mixtures in Reference 31. The Onsager-Casimer relations are also proven within the context of this formulation.

In order to apply a model in the Chapman-Enskog method, one always has to evaluate collision integrals. The problems in doing this are first to derive a form for the collision cross section and second to perform the integrations over colliding particles' momenta and orientations. In Chapter 4 we give forms for the cross section for both soft spheres and rigid ovaloids. We generalize these results by approximating the form of a generalized cross section for a nonspherical soft model to include attributes of the two limiting cases of soft spheres and rigid ovaloids. The assumed form of the generalized cross section can be related to a Kihara (34) type collision model for which the molecules are assumed to possess generally shaped cores which interact through a soft potential. This potential is determined by the shortest distance between the cores. The significance of the cores is that when they touch the potential is zero. Hoffman (35) has shown for rigid ovaloid models how the momentum integrations of the collision integrals can be performed. We apply this method to the momentum integrations for the general soft model. We also extend this work on rigid convex models to derive a more convenient form for the results of the momentum integrations.

In Chapter 5 we show the details and results of the application of a rigid convex model to the calculation of the Senftleben-Beenakker effect on CX_4 molecules. The separation of the integrand in order to facilitate the orientation integrations is given. The parameters of the model are optimized and the resulting fits of the data are found to be comparable to those of Cooper and Hoffman (29) on linear molecules.

In Chapter 6 we show the results of the application of the soft ellipsoidal model to the phenomenon of thermal diffusion in binary isotopic mixtures of CO. The parameters of the model can be chosen to reproduce every major feature of the data (15). Using the same parameters, thermal conductivity of pure CO is matched exactly and isotopic binary diffusion is matched fairly well.

CHAPTER 2. DERIVATION OF THE BOLTZMANN EQUATION

Hoffman and Dahler (26) have derived a Boltzmann equation for classical particles with translational and rotational degrees of freedom. What appears here is an expanded version of that treatment. It is included here for completeness.

For simplicity we consider a system containing a single species. We define a 12-N dimensional phase space whose points specify the linear and angular coordinates of position and momentum of the N particles in the system. For each particle, i , $\underline{x}_i$ specifies the position of the center of mass, $\underline{p}_i$ is the momentum conjugate to $\underline{x}_i$, $\underline{\alpha}_i$ is the set of Eulerian angles of orientation of the particle and $\underline{\mathfrak{p}}_i$ is the momentum conjugate to $\underline{\alpha}_i$. We now consider a representative ensemble of the system and define D as the density function describing the distribution of the ensemble systems in phase space. This distribution function is normalized to unity over all phase space and is symmetric in all particles of a system. Within a differential volume in phase space at a given time there are phase points of systems in the ensemble. It is a standard result from classical mechanics that a volume of phase space does not change in size as it evolves in time. (See, for instance, Goldstein (36)). Since the number of systems under consideration also does not change, the ensemble distribution function does not change along the trajectory of the differential volume, i.e.

$$\frac{dD}{dt} = \frac{\partial D}{\partial t} + \sum_{i=1}^{N} \left[\frac{\partial D}{\partial \underline{x}_i} \cdot \frac{d\underline{x}_i}{dt} + \frac{\partial D}{\partial \underline{p}_i} \cdot \frac{d\underline{p}_i}{dt} + \frac{\partial D}{\partial \underline{\alpha}_i} \cdot \frac{d\underline{\alpha}_i}{dt} \right.$$

$$\left. + \frac{\partial D}{\partial j_i} \cdot \frac{dj_i}{dt} \right] = 0 \quad . \tag{2.1}$$

The Hamiltonian of an N particle system is given by

$$H^{(N)} = \sum_{i=1}^{N} \left(\frac{p_i^2}{2m_i} + H_i^{rot} \right) + \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} V_{ij} \tag{2.2}$$

where m_i is the mass of particle i, H_i^{rot} is the rotational kinetic energy contribution to the Hamiltonian of particle i and V_{ij} is the interaction potential between particle i and particle j. We assume in Equation 2.2 that the forces between particles are pairwise additive. Using Hamilton's equations we can write that

$$\frac{\partial D}{\partial t} + [D, H^{(N)}] = 0 \tag{2.3}$$

where the bracketed quantity, called the Poisson bracket, is given by

$$[D, H^{(N)}] = \sum_{i=1}^{N} \left(\frac{\partial D}{\partial \underline{x}_i} \cdot \frac{\partial H^{(N)}}{\partial \underline{p}_i} + \frac{\partial D}{\partial \underline{\alpha}_i} \cdot \frac{\partial H^{(N)}}{\partial j_i} - \frac{\partial D}{\partial \underline{p}_i} \cdot \frac{\partial H^{(N)}}{\partial \underline{x}_i} - \frac{\partial D}{\partial j_i} \cdot \frac{\partial H^{(N)}}{\partial \underline{\alpha}_i} \right) . \tag{2.4}$$

The expression in Equation 2.3 is the usual form of the Liouville theorem.

We can define a set of distribution functions for any n $(<N)$ particles of the system as follows:

$$f_n \equiv \frac{N!}{(N-n)!} \int d\underline{Y}_N \int d\underline{Y}_{N-1} \cdots \int d\underline{Y}_{n+1} \; D \tag{2.5}$$

where $d\underline{Y}_i = d\underline{x}_i \, d\underline{p}_i \, d\underline{\alpha}_i \, d\mathfrak{j}_i$ and the factorials arise from the indistinguishability of particles. The quantity defined by Equation 2.5 is a function of the positions, orientations and momenta of n particles and gives the probability density of finding any n particle subset of the total number with these coordinates and momenta. If one performs the integrations of Equation 2.5 on both sides of Equation 2.3, the result is

$$\frac{\partial f_n}{\partial t} + [f_n, H^{(n)}] = \sum_{i=1}^{n} \int d\underline{Y}_{n+1} \left\{ \frac{\partial}{\partial \underline{x}_i} \cdot \left(f_{n+1} \frac{\partial V_{i,n+1}}{\partial \underline{p}_i} \right) + \frac{\partial}{\partial \underline{\alpha}_i} \cdot \left(f_{n+1} \frac{\partial V_{i,n+1}}{\partial \mathfrak{j}_i} \right) \right.$$

$$\left. - \frac{\partial}{\partial \underline{p}_i} \cdot \left(f_{n+1} \frac{\partial V_{i,n+1}}{\partial \underline{x}_i} \right) - \frac{\partial}{\partial \mathfrak{j}_i} \cdot \left(f_{n+1} \frac{\partial V_{i,n+1}}{\partial \underline{\alpha}_i} \right) \right\} . \tag{2.6}$$

This set of equations is called the BBGKY coupled hierarchy of equations. As a practical matter, it is impossible to solve for D from Equation 2.3 and to hence find $f_{N-1}, f_{N-2} \cdots \cdot f_1$ from Equation 2.5. Instead, by using approximations appropriate to a dilute gas, we derive the Boltzmann equation, which is a closed equation for f_1, the singlet distribution function.

As O'Toole and Dahler (37) point out, the singlet distribution function which appears in the Boltzmann equation does not include particles which are in the process of collision. In order to define when a collision is occurring, we construct a geometrical convex surface, σ_{ij}, about the center of mass of particle i such that it exceeds the range of the intermolecular forces. Whenever the center of mass of any particle j crosses σ_{ij}, we consider it as having entered into collision with i. The singlet distribution function, $\tilde{f}_1$, appropriate to isolated particles (i.e., those not in collision) can be written by Equation 2.5 as

$$\tilde{f}_1(\underline{1}) = N \int d\underline{Y}_2 \cdots\cdots \int d\underline{Y}_N \left(\prod_{j=1}^{N} \xi_{1j} \right) D \tag{2.7}$$

where ξ_{1j} is zero whenever the center of mass of j lies within σ_{1j} but is unity otherwise. The dependence of on the variables of body 1 is indicated explicitly. The integral transform which is applied to D in Equation 2.7 can be applied to the Liouville theorem with the result that

$$\frac{\partial \tilde{f}_1(\underline{1})}{\partial t} + N \int d\underline{Y}_2 \cdots \int d Y_N \prod_{j=2}^{N} \xi_{1j} \left[D, \sum_{i=1}^{N} H_{ii} \right] =$$

$$-N \int d\underline{Y}_2 \cdots \int d\underline{Y}_N \prod_{j=2}^{N} \xi_{1j} \left[D, \frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{N} V_{ik} \right] \tag{2.8}$$

where $H_{ii} \equiv \left(\frac{p_i^2}{2m_i}\right) + H_i^{rot}$. Using the fact that the particles are indistinguishable and integrating by parts, we can write Equation 2.8 as

$$\frac{\partial \tilde{f}_1(\underline{1})}{\partial t} + [\tilde{f}_1, H_{11}] - \int d\underline{Y}_2 \, \tilde{f}_2(\underline{1}, \underline{2}) [\xi_{12}, H_{11} + H_{22}]$$

$$= -N \int d\underline{Y}_2 \cdots \int d\underline{Y}_N \prod_{j=2}^{N} \xi_{1j} \left[D, \frac{1}{2} \sum_{i=1}^{N} \sum_{k=1}^{N} V_{ik} \right] \tag{2.9}$$

where $\tilde{f}_2$ is the distribution function for pairs of particles, one of which is isolated as described above. This function is given by

$$\tilde{f}_2(\underline{1}, \underline{2}) = \frac{N!}{(N-2)!} \int d\underline{Y}_3 \cdots \int d\underline{Y}_N \prod_{j=3}^{N} \xi_{1j} D \ . \tag{2.10}$$

The nonzero domains of ξ_{1j} and V_{1j} do not overlap. The right hand side of Equation 2.9 is therefore zero and we have that

$$\frac{\partial \tilde{f}_1(\underline{1})}{\partial t} + [\tilde{f}_1(\underline{1}), H_{11}] = \partial_c \tilde{f}_1(\underline{1}) \tag{2.11}$$

where

$$\partial_c \tilde{f}_1(\underline{1}) = \int d\underline{Y}_2 \, \tilde{f}_2(\underline{1}, \underline{2}) [\xi_{1,2}, H_{11} + H_{22}] \ . \tag{2.12}$$

The implication of Equation 2.11 is that the collisional rate of change of the singlet distribution function of free particles is equal to the difference between the rate that pairs of particles involved in isolated binary collisions disengage by particle 2 passing outwardly through σ_{12} and the rate that isolated particles engage by particle 2 passing inwardly through σ_{12}.

The description of the convex surface σ_{12} can be given in terms of its supporting function, h (see Appendix A). The surface may be scaled by multiplying h by a scaling factor, ρ, wherever it appears in Appendix A. Specifically, the differential surface area of the scaled surface is $\rho^2 S \, d\hat{k}$ where S is the ratio of the area on the original surface corresponding to a unit solid angle of the surface normal $\hat{k}$. The position of the center of mass of body 2 with respect to the center of mass of body 1 can be specified by giving the instantaneous ρ value for the scaled surface on which the center of mass of body 2 lies and $\hat{k}$ at that point. Thus the differential volume, $d\underline{x}_2$, for the position vector of $\underline{2}$ is given by

$$d\underline{x}_2 = \rho^2 h \, S \, d\rho \, d\hat{k} \quad . \tag{2.13}$$

The scaling parameter is unity at the instant that particle 2 passes through σ_{12}. We can use this fact to write ξ_{12}

in the form

$$\xi_{12} = \hat{\eta}(\rho - 1) \qquad (2.14)$$

where $\hat{\eta}$ is the unit step function whose discontinuity occurs at $\rho = 1$. The time derivative of the step function is the delta function. Explicitly taking the time derivative of ξ_{12}, we obtain that

$$\frac{d\xi_{12}}{dt} = \delta(\rho - 1)\dot{\rho} \; . \qquad (2.15)$$

When Equations 2.13 and 2.15 are substituted into Equation 2.12, we have that

$$\partial_c \tilde{f}_1(\underline{1}) = \partial_c f_1(\underline{1}) = \int d\underline{2} \int d\hat{k}\, S \dot{\rho}\, h\, \tilde{f}_2(\underline{1}, \underline{2}) \qquad (2.16)$$

where $d\underline{i} = d\underline{p}_i\, d\underline{a}_i\, d\mathfrak{J}_i$. In this equation the first equality results from the fact that the difference between $\tilde{f}_1$ and f_1 can be dropped for dilute gases in which permanently bound molecular pairs do not exist to an appreciable extent.

Up to this point, what we have done has been rigorous. Now it is convenient to make the first of three assumptions which are based on Bogoliubov's (38) description of the approach to equilibrium. Briefly this view concerns three time scales: the time scale appropriate to a time of the duration of a single collision, τ_c, when all of the f_n $(n > 1)$ become functionals of f_1 (which does not change on this time scale); the time scale appropriate to a time, τ_*, during which a particle travels between collisions and local equilibrium is established; and the time scale appropriate to a time, τ_m, during which macroscopic changes occur and establish equilibrium. It is then reasonable to assume that f_1 is independent of events which occur on the τ_c time scale and the $\left|\frac{p_2}{m_2} - \frac{p_1}{m_1}\right| \tau_c$ length scale. A consequence of this assumption is that we can choose an arbitrary shape for σ_{12}; a sphere is most convenient.

For spheres h is a constant and

$$\dot{\rho} h = \left(\frac{p_2}{m_2} - \frac{p_1}{m_1}\right)\cdot\hat{k} \quad . \tag{2.17}$$

The differential surface area of the spherical surface, σ_{12}, of radius R is $R^2 d\hat{k}$. We can then rewrite Equation 2.11 using Equation 2.16 to obtain

$$\frac{\partial f_1}{\partial t}(\underline{1}) + [f_1(\underline{1}), H_{11}] =$$

$$R^2 \int d\underline{2} \int d\hat{k} \left(\frac{\hat{p}_2}{m_2} - \frac{\hat{p}_1}{m_1}\right)\cdot\hat{k}\, f_2(\underline{1},\underline{2}) \quad . \tag{2.18}$$

For any relative velocity of the centers of mass of the two particles, the sphere σ_{12} can be divided into precollision and postcollision regions. When we separate the integration over $d\hat{k}$ into these regions, Equation 2.18

becomes

$$\partial_c f_1(\underline{1}) = R^2 \int d\underline{2} \int d\hat{k} \, \Big[\gamma\Big(\Big(\frac{p_2}{m_2} - \frac{p_1}{m_1}\Big)\cdot\hat{k}\Big) \, \tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{post} - \gamma\Big(-\Big(\frac{p_2}{m_2} - \frac{p_1}{m_1}\Big)\cdot\hat{k}\Big) \, \tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{pre} \Big] \tag{2.19}$$

where $\gamma(x) = x\,\eta(x)$ and the "pre" and "post" subscripts indicate on which hemisphere the variables of $\underline{1}$ and $\underline{2}$ are evaluated. By changing the variable of integration $\hat{k}$ to $-\hat{k}$ in the precollision term of Equation 2.19, we obtain

$$\partial_c f_1(\underline{1}) = R^2 \int d\underline{2} \int d\hat{k} \, \gamma\Big(\Big(\frac{p_2}{m_2} - \frac{p_1}{m_1}\Big)\cdot\hat{k}\Big) \Big[\tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{post} - \tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 - R\hat{k}, \underline{2}; t)_{pre} \Big] \, . \tag{2.20}$$

The second assumption is that the collisions are isolated binary events. This means that corresponding to every postcollisional state $(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{post}$ there is a unique precollisional (starred) state $(\underline{x}_1^*, \underline{1}^*; \underline{x}_1^* + R\hat{k}^*, \underline{2}^*; t-\tau_c)_{pre}$ from which that postcollisional state evolves. We can then replace $\tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{post}$ with $\tilde{f}_2(\underline{x}_1^*, \underline{1}^*; \underline{x}_1^* + R\hat{k}^*, \underline{2}^*; t-\tau_c)$ in Equation 2.19. The third assumption is that of molecular chaos; that is, on the precollision hemisphere there is no correlation of states of colliding molecules. Thus we can factor $\tilde{f}_2(\underline{x}_1, \underline{1}; \underline{x}_1 + R\hat{k}, \underline{2}; t)_{pre}$ into $f_1(\underline{1}) f_1(\underline{2})$. Upon application of all three assumptions on Equation 2.20, we have that

$$\partial_c f_1(\underline{1}) = R^2 \int d\underline{2} \int d\hat{k}\ \gamma\left(\left(\frac{p_2}{m_2} - \frac{p_1}{m_1}\right)\cdot\hat{k}\right)$$

$$\left[f_1(\underline{1}) f_1(\underline{2}) - f_1(\underline{1}^*) f_1(\underline{2}^*) \right] \quad . \qquad (2.21)$$

Both sides of Equation 2.21 may be multiplied by $\delta(\underline{1}' - \underline{1}^*)\ \delta(\underline{2}' - \underline{2}^*)$ and integrated over the variables $\underline{1}'$ and $\underline{2}'$ to yield

$$\partial_c f_1(\underline{1}) = R^2 \int d\underline{1}' \int d\underline{2}' \int d\underline{2} \int d\hat{k}\ \gamma\left(\left(\frac{p_2}{m_2} - \frac{p_1}{m_1}\right)\cdot\hat{k}\right) \delta(\underline{1}' - \underline{1}^*)$$

$$\delta(\underline{2}' - \underline{2}^*) \left[f_1(\underline{1}) f_1(\underline{2}) - f_1(\underline{1}') f_2(\underline{2}') \right] \qquad (2.22)$$

where the primed states refer to any precollisional state and $\delta(\underline{i}' - \underline{i}^*) = \delta(\underline{\alpha}_i' - \underline{\alpha}_i^*)\, \delta(p_i' - p_i^*)\, \delta(j_i' - j_i^*)$.

We can change from a postcollision hemisphere of radius R to a cylinder whose axis is mounted along $\frac{p_2}{m_2} - \frac{p_1}{m_1}$. The head of the cylinder is mounted at a distance R'' from the center of molecule 1 and is called the postcollision impact plane which is specified by the impact parameter $\underline{b}$.

In terms of the impact plane Equation 2.22 can be rewritten as

$$\partial_c f_1(\underline{1}) = \int d\underline{1}' \int d\underline{2}' \int d\underline{2} \int d^2\underline{b} \ \left| \frac{p_2}{m_2} - \frac{p_1}{m_1} \right| \delta(\underline{1}' - \underline{1}^*)$$

$$\delta(\underline{2}' - \underline{2}^*) \ [f_1(\underline{1}) f_1(\underline{2}) - f_1(\underline{1}') f_1(\underline{2}')] \qquad (2.23)$$

where all the variables are evaluated at R''. This is not yet the desired form of the Boltzmann equation. In order to proceed, we must define and investigate the properties of the specific transition rate.

The specific transition rate, $w_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\underline{2}'\,R)$, is the rate (per unit concentration of reactant states and per unit extension in the phase space of the final states) of the binary collision process $\underline{1}'\underline{2}'(R) \rightarrow \underline{1}\,\underline{2}(R)$ in the presence of an external field F. The functional form of w_F has certain restrictions. The transition rate exhibits Galilean invariance and hence can only depend on the velocity of the center of mass and the pre and postcollision relative linear velocities between the two colliding particles. Conservation of linear momentum of the center of mass in collision requires that w_F be proportional to $\delta(\underline{G} - \underline{G}')$ where $G = (p_2 + p_1)/(m_2 + m_1)$. Conservation of energy requires that w_F be proportional to $\delta(E - E')$ where E is the total energy of the pair.

From the properties of classical collisions, the actions of the time reversal operator, $\hat{T}$, and the parity reversal operator, $\hat{P}$, on the collision situation lead respectively to the following conditions on w_F :

$$w_F(\underline{1}\ \underline{2}\ R\,|\,\underline{1}'\ \underline{2}'R) = w_{\hat{P}F}(\hat{P}\underline{1}\ \hat{P}\underline{2}R\,|\,\hat{P}\underline{1}'\ \hat{P}\underline{2}'R) \qquad (2.24)$$

and

$$w_F(\underline{1}\ \underline{2}\ R\,|\,\underline{1}'\ \underline{2}'R) = w_{\hat{T}F}(\hat{T}\underline{1}'\ \hat{T}\underline{2}'R\,|\,\hat{T}\underline{1}\ \hat{T}\underline{2}R) \ . \qquad (2.25)$$

An additional important property of w_F , proved in Appendix B, is that of bilateral normalization

$$\int d\underline{1} \int d\underline{2}\ w_F(\underline{1}\ \underline{2}\ R\,|\,\underline{1}'\ \underline{2}'R) =$$

$$\int d\underline{1} \int d\underline{2}\ w_F(\underline{1}'\underline{2}'R\,|\,\underline{1}\ \underline{2}\ R) \ . \qquad (2.26)$$

In order to get an explicit form for w_F, we consider a steady state scattering experiment in which one has a uniform unit density beam of particles in state $\underline{1}'$ colliding with a similar beam of particles in state $\underline{2}'$. It is specified that the particles have only the single isolated binary collision. The type $\underline{1}'$ particles have an observational sphere around them and the postcollision impact plane can be designated in the usual way. The ensemble density associated with this experiment, Z, is the solution to the two particle Liouville theorem, $[Z, H^{(2)}] = 0$, and satisfies the boundary condition $Z = \delta(\underline{1} - \underline{1}')\ \delta(\underline{2} - \underline{2}')$ on the precollision impact plane and $Z = \delta(\underline{1}' - \underline{1}^*)\ \delta(\underline{2}' - \underline{2}^*)$ on the postcollision impact plane. By the definitions of specific transition rate, ensemble density and steady state scattering experiment, we can express W_F as

$$W_F(\underline{1}\ \underline{2}\ R'' \mid \underline{1}'\ \underline{2}'\ R'') = \int d^2\underline{b}\ \left| \frac{p_2}{m_2} - \frac{p_1}{m_1} \right| \cdot$$

$$\delta(\underline{1}' - \underline{1}^*)\ \delta(\underline{2}' - \underline{2}^*) \tag{2.27}$$

which is recognized as a portion of Equation 2.23. By substitution of Equation 2.27 into Equation 2.23, we can write Equation 2.18 as

$$\frac{\partial f_1(\underline{1})}{\partial t} + [f_1(\underline{1}), H_{11}] = \int d\underline{1}' \int d\underline{2}' \int d\underline{2}\ W_F(\underline{1}\ \underline{2}\ R'' \mid \underline{1}'\ \underline{2}'\ R'')$$

$$[f_1(\underline{1})\ f_1(\underline{2}) - f_1(\underline{1}')\ f_1(\underline{2}')] \ . \tag{2.28}$$

The orientations of the particles typically change at a rate much faster than τ_a. We have assumed that $f_1(\underline{1})$ is independent of such events. Therefore Equation 2.28 can be integrated over $\underline{\alpha}_1$ to obtain

$$\frac{\partial f_1(\bar{\underline{1}})}{\partial t} + [f_1(\bar{\underline{1}}), \bar{H}_{11}] = \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}}\ W_F(\bar{\underline{1}}\ \bar{\underline{2}} \mid \bar{\underline{1}}'\ \bar{\underline{2}}')$$

$$[f_1(\bar{\underline{1}})\ f_1(\bar{\underline{2}}) - f_1(\bar{\underline{1}}')\ f_1(\bar{\underline{2}}')] \tag{2.29}$$

where $d\bar{\underline{i}} = d\underline{p}_i \, d\underline{q}_i$, $f_1(\bar{\underline{i}}) = \Delta_i \, f_1(\underline{i})$, $\Delta_i = \int d\underline{\alpha}_i$,

$\bar{H}_{ii} = \frac{1}{\Delta_i} \int d\underline{\alpha}_i \, H_{ii}$ and

$$W_F(\bar{\underline{1}}\,\bar{\underline{2}} \mid \bar{\underline{1}}'\,\bar{\underline{2}}') = \frac{1}{\Delta_1 \Delta_2} \int d\underline{\alpha}_1 \int d\underline{\alpha}_2 \int d^2\underline{b} \, \left| \frac{\underline{p}_2}{m_2} - \frac{\underline{p}_1}{m_1} \right|$$

$$\delta(\bar{\underline{1}}' - \bar{\underline{1}}^*) \, \delta(\bar{\underline{2}}' - \bar{\underline{2}}^*) \quad . \tag{2.30}$$

The expression of Equation 2.29 is the desired form of the Boltzmann equation.

CHAPTER 3. LINEAR PHENOMENOLOGICAL DESCRIPTION OF THE FLUID

The form of the Boltzmann equation given in Equation 2.29 can be generalized easily at this point to cover the situation in mixtures. In this case, the right hand side of Equation 2.29 becomes an expression for the time rate of change along a phase trajectory of f_{1i} where the second subscript i refers to the species. On the left hand side one must account for the collisional change in f_{1i} caused by collisions with all species. Thus the Boltzmann equation for a mixture is

$$\frac{\partial f_{1i}}{\partial t}(\bar{\underline{1}}) + [f_{1i}(\bar{\underline{1}}), \bar{H}_{11}] = \sum_{j} \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}}\, W_F(\bar{\underline{1}}\bar{\underline{2}}|\bar{\underline{1}}'\bar{\underline{2}}')$$

$$[f_{1i}(\bar{\underline{1}}) f_{1j}(\bar{\underline{2}}) - f_{1i}(\bar{\underline{1}}') f_{1j}(\bar{\underline{2}}')] . \qquad (3.1)$$

The left hand side of Equation 3.1 can be rewritten as

$$\frac{\partial f_{1i}}{\partial t}(\bar{\underline{1}}) + \frac{\partial f_{1i}}{\partial \underline{\alpha}_1}(\bar{\underline{1}}) \cdot \underline{c}_1 + \frac{\partial f_{1i}}{\partial \underline{c}_1}(\bar{\underline{1}}) \cdot \hat{F}_i^e + \frac{\partial f_{1i}}{\partial \underline{L}_1}(\bar{\underline{1}}) \cdot \bar{\underline{\mu}}_i(\underline{1}) \times \underline{\mathcal{E}}$$

where $\hat{F}_i^e$ is the body force per unit mass acting on the center of mass of i species molecules, $\underline{L}_1$ is the angular momentum vector of body 1 and $\bar{\underline{\mu}}_i(\underline{1}) \times \underline{\mathcal{E}}$ is the torque of the applied field $\underline{\mathcal{E}}$ on the i species molecules whose orientation averaged moment at constant $\underline{L}_1$ is $\bar{\underline{\mu}}_i$.

The Chapman-Enskog normal solution to the Boltzmann equation derives from consideration of the relative magnitudes of the terms in that equation. Using the transformed left hand side above, we rearrange Equation 3.1 as

$$\frac{\partial f_{1i}(\bar{\underline{1}})}{\partial t} + \frac{\partial f_{1i}(\bar{\underline{1}})}{\partial \underline{x}_1} \cdot \underline{c}_1 + \frac{\partial f_{1i}(\bar{\underline{1}})}{\partial \underline{c}_1} \cdot \hat{F}_i^e = -\frac{\partial f_{1i}(\bar{\underline{1}})}{\partial \underline{L}_1} \cdot$$

$$\bar{\underline{\mu}}_i(\underline{1}) \times \underline{\mathcal{H}} + \sum_j \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}} \; W_F(\bar{\underline{1}}\,\bar{\underline{2}} \mid \bar{\underline{1}}'\bar{\underline{2}}')$$

$$\left[f_{1i}(\bar{\underline{1}})\, f_{1j}(\bar{\underline{2}}) - f_{1i}(\bar{\underline{1}}')\, f_{1j}(\bar{\underline{2}}') \right] . \tag{3.2}$$

We now assume that the gradients and the body forces are small. By dimensional analysis, Hoffman and Dahler (26) show that the terms of the left hand side of Equation 3.2 are of the same magnitude but they are all much smaller than the terms on the right hand side (for possible large values of the applied field strength). We define ϵ as a marking parameter to identify the small terms (ultimately $\epsilon = 1$). The standard method is to multiply the left hand side of Equation 3.2 by ϵ and to expand the singlet distribution functions and $\frac{\partial}{\partial t}$ in terms whose magnitudes can also be marked by powers of ϵ as follows:

$$f_{1i}(\bar{\underline{1}}) = f_{1i}^{[0]}(\bar{\underline{1}}) + \epsilon f_{1i}^{[1]}(\bar{\underline{1}}) + \epsilon^2 f_{1i}^{[2]}(\bar{\underline{1}}) \cdots \tag{3.3}$$

and

$$\frac{\partial}{\partial t} = \frac{\partial}{\partial_0 t} + \epsilon \frac{\partial}{\partial_1 t} + \epsilon^2 \frac{\partial}{\partial_2 t} \cdots \quad . \tag{3.4}$$

This done, the expressions in Equation 3.2 yield an equation which must be obeyed to all powers of ϵ .

The equation which is formed by the terms of zero power of ϵ is

$$0 = - \frac{\partial f_{1i}^{[0]}(\bar{\underline{1}})}{\partial \underline{\underline{L}}_1} \cdot \underline{K}_i(\bar{\underline{1}}) \times \underline{\xi} + \sum_j \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}}$$

$$W_F(\bar{\underline{1}}\,\bar{\underline{2}} \mid \bar{\underline{1}}'\,\bar{\underline{2}}') \; [\, f_{1i}^{[0]}(\bar{\underline{1}}) \; f_{1j}^{[0]}(\bar{\underline{2}})$$

$$- f_{1i}^{[0]}(\bar{\underline{1}}') \; f_{1j}^{[0]}(\bar{\underline{2}}') \,] \quad . \tag{3.5}$$

It is generally true that the solution to Equation 3.5 is the Maxwell-Boltzmann equilibrium distribution function. For a particle of general symmetry, the equilibrium singlet distribution function is given by

$$f_{1i}^{[0]}(\bar{\underline{1}}) = n_i \, m_i^{3/2} \, (2\pi kT)^{-3/2} \; Z_{rot}^{-1}$$

$$\exp\left(\left(\frac{1}{2kT}\right) (m_i \, (\underline{c}_1 - \underline{u})^2 + H_1^{rot}) \right) \tag{3.6}$$

where Z_{rot} is the rotational partition function and where n_i , T and u are arbitrary constants. For the linear and spherical top molecules with which we are concerned, this distribution function is of the form

$$f_{1i}^{[0]}(\underline{\bar{1}}) = n_i m_i^{3/2} (2\pi kT)^{-3/2} (4 I_i kT)^{-1} \exp\left(\frac{(\underline{c}_1-\underline{u})^2 m_i}{2kT} + \frac{(\underline{L}_1 - L_{1m}\hat{e}_{1m})^2}{2 I_i kT} \right)$$

(linear top)

(3.7)

$$f_{1i}^{[0]}(\underline{\bar{1}}) = n_i m_i^{3/2} (2\pi kT)^{-3/2} (2 I_i \pi kT)^{-3/2} \exp\left(\frac{(\underline{c}_1-\underline{u})^2 m_i}{2kT} + \frac{L_1^2}{2 I_i kT} \right)$$

(spherical top)

(3.8)

where I_i is the moment of inertia of the active degrees of freedom and for linear tops L_{1m} is the angular momentum component along the major axis (the $\hat{e}_{1m}$ direction) due to the electrons. If it is required that the function $f_{1i}^{[k]}(\underline{\bar{1}})$; $k \geq 1$ not contribute to the local equilibrium values of number density of species i , the temperature and streaming velocity, we can identify these quantities as n_i , T and u , respectively. The higher order terms ($k \geq 1$) in the expansion of f_{1i} can be written in terms of distortions, $\bar{\Phi}_i^{[k]}$, from equilibrium as follows:

$$f_{1i}^{[k]}(\underline{\bar{1}}) = f_{1i}^{[0]}(\underline{\bar{1}}) \; \bar{\Phi}_i^{[k]}(\underline{\bar{1}}) \quad . \tag{3.9}$$

The above identification of n_i , T and u imposes the subsidiary conditions on the distortions

$$\begin{aligned} 0 &= \int d\bar{\underline{1}}\; f_{1i}^{[0]}(\bar{\underline{1}})\; \bar{\Phi}_i^{[k]}(\bar{\underline{1}}) \\ &= \sum_i \int d\bar{\underline{1}}\; f_{1i}^{[0]}(\bar{\underline{1}})\; \bar{\Phi}_i^{[k]}(\bar{\underline{1}})\; m_i(\underline{c}_1-\underline{u}) \\ &= \sum_i \int d\bar{\underline{1}}\; f_{1i}^{[0]}(\bar{\underline{1}})\; \bar{\Phi}_i^{[k]}(\bar{\underline{1}})\left(\frac{m_i}{2}(\underline{c}_1-\underline{u})^2+H_1^{rot}\right) \end{aligned} \tag{3.10}$$

where the summations over i extend over all species. We require also that the internal angular momentum density of each species be zero so that

$$\int d\bar{\underline{1}}\;\; \underline{L}_1\; f_{1i}^{[0]}(\bar{\underline{1}})\;\; \bar{\Phi}_i^{[k]}(\bar{\underline{1}}) = 0 \quad . \tag{3.11}$$

The equation formed from the terms first order in ϵ in Equation 3.2 is

$$\begin{aligned} &\frac{\partial f_{1i}^{[0]}(\bar{\underline{1}})}{\partial_0 t} + \frac{\partial f_{1i}^{[0]}(\bar{\underline{1}})}{\partial \underline{x}_1}\cdot \underline{c}_1 + \frac{\partial f_{1i}^{[0]}(\bar{\underline{1}})}{\partial \underline{c}_1}\cdot \hat{F}_i^{e} = \\ &\quad - f_{1i}^{[0]}(\bar{\underline{1}})\; \bar{\underline{\omega}}_i(\bar{\underline{1}}) \times \bar{\underline{r}} \cdot \frac{\partial}{\partial \underline{L}_1}\bar{\Phi}_i^{[1]}(\bar{\underline{1}}) \\ &\quad + \sum_j \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}}\;\; W_r(\bar{\underline{1}}\,\bar{\underline{2}} \,|\, \bar{\underline{1}}'\,\bar{\underline{2}}')\; f_{1i}^{[0]}(\bar{\underline{1}})\, f_{1j}^{[0]}(\bar{\underline{2}}) \\ &\quad\quad \left[\,\bar{\Phi}_i^{[1]}(\bar{\underline{1}}) + \bar{\Phi}_j^{[1]}(\bar{\underline{2}}) - \bar{\Phi}_i^{[1]}(\bar{\underline{1}}') - \bar{\Phi}_j^{[1]}(\bar{\underline{2}}')\right] \quad . \end{aligned} \tag{3.12}$$

For a linear phenomenological description of the gas, we do not need to consider terms of higher than first order in ϵ. There is an equation of the same form as Equation

3.12 for each species. This set of equations can be compactly given by

$$(\underline{D}(\underline{\bar{1}}))_i = (K^{(0)}(\underline{\bar{1}}))_{ij} (\bar{\Phi}^{[1]}(\underline{\bar{1}}))_j + \int d\underline{\bar{\ell}} \, (K^{(1)}(\underline{\bar{1}},\underline{\bar{\ell}})$$

$$K^{(2)}(\underline{\bar{1}},\underline{\bar{\ell}}) + K^{(3)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij} \, (\bar{\Phi}^{[1]}(\underline{\bar{1}}))_j \qquad (3.13)$$

where

$$(\underline{D}(\underline{\bar{1}}))_i = \frac{\partial f_{1i}^{[0]}(\underline{\bar{1}})}{\partial t} + \frac{\partial f_{1i}^{[0]}(\underline{\bar{1}})}{\partial \underline{x}_1} \cdot \underline{c}_1$$

$$+ \frac{\partial f_{1i}^{[0]}(\underline{\bar{1}})}{\partial \underline{c}_1} \cdot \hat{F}_i^e \quad , \qquad (3.14)$$

$$(K^{(0)}(\underline{\bar{1}}))_{ij} = \delta_{ij} \sum_{\gamma} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}} \; f_{1i}^{[0]}(\underline{\bar{1}})$$

$$f_{1\gamma}^{[0]}(\underline{\bar{2}}) \; W_F(\underline{\bar{1}}\,\underline{\bar{2}} \mid \underline{\bar{1}}'\,\underline{\bar{2}}') \quad , \qquad (3.15)$$

$$(K^{(2)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij} = -\delta_{ij} \sum_{\gamma} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}} \; f_{1i}^{[0]}(\underline{\bar{1}})$$

$$f_{1\gamma}^{[0]}(\underline{\bar{2}}) \; W_F(\underline{\bar{1}}\,\underline{\bar{2}} \mid \underline{\bar{1}}'\underline{\bar{2}}') \; \delta(\underline{\bar{1}}' - \underline{\bar{\ell}}) \quad , \qquad (3.16)$$

$$(K^{(2)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij} = \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}}\; f_{1i}^{[0]}(\underline{\bar{1}})\; f_{1j}^{[0]}(\underline{\bar{2}})$$

$$w_F(\underline{\bar{1}}\,\underline{\bar{2}}|\underline{\bar{1}}'\underline{\bar{2}}')\,[\delta(\underline{\bar{2}}-\underline{\bar{\ell}}) - \delta(\underline{\bar{2}}'-\underline{\bar{\ell}})] \quad , \tag{3.17}$$

$$(K^{(3)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij} = -\delta_{ij}\,\delta(\underline{\bar{1}}-\underline{\bar{\ell}})\; f_{1i}^{[0]}(\underline{\bar{1}})$$

$$\underline{\bar{\mathcal{M}}}_i(\underline{\bar{1}}) \times \underline{\mathfrak{H}} \cdot \frac{\partial}{\partial \underline{L}_1} \quad , \tag{3.18}$$

$$(\underline{\Phi}^{[1]})_i = \underline{\Phi}_i^{[1]} \tag{3.19}$$

and where $\underline{\bar{\ell}}$ is a dummy momentum variable of integration. Beginning with Equations 3.13-3.19 we adopt the convention that a subscript to the right of an expression in parentheses refers to a component of a tensor defined over composition space. Composition space has the same dimension as the number of species. For instance the ij component of the second rank composition tensor $(K^{(2)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij}$ is that component for which molecule 1 is species i and molecule ℓ is species j. Tensors in the function space of the coordinates of the molecules are written in the usual way with an underscore for each rank. The Einstein summation convention is assumed for indices in composition space. The sums over ν in Equations 3.15 and 3.16 extend over the number of species n_s. In this form of Equation

3.13, we can see that it is a linear integral equation of the second kind to which the Fredholm theorems (39) can be applied.

The first step in the application of these theorems is to determine the solutions, $(\chi^{(i)})_j$, of the homogeneous form of Equation 3.13. Likely candidates for such solutions based on the form of the terms of Equation 3.13 defined in Equations 3.15, 3.16 and 3.17 are the collisional invariants of mass of each species, linear momentum and energy. The collisional invariants, in addition to causing the terms defined in Equations 3.15, 3.16 and 3.17 to sum to zero, give a zero result for the field term of Equation 3.18 and hence are indeed solutions to the homogeneous form of Equation 3.13. In terms of vectors in composition space the solutions, $(\chi^{(i)})_j$, are

$$\begin{pmatrix} m_1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \cdots \begin{pmatrix} 0 \\ 0 \\ \vdots \\ m_{n_s} \end{pmatrix}, \begin{pmatrix} m_1 \underline{c}_1 \\ m_2 \underline{c}_2 \\ \vdots \\ m_{n_s} \underline{c}_{n_s} \end{pmatrix}, \begin{pmatrix} \frac{m_1 c_1^2}{2} + H_1^{rot} \\ \vdots \\ \frac{m_{n_s} c_{n_s}^2}{2} + H_{n_s}^{rot} \end{pmatrix} .$$

The Fredholm theorems which apply are determined by the fact that these solutions to the homogeneous equation are nonzero.

The next step in the application of the appropriate theorems is to find the solutions to the "transposed" homogeneous equations given by

$$0 = \left(K^{(0)}(\bar{\underline{1}})\right)_{ij} \left(\bar{\Phi}^{[1]}(\bar{\underline{1}})\right)_j + \int d\bar{\underline{\ell}} \, \Big(K^{(1)}(\bar{\underline{\ell}}, \bar{\underline{1}})$$

$$+ K^{(2)}(\bar{\underline{\ell}}, \bar{\underline{1}}) + K^{(3)}(\bar{\underline{\ell}}, \bar{\underline{1}})\Big)_{ij} \left(\bar{\Phi}^{[1]}(\bar{\underline{1}})\right)_j \, . \qquad (3.20)$$

The quotation marks around the word "transposed" mean that we interchange the roles of $\bar{\underline{1}}$ and $\bar{\underline{\ell}}$ in Equations 3.16, 3.17 and 3.18 rather than perform the usual transposition of the indices of a tensor. Using the conservation of mass, of linear momentum and of kinetic energy, bilateral normalization and the definition of an adjoint of a linear operator (designated by a dagger superscript), we can write Equation 3.20 as

$$0 = \left(K^{(0)}(\bar{\underline{1}})\right)_i \left(\Phi^{[1]}(\bar{\underline{1}})\right)_i + \int d\bar{\underline{\ell}} \, \Big(K^{(1)^{\dagger}}(\bar{\underline{1}}, \bar{\underline{\ell}}) + K^{(2)^{\dagger}}(\bar{\underline{1}}, \bar{\underline{\ell}})$$

$$- K^{(3)^{T}}(\bar{\underline{1}}, \bar{\underline{\ell}})\Big)_{ij} \left(\bar{\Phi}^{[1]}(\bar{\underline{1}})\right)_j \qquad (3.21)$$

where

$$\left(K^{(1)^{\dagger}}(\bar{\underline{1}}, \bar{\underline{\ell}})\right)_{ij} = -\delta_{ij} \sum_{\gamma} \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}} \; f^{[0]}_{1i}(\bar{\underline{1}}) \; f^{[0]}_{2\gamma}(\bar{\underline{2}})$$

$$W_F(\bar{\underline{1}}'\bar{\underline{2}}' \mid \bar{\underline{1}}\,\bar{\underline{2}}) \; \delta(\bar{\underline{1}}' - \bar{\underline{\ell}}) \quad , \qquad (3.22)$$

$$(K^{(2)\dagger}(\bar{\underline{1}}, \bar{\underline{\ell}}))_{ij} = \int d\bar{\underline{1}}' \int d\bar{\underline{2}}' \int d\bar{\underline{2}} \; f_{1i}^{[0]}(\bar{\underline{1}}) \; f_{1j}^{[0]}(\bar{\underline{2}})$$

$$w_F(\bar{\underline{1}}' \bar{\underline{2}}' \,|\, \bar{\underline{1}} \bar{\underline{2}})(\delta(\bar{\underline{1}}-\bar{\underline{\ell}}) - \delta(\bar{\underline{2}}'-\bar{\underline{\ell}})) \qquad (3.23)$$

and

$$(K^{(3)\dagger}(\bar{\underline{1}}, \bar{\underline{\ell}}))_{ij} = \delta_{ij} \; \delta(\bar{\underline{1}}-\bar{\underline{\ell}}) \; f_{1i}^{[0]}(\bar{\underline{1}}) \; \bar{\underline{\mu}}_i(\bar{\underline{1}}) \times \underline{F} \cdot \frac{\partial}{\partial \underline{L}_1} \; . \qquad (3.24)$$

One can readily verify that the solutions of the "transposed" homogeneous equations are also $(\chi^{(j)})_i$. The Fredholm theorems then state that the necessary and sufficient conditions under which Equation 3.13 possesses a solution are that

$$\int d\bar{\underline{1}} \; (\mathfrak{D}(\bar{\underline{1}}))_i \; (\chi^{(j)}(\bar{\underline{1}}))_i \qquad (3.25)$$

for all j . The final information that the theorems give is that any solution to the inhomogeneous equation could possibly include an additive combination of the solutions to the homogeneous equation. The subsidiary conditions of Equations 3.10 prevent a nonzero combination of the $(\chi^{(j)})_i$ from being included in the solution to the inhomogeneous equation because Equations 3.10 are statements of orthogonality between $(\bar{\Phi}^{[1]}(\underline{1}))_i$ and $(\chi^{(j)})_i$ for all values of j .

When the general expression of Equation 3.6 for is substituted into Equation 3.13, the inhomogeneity becomes

$$(\mathcal{D}(\underline{1}))_i = f_{1i}^{[0]}(\underline{1}) \Big[n_i^{-1} \left(\frac{\partial}{\partial_0 t} + \underline{c}_1 \cdot \underline{\nabla}_1 \right) n_i + T^{-1} \Big\{ \frac{m_i C_1^2}{2kT}$$

$$- \frac{3}{2} + [H_1^{rot} - \bar{H}_1^{rot}] \Big\} \left(\frac{\partial}{\partial_0 t} + \underline{c}_1 \cdot \underline{\nabla}_1 \right) T + \frac{m_i}{kT} \Big\{ \Big(\frac{\partial}{\partial_0 t} +$$

$$\underline{c}_1 \cdot \underline{\nabla}_1 \Big) \underline{u} - \hat{F}_i^e \Big\} \underline{C}_1 \Big] \tag{3.26}$$

with $\underline{\nabla}_1 = \frac{\partial}{\partial \underline{x}_1}$ and $\underline{C}_1 = \underline{c}_1 - \underline{u}$ and where $\bar{H}_i^{rot}$ is the average local equilibrium value of H_i^{rot}. When this form of the inhomogeneity is inserted into the solubility conditions of Equation 3.25, the fluid dynamic equations to lowest order in ϵ are obtained. Thus we find that

$$\frac{\partial n_i}{\partial_0 t} = -\underline{\nabla}_1 \cdot n_i \underline{u} \quad , \tag{3.27}$$

$$\frac{\partial \underline{u}}{\partial_0 t} = -\underline{u} \cdot \underline{\nabla}_1 \underline{u} - \rho^{-1} \underline{\nabla}_1 p + \sum_i \frac{\rho_i}{\rho} \hat{F}_i^e \quad , \tag{3.28}$$

and

$$\frac{\partial T}{\partial_0 t} = -\underline{u} \cdot \underline{\nabla}_1 T - \left(\frac{p}{c_v} \right) \underline{\nabla}_1 \cdot \underline{u} \tag{3.29}$$

with $\rho_i = m_i n_i$, $\rho = \sum_i \rho_i$, $p = n k T$, $c_v = \frac{3}{2} n k T + \hat{c}_i$ and $n = \sum_i n_i$ and where $\hat{c}_i$ is the contribution of the rotational degrees of freedom to the heat capacity per molecule of species i . Using Equations 3.27, 3.28 and 3.29 to evaluate the time derivatives which appear in Equation 3.26, we have the result that

$$\left(\mathcal{D}(\underline{1}) \right)_i = f_{1i}^{[0]}(\underline{1}) \Big\{ \left(\frac{n}{n_i}\right) \underline{C}_1 \cdot \underline{d}_i + \Big(W_1^2 + H_1^{rot^*} - \frac{5}{2} - \bar{H}_1^{rot^*} \Big) \underline{C}_1 \cdot \left(\frac{\underline{\nabla}_1 T}{T} \right) + \Big(2 \underline{W}_1 \underline{W}_1 - \underline{\underline{\delta}}^{(3)} \Big[\left(\frac{p}{i c_v} \right) \left(W_1^2 + H_1^{rot^*} - \frac{3}{2} - \bar{H}_1^{rot^*} \right) + 1 \Big] \Big) : \underline{\nabla}_1 \underline{u} \tag{3.30}$$

with $\underline{W}_i = (m_i/2kT)^{1/2} \underline{C}_1$, $H_i^{rot^*} = H_i^{rot} / kT$, $\bar{H}_1^{rot^*} = \bar{H}_1^{rot} / kT$ and $\underline{\underline{\delta}}^{(b)}$ is the second rank unit tensor over a b dimensional space and where the generalized diffusion forces, $\underline{d}_i$, are defined by

$$\underline{d}_i = \frac{\underline{\nabla}_1 n_i}{n} + \left(\frac{n_i}{n} - \frac{\rho_i}{\rho} \right) \frac{\underline{\nabla}_1 p}{p} - \frac{\rho_i}{\rho p} \left(\rho \hat{F}_i^e - \sum_j \rho_j \hat{F}_j^e \right) . \tag{3.31}$$

They satisfy the condition of linear dependence that $\sum_i \underline{d}_i = 0$.

The operators on the right hand side of Equation

3.13 are all linear and by Equation 3.30 the left hand side of that equation is seen to be linearly dependent upon the generalized forces $\underline{d}_i$, $\underline{\nabla}_1 T$ and $\overline{\overline{\underline{\nabla}_1 u_o}}$ where the double bar over the last force indicates the symmetric part of the tensor. The function, $(\Phi^{[1]})_i$, appearing on the right hand side of Equation 3.13 can thus also be written as a linear combination of these forces. That is

$$(\bar{\Phi}^{[1]}(\bar{\underline{I}}))_i = -(2kT)^{1/2}(\underline{A})_i \cdot \underline{\nabla}_1 \ln T - (\bar{\underline{\underline{B}}})_i : \overline{\overline{\underline{\nabla}_1 \underline{u}}}$$

$$+ n \sum_j (\underline{\zeta}^{(j)})_i \cdot \frac{\underline{d}_j}{\rho_j} \quad . \qquad (3.32)$$

It is now convenient to divide $(\bar{\underline{\underline{B}}})_i$ as follows:

$$(\bar{\underline{\underline{B}}})_i = (\overset{\circ}{\bar{\underline{\underline{B}}}})_i + \frac{1}{3}(\bar{\underline{\underline{B}}})_i : \underline{\underline{\delta}}^{(3)}\,\underline{\underline{\delta}}^{3} \equiv (\overset{\circ}{\bar{\underline{\underline{B}}}})_i + (D)_i\,\underline{\underline{\delta}}^{(3)} \qquad (3.33)$$

where the super naught indicates a traceless tensor. With this division, Equation 3.32 becomes

$$(\bar{\Phi}^{[1]}(\bar{\underline{I}}))_i = -(2kT)^{1/2}(\underline{A})_i\,\underline{\nabla}_1 \ln T - (\overset{\circ}{\underline{\underline{B}}})_i : \underline{\underline{S}}$$

$$- (D)_i\,\underline{\nabla}_1 \cdot \underline{u} + n \sum_j (\underline{\zeta}^{(j)})_i \cdot \frac{\underline{d}_j}{\rho_j} \qquad (3.34)$$

where $\underline{\underline{S}} = \overset{\circ}{\overline{\overline{\underline{\nabla}_1 \underline{u}}}}$. The linear dependence of the $\underline{d}_j$ causes an arbitrariness in the definition of the $(\underline{\zeta}^{(j)})_i$

which we remove by requiring that $\sum_j (\underline{\zeta}^{(j)})_i = 0$ for all i.

The substitution of both the expression for the first order distortion of Equation 3.34 and the expression for the inhomogeneity of Equation 3.30 into Equation 3.12 yields an equation which is linear in the generalized forces. These forces are independent except for the aforementioned linear dependence of the $\underline{d}_j$, which we remove by changing from $\underline{d}_j$ to the $n_s - 1$ independent forces $((\underline{d}_j/\rho_j) - (\underline{d}_k/\rho_k))$, $j \neq k$, where k is arbitrary. Then separate equations can be formed by equating coefficients of the forces as follows:

$$(\underline{D}^{(\underline{A})})_i = (\hat{\Lambda})_{ij} (\underline{A})_j \qquad (D^{(D)}) = (\hat{\Lambda})_{ij} (D)_j$$

$$(\underline{\underline{D}}^{(\overset{\circ}{\underline{\underline{B}}})})_i = (\hat{\Lambda})_{ij} (\overset{\circ}{\underline{\underline{B}}})_j \qquad (\underline{D}^{(\underline{\zeta}^{(k)})})_i = (\hat{\Lambda})_{ij} (\underline{\zeta}^{(k)})_j \tag{3.35}$$

with

$$(\underline{D}^{(\underline{A})})_i = m_i^{-1/2} f_{1i}^{[0]} [\underline{W}_1 (W_1^2 + H_1^{rot*} - \tfrac{5}{2} - \bar{H}_1^{rot*}] , \tag{3.36}$$

$$(\underline{\underline{D}}^{(\overset{\circ}{\underline{\underline{B}}})})_i = 2 f_{1i}^{[0]} (\underline{\bar{1}}) [\underline{W}_1]^{(2)} , \tag{3.37}$$

$$(D^{(D)})_i = f_{1i}^{[0]} (\underline{\bar{1}}) \{ (\tfrac{2}{3} - \tfrac{p}{c_v T}) W_1^2 - \tfrac{p}{c_v T} [H_1^{rot*} - \bar{H}_1^{rot*} - \tfrac{3}{2}] + 1 \} , \tag{3.38}$$

$$(\underline{D}^{(\underline{\varsigma}^{(k)})} = f_{1i}^{[0]}(\underline{1})\, m_i\, \underline{C}_1 \left(-\delta_{ik} + \frac{\rho_k}{\rho}\right) \tag{3.39}$$

and

$$(\hat{\Lambda})_{ij} = n_i\,(\hat{\theta})_{ij} + n_i n_j\,(\hat{\mu})_{ij} \tag{3.40}$$

and where

$$n_i\,(\hat{\theta})_{ij} = \int d\bar{\underline{l}}\,\left(K^{(3)}(\underline{1},\underline{l})\right)_{ij} \tag{3.41}$$

and

$$n_i n_j\,(\hat{\mu})_{ij} = \left(K^{(0)}(\underline{1})\right)_{ij} + \int d\bar{\underline{l}}$$

$$\left(K^{(1)}(\underline{1},\underline{l}) + K^{(2)}(\underline{1},\underline{l})\right)_{ij} \tag{3.42}$$

The symbol $[\,\underline{X}\,]^{(p)}$ signifies the highest weight irreducible part of the polyad formed from p $\underline{X}$'s.

The first order distortion in terms of independent forces can be inserted into Equations 3.10 and 3.11 with the result that

$$\int d\bar{\underline{1}}\,\left(f_1^{[0]}(\underline{1})\,\mathcal{D}\right)_i \left(\xi^{(j)}\right)_i = 0 \tag{3.43}$$

where $(\mathcal{D})_i$ can be $(\underline{A})_i$, $(\overset{\circ}{\underline{\underline{B}}})_i$, $(D)_i$ or $(\underline{\varsigma}^{(k)})_i$ and $(\xi^{(j)})_i$ includes all the $(\chi^{(j)})_i$ and in addition

$$\begin{pmatrix} \underline{L}_1 \\ 0 \\ \vdots \\ 0 \end{pmatrix} \cdots \begin{pmatrix} 0 \\ \vdots \\ 0 \\ \underline{L}_{n_s} \end{pmatrix} .$$

In general the flux of any property can be written as an integral over all momentum space of a particle, whose integrand is the product of the distribution function, the relative velocity, $\underline{C}$, and the property under consideration. In our situation we can write the fluxes of mass, linear momentum and kinetic energy respectively as

$$(\underline{J})_i = \int d\underline{\bar{1}} \left(f_1^{[0]}(\underline{\bar{1}}) \, \bar{\Phi}^{[1]}(\underline{\bar{1}}) \, m\underline{C}_1 \right)_i , \qquad (3.44)$$

$$\underline{\underline{P}} = p \, \underline{\underline{\delta}}^{(3)} + \overset{\circ}{\underline{\underline{\tilde{\pi}}}} + \tilde{\pi} \, \underline{\underline{\delta}}^{(3)} \qquad (3.45)$$

and

$$\underline{Q} = (\underline{J})_i \, (\tilde{H})_i + \underline{Q}' \qquad (3.46)$$

where

$$\overset{\circ}{\underline{\underline{\tilde{\pi}}}} = \int d\underline{\bar{1}} \left(f_1^{[0]}(\underline{\bar{1}}) \, \bar{\Phi}^{[1]}(\underline{\bar{1}}) \right)_i \left(m[\underline{C}_1]^{(2)} \right)_i , \qquad (3.47)$$

$$\tilde{\pi} = \frac{1}{3} \int d\underline{\bar{1}} \left(f_1^{[0]}(\underline{\bar{1}}) \, \bar{\Phi}^{[1]}(\underline{\bar{1}}) \right)_i \left(m C_1^2 \right)_i , \qquad (3.48)$$

$$\underline{Q}' = \int d\underline{\bar{1}} \; (f_1^{[0]}(\underline{\bar{1}}) \; \underline{\bar{\Phi}}^{[1]}(\underline{\bar{1}}))_i \; (\underline{C}_1 \; (\frac{mC_1^2}{2} + H_1^{rot} - \frac{5}{2} kT - \bar{H}_1^{rot}))_i \tag{3.49}$$

and

$$(\tilde{H})_i = m^{-1} (\frac{5}{2} kT + \bar{H}_1^{rot}) \quad . \tag{3.50}$$

The flux of kinetic energy given by Equation 3.46 is divided into a convective term $(\underline{J})_i (\tilde{H})_i$ and a conductive term Q'. The integrands of Equations 3.44, 3.47, 3.48 and 3.49 can be related to the expressions for the inhomogeneities given in Equations 3.36-3.39. By Equation 3.35 we have that

$$(\underline{J})_i = - \int d\underline{\bar{1}} \; (\underline{\bar{\Phi}}^{[1]}(\underline{\bar{1}}))_j \; (\underline{D}^{(\underline{\zeta}^{(i)})}(\underline{\bar{1}}))_j = - \{\{ \underline{\bar{\Phi}}^{[1]}, \underline{\zeta}^{(i)} \}\}$$

$$\overset{\circ}{\underline{\underline{\Pi}}} = kT \int d\underline{\bar{1}} \; (\underline{\bar{\Phi}}^{[1]}(\underline{\bar{1}}))_j \; (\underline{\underline{D}}^{(\overset{\circ}{\underline{\underline{B}}})}(\underline{\bar{1}}))_j = kT \{\{ \underline{\bar{\Phi}}^{[1]}, \overset{\circ}{\underline{\underline{B}}} \}\}$$

$$\pi = kT \int d\underline{\bar{1}} \; (\underline{\bar{\Phi}}^{[1]}(\underline{\bar{1}}))_j \; (D^{(0)}(\underline{\bar{1}}))_j = kT \{\{ \underline{\bar{\Phi}}^{[1]}, D \}\} \tag{3.51}$$

and

$$\underline{Q}' = (kT)\,(2kT)^{1/2} \int d\underline{\bar{\imath}} \;\; (\bar{\Phi}^{[1]}(\underline{\bar{\imath}}))_j \, (\underline{D}^{(A)}(\underline{\bar{\imath}}))_j$$

$$= kT\,(2kT)^{1/2} \,\{\{ \bar{\Phi}^{[1]}, \underline{A} \}\}$$

where the double brackets signify for two tensors $\underline{\underline{a}}$ and $\underline{\underline{b}}$

$$\{\{ \underline{\underline{a}}, \underline{\underline{b}} \}\} \equiv (\, (\underline{\underline{a}})_i \,,\, (\hat{\Lambda})_{ij}\, (\underline{\underline{b}})_j \,)$$

$$\equiv \int d\underline{\bar{\imath}}\, (\underline{a})_i\, (\hat{\Lambda})_{ij}\, (\underline{\underline{b}})_j \quad . \tag{3.52}$$

By substituting the expression for $\Phi^{[1]}$ of Equation 3.34, we derive the general force flux relationships as follows:

$$(\underline{J})_i = \left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, \underline{C}^{(i)} \}\} + \underline{\underline{S}} : \{\{ \overset{\circ}{\underline{\underline{B}}}, \underline{C}^{(i)} \}\}$$

$$+ \underline{\nabla}_1 \cdot \underline{u}\, \{\{ D, \underline{C}^{(i)} \}\} - n \sum_j \frac{\underline{d}_j}{\rho_j}\, \{\{ \underline{C}^{(j)}, \underline{C}^{(i)} \}\} \quad ,$$

$$\overset{\circ}{\underline{\underline{\Pi}}} = -kT \left[\left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, \overset{\circ}{\underline{\underline{B}}} \}\} + \underline{\underline{S}} : \{\{ \overset{\circ}{\underline{\underline{B}}}, \overset{\circ}{\underline{\underline{B}}} \}\} \right.$$

$$\left. + \underline{\nabla}_1 \cdot \underline{u}\, \{\{ D, \overset{\circ}{\underline{\underline{B}}} \}\} - n \sum_j \frac{\underline{d}_j}{\rho_j} \cdot \{\{ \underline{C}^{(j)}, \overset{\circ}{\underline{\underline{B}}} \}\} \right] \quad ,$$

$$\pi = -kT \left[\left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, D \}\} + \underline{\underline{S}} : \{\{ \overset{\circ}{\underline{\underline{B}}}, D \}\} \right.$$

$$\left. + \underline{\nabla}_1 \cdot \underline{u}\, \{\{ D, D \}\} - n \sum_j \frac{\underline{d}_j}{\rho_j} \cdot \{\{ \underline{C}^{(j)}, D \}\} \right] \tag{3.53}$$

and

$$\underline{Q}' = -kT\ (2kT)^{1/2}\left[\ \left(\frac{2k}{T}\right)^{1/2}\underline{\nabla}_1 T\cdot\{\{\underline{A},\underline{A}\}\} + \underline{\underline{S}} : \{\{\mathring{\underline{\underline{B}}},\underline{A}\}\}\right.$$

$$+\ \underline{\nabla}_1\cdot\underline{u}\ \{\{0,\underline{A}\}\} - n\sum_j\frac{\underline{d}_j}{\rho_j}\cdot\{\{\underline{C}^{(j)},\underline{A}\}\}\ .$$

The operation of parity reversal on the fluxes, which are all polar quantities, has the result that

$$\hat{P}\,(\underline{J})_i = -(J)_i \qquad\qquad \hat{P}\,\mathring{\tilde{\underline{\underline{\pi}}}} = \mathring{\tilde{\underline{\underline{\pi}}}}$$

$$\hat{P}\ \underline{Q}' = -\underline{Q}' \qquad\qquad \hat{P}\ \tilde{\pi} = \tilde{\pi}\ . \tag{3.54}$$

Since the parity of the forces in Equations 3.53 is readily apparent, these equations can be used to determine the parity of the bracketed expressions therein. The bracketed expressions are unaffected by rotations perpendicular to the direction, $\hat{k}_f$, of the applied field, $\underline{\mathfrak{F}}$, and can therefore be expanded in the appropriate tensors given in Reference 27. These tensors in the expansion must all have the same parity as the bracket in order to have nonzero coefficients. The parity of such tensors can be determined from the facts that a magnetic field is unaffected by parity and an electric field reverses direction under parity. It is useful to note the additional property of the double bracketed expressions that $\{\{\underline{\underline{a}},\underline{\underline{b}}\}\}=0$ if $\underline{\underline{a}}$ and $\underline{\underline{b}}$ are of different parity. The proof of this statement follows easily if $\hat{P}$ and $(\hat{\Lambda})_{ij}$ can be shown to commute. That these two operators commute can be established by examining the effect of $\hat{P}$ on the separate parts of $(\hat{\Lambda})_{ij}$ in Equation 3.40: $(\hat{\theta})_{ij}$ is unaffected by parity reversal because the energy of the dipole $(= -\underline{\mu}\cdot\underline{\mathcal{E}})$ is unaffected as is $\underline{\underline{L}}$, an axial vector. The operator $(\hat{p})_{ij}$ is invariant to parity reversal by Equation 2.26. The sequence of the proof that $\{\{\underline{\underline{a}},\underline{\underline{b}}\}\}=0$ if $\underline{\underline{a}}$ and $\underline{\underline{b}}$ are of different parity with eigenvalues ζ_a^p and ζ_b^p under parity is

$$\begin{aligned}((\underline{\underline{a}})_i, (\hat{\Lambda})_{ij}(\underline{\underline{b}})_j) &= \zeta_b^p((\underline{\underline{a}})_i, (\hat{\Lambda})_{ij}\hat{P}(\underline{\underline{b}})_j) \\ &= \zeta_b^p((\underline{\underline{a}})_i, \hat{P}(\hat{\Lambda})_{ij}(\underline{\underline{b}})_j) = \zeta_b^p(\hat{P}(\underline{\underline{a}})_i, (\hat{\Lambda})_{ij}(\underline{\underline{b}})_j) \\ &= \zeta_a^p\zeta_b^p((\underline{\underline{a}})_i, (\hat{\Lambda})_{ij}(\underline{\underline{b}})_j)\end{aligned} \tag{3.56}$$

where the self-adjointness of $\hat{P}$ is utilized.

Time reversal also leads to a useful property of the double brackets. Proof of this property requires that we first show that

$$\hat{T}\,(\hat{\Lambda})_{ij} = (\hat{\Lambda}^{+})_{ij}\,\hat{T} \quad . \tag{3.57}$$

The time reversal operator can be broken up into a product of an operator on the applied field and of an operator on the momentum, $\hat{T} = \hat{T}_F \hat{T}_m$. With the aid of Equation 2.25 and the conservation of linear momentum and of energy, we can operate on the individual terms of $(\Lambda)_{ij}$ given in Equation 3.40 with $\hat{T}$ and show Equation 3.57. As an example we give the proof sequence for $(K^{(1)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij}$

$$\hat{T} \int d\underline{\bar{\ell}}\ (K^{(1)}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij} = -\delta_{ij} \sum_{\gamma} \int d\underline{\bar{\ell}} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}}\ W_{\hat{T}_F} (\hat{T}_m \underline{\bar{1}}\, \underline{\bar{2}} | \underline{\bar{1}}' \underline{\bar{2}}')$$

$$f^{[0]}_{1i} (\hat{T}_m \underline{\bar{1}})\ f^{[0]}_{1\gamma} (\underline{\bar{2}})\ \delta(\underline{\bar{1}}' - \underline{\bar{\ell}})\ \hat{T}$$

$$= -\delta_{ij} \sum_{\gamma} \int d\hat{T}_m^{-1} \underline{\bar{\ell}} \int d\hat{T}_m^{-1} \underline{\bar{1}}' \int d\hat{T}_m^{-1} \underline{\bar{2}}' \int d\hat{T}_m^{-1} \underline{\bar{2}}$$

$$W_{\hat{T}_F} (\hat{T}_m \underline{\bar{1}}\, \underline{\bar{2}} | \underline{\bar{1}}' \underline{\bar{2}}')\ f^{[0]}_{1i} (\hat{T}_m \underline{\bar{1}})\ f^{[0]}_{1\gamma} (\underline{\bar{2}})\ \delta(\underline{\bar{1}}' - \underline{\bar{\ell}})\ \hat{T}$$

$$= -\delta_{ij} \sum_{\gamma} \int d\underline{\bar{\ell}} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}}\ W_{\hat{T}_F} (\hat{T}_m \underline{\bar{1}}\, \hat{T}_m \underline{\bar{2}} | \hat{T}_m \underline{\bar{1}}'\, \hat{T}_m \underline{\bar{2}}')$$

$$f^{[0]}_{1i} (\hat{T}_m \underline{\bar{1}})\ f^{[0]}_{1\gamma} (\hat{T}_m \underline{\bar{2}})\ \delta(\hat{T}_m \underline{\bar{1}}' - \hat{T}_m \underline{\bar{\ell}})\ \hat{T}$$

$$= -\delta_{ij} \sum_{\gamma} \int d\underline{\bar{\ell}} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}' \int d\underline{\bar{2}}\ W_F (\underline{\bar{1}}' \underline{\bar{2}}' | \underline{\bar{1}}\, \underline{\bar{2}})$$

$$f^{[0]}_{1i} (\underline{\bar{1}})\ f^{[0]}_{1\gamma} (\underline{\bar{2}})\ \delta(\underline{\bar{1}}' - \underline{\bar{\ell}})\ \hat{T}$$

$$= \int d\underline{\bar{\ell}}\ (K^{(1)^+}(\underline{\bar{1}},\underline{\bar{\ell}}))_{ij}\ \hat{T}$$

The theorem which we wish to prove is that for any tensors $(\underline{a})_i$ and $(\underline{b})_i$

$$\{\{\underline{\underline{a}},\underline{\underline{b}}\}\} = \tau_a \tau_b \hat{T}_F \{\{\underline{\underline{b}},\underline{\underline{a}}\}\}^T \tag{3.58}$$

where τ_a and τ_b are the time operator eigenvalues of $(\hat{\Lambda})_{ij}(\underline{\underline{a}})_j$ and $(\hat{\Lambda})_{ij}(\underline{\underline{b}})_j$ respectively and the superscript T refers to the bulk transposition of function space indices. The steps of the proof of Equation 3.58 utilize the self-adjointness of $\hat{T}_m$ and are

$$\{\{\underline{\underline{a}},\underline{\underline{b}}\}\} = ((\underline{\underline{a}})_i, \hat{T}\hat{T}(\hat{\Lambda})_{ij}(\underline{\underline{b}})_j)$$

$$= \tau_b \hat{T}_F \hat{T}_F ((\underline{\underline{a}})_i, \hat{T}_F \hat{T}_m (\hat{\Lambda})_{ij}(\underline{\underline{b}})_j) = \tau_b \hat{T}_F (\hat{T}_F (\underline{\underline{a}})_i, \hat{T}_m (\hat{\Lambda})_{ij}(\underline{\underline{b}})_j)$$

$$= \tau_b \hat{T}_F ((\hat{\Lambda}^+)_{ji} \hat{T}_m \hat{T}_F (\underline{\underline{a}})_i, (\underline{\underline{b}})_j) = \tau_a \tau_b \hat{T}_F \{\{\underline{\underline{b}},\underline{\underline{a}}\}\}^T .$$

The time reversal eigenvalues of $(\hat{\Lambda})_{ij}(\underline{H})_j$ may be found through Equations 3.35 by considering the equivalent problem of how the time reversal operator affects the $(\mathfrak{D}^{(\gamma)})_i$. By this means we find that

$$\hat{T}(\hat{\Lambda})_{ij}(\underline{A})_j = -(\hat{\Lambda})_{ij}(\underline{A})_j \quad ,$$

$$\hat{T}(\hat{\Lambda})_{ij}(\mathring{\underline{\underline{B}}})_j = (\Lambda)_{ij}(\mathring{\underline{\underline{B}}})_j \quad ,$$

$$\hat{T}(\hat{\Lambda})_{ij}(D)_j = (\hat{\Lambda})_{ij}(D)_j \tag{3.59}$$

and

$$\hat{T}\,(\hat{\Lambda})_{ij}\,(\underline{\zeta}^{(a)})_j = -\,(\hat{\Lambda})_{ij}\,(\underline{\zeta}^{(b)})_j \;.$$

We now examine the double brackets of Equations 3.53 in a two-fold process. The first step, as we have already mentioned, is to establish which tensors of Reference 27 have the appropriate parity for the expansion of a given double bracket. The second step is to apply the theorem of Equation 3.58 to derive the Onsager-Casimer relationships. The application of this process results in the following statements:

(i) The second rank tensors $\{\{\underline{A},\underline{\zeta}^{(i)}\}\}$, $\{\{\underline{\zeta}^{(i)},\underline{A}\}\}$, $\{\{\underline{\zeta}^{(i)},\underline{\zeta}^{(j)}\}\}$ and $\{\{\underline{A},\underline{A}\}\}$ can be expanded linearly in the three tensors (27) $\underline{\underline{J}}^{i}$ with coefficients $L_{\perp}$, $L_{\parallel}$ and L_{tr} respectively. The coefficients $L_{\perp}$ and $L_{\parallel}$ are nonzero for any applied field. For the case $\underline{\mathcal{F}} = \underline{H}$ (magnetic field case), L_{tr} is nonzero and is an odd function of $\underline{H}$; for $\underline{\mathcal{F}} = \underline{E}$ (electric field case) L_{tr} is zero. The relations between these double brackets are $\{\{\underline{A},\underline{\zeta}^{(i)}\}\} = \{\{\underline{\zeta}^{(i)},\underline{A}\}\}$ and $\{\{\underline{\zeta}^{(i)},\underline{\zeta}^{(j)}\}\} = \{\{\underline{\zeta}^{(j)},\underline{\zeta}^{(i)}\}\}$.

(ii) The vectors $\{\{\underline{A},D\}\}$, $\{\{D,\underline{A}\}\}$, $\{\{D,\underline{\zeta}^{(i)}\}\}$ and $\{\{\underline{\zeta}^{(i)},D\}\}$ are proportional to $\hat{k}_f$. In a magnetic field the coefficients of proportionality are zero and in an electric field they are nonzero. The relationships between these double brackets are $\{\{\underline{A},D\}\} = \{\{D,\underline{A}\}\}$ and $\{\{D,\underline{\zeta}^{(i)}\}\} = \{\{\underline{\zeta}^{(i)},D\}\}$.

(iii) The third rank tensors $\{\{\underline{A}, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\}$, $\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, \underline{A}\}\}^T$, $\{\{\underline{\varsigma}^{(i)}, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\}$ and $\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, \underline{\varsigma}^{(i)}\}\}^T$ can be expanded in the three tensors (27) $\underline{\underline{F}}^{(i)}$ which are traceless and symmetric on their last two indices. All scalar coefficients of these tensors are zero in a magnetic field. In an electric field $F^{(1)}$ and $F^{(2)}$ have nonzero coefficients. The relationships between these double brackets are $\{\{\underline{A}, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\} = -\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, \underline{A}\}\}^T$ and $\{\{\underline{\varsigma}^{(i)}, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\} = -\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, \underline{\varsigma}^{(i)}\}\}^T$.

(iv) The second rank tensors $\{\{D, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\}$ and $\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, D\}\}$ are proportional with nonzero coefficient to the traceless and symmetric tensor (27) $\underline{\underline{j}}$. The relationship between these tensors is $\{\{D, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\} = \{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, D\}\}$.

(v) The fourth rank tensor $\{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}, \overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\}$ can be linearly expanded in terms of the five fourth rank tensors $\underline{\underline{\underline{\underline{B}}}}^{a}_{0}(2)$, $\underline{\underline{\underline{\underline{B}}}}^{a}_{1}(2)$, $\underline{\underline{\underline{\underline{B}}}}^{a}_{2}(2)$, $\underline{\underline{\underline{\underline{B}}}}^{b}_{1}(2)$ and $\underline{\underline{\underline{\underline{B}}}}^{b}_{2}(2)$ which are defined in Reference 40. These tensors possess the required symmetry and tracelessness and in addition they have the orthogonality properties mentioned in that reference. All five tensors contribute in a magnetic field and all but $\underline{\underline{\underline{\underline{B}}}}^{b}_{1}(2)$ and $\underline{\underline{\underline{\underline{B}}}}^{b}_{2}(2)$ in an electric field.

At this point we are ready to identify the transport properties from the force flux relations of Equation 3.53 and to form and solve the kinetic equations. The two distinct experimental situations of concern in this work are (i) the effect of a magnetic field on the viscosity and thermal conductivity of a gas composed of spherical top molecules and (ii) the thermal conductivity, thermal diffusion and diffusion occurring in binary isotopic gas mixtures composed of linear molecules. We treat these two situations in the following subsections.

Solution of the Kinetic Equations for Viscosity and Thermal Conductivity of a Pure Gas Composed of Spherical Top Molecules in the Presence of a Magnetic Field

From Equations 3.45 and 3.53, the total pressure tensor for this situation is given by

$$\begin{aligned}\underline{\underline{p}} = p\,\underline{\underline{\delta}}^{(3)} &- kT\,\underline{\underline{S}} : \{\{\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}\}\} - kT\,\underline{\nabla}_1 \cdot \underline{u}\,\{\{D, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}\}\} \\ &- kT\,\underline{\underline{S}} : \{\{\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, D\}\}\,\underline{\underline{\delta}}^{(3)} - kT\,\underline{\nabla}_1 \cdot \underline{u}\,\{\{D, D\}\}\,\underline{\underline{\delta}}^{(3)} \qquad (3.60)\end{aligned}$$

where we have omitted terms which do not contribute in the case of a pure gas in the presence of a magnetic field. For a pure gas there is only one component and we can drop the composition space indices. The identification of viscosity requires the following manipulation:

$$\begin{aligned}\underline{\underline{S}} : \{\{\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}\}\} &= \underline{\underline{S}} : (\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \hat{\Lambda}\,\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}) = \underline{\underline{S}} : (\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \hat{T}\hat{\Lambda}\,\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}) \\ &= \underline{\underline{S}} : (\hat{\Lambda}^{\dagger}\hat{T}\,\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}) = \underline{\underline{S}} : (\hat{T}\hat{\Lambda}\,\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}) \\ &= \{\{\overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}, \overset{\circ}{\bar{\bar{\underline{\underline{B}}}}}\}\} : \underline{\underline{S}} \qquad (3.61)\end{aligned}$$

where we have used Equation 3.57 and part of Equation 3.59. The standard macroscopic formula for the pressure tensor (21) is

$$\underline{\underline{P}} = p\,\underline{\underline{\delta}}^{(3)} - 2\,\underline{\underline{\eta}} : \underline{\underline{S}} - \kappa\,\underline{\nabla}_1 \cdot \underline{u}\,\underline{\underline{\delta}}^{(3)} + \underline{\underline{L}}^{(0,2)}_{\pi,\pi} : \underline{\underline{S}}\,\underline{\underline{\delta}}^{(3)}$$

$$+ \underline{\underline{L}}^{(2,0)}_{\pi,\pi}\,\underline{\nabla}_1 \cdot \underline{u} \qquad (3.62)$$

where $\underline{\underline{\eta}}$ is the shear viscosity, κ is the bulk viscosity, and $\underline{\underline{L}}^{(0,2)}_{\pi,\pi}$ and $\underline{\underline{L}}^{(2,0)}_{\pi,\pi}$ are the coefficients of coupling between the bulk and shear forces. Since shear viscosity is the only property to be studied, we need only identify it (though the other identifications are apparent). Using Equations 3.60-3.62 we find that

$$\underline{\underline{\eta}} = \left(\frac{kT}{2}\right) \{\{\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\,,\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}\}\} \,. \qquad (3.63)$$

According to the method originated by Kagan and Maksimov (41), the tensor $\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}}$ is expanded in the infinite series

$$\overset{\circ}{\overline{\overline{\underline{\underline{B}}}}} = \sum_{pqst} [\underline{W}_1]^{(p)}\,[\underline{\Omega}_1]^{(q)}\,S^{(s)}_{p+\frac{1}{2}}(W_1^2)\,S^{(t)}_{q+\frac{1}{2}}(\Omega_1^2)$$

$$\odot^{p+q}\,\underline{\underline{B}}^{pqst} \qquad (3.64)$$

where for spherical tops $\underline{\Omega}_1 = (2 I_i kT)^{-1/2}\,\underline{\underline{L}}_1$, $\odot^{p+q}$

indicates nested indicial collapse (42) of the $p+q$ function space indices, $S^{(n)}_{m}(X)$ is a Sonine polynomial (42) of the function X and the tensor coefficients $\underline{\underline{B}}^{pqst}$ of rank $p+q+2$ are independent of microscopic variables. The expansion of Equation 3.64 can be inserted into $\{\{\mathring{\bar{\underline{\underline{B}}}}, \mathring{\bar{\underline{\underline{B}}}}\}\}$ and after some rearrangement we obtain

$$\{\{\mathring{\bar{\underline{\underline{B}}}}, \mathring{\bar{\underline{\underline{B}}}}\}\} = (\hat{\lambda}\mathring{\bar{\underline{\underline{B}}}}, \mathring{\bar{\underline{\underline{P}}}}) = (\underline{\underline{D}}^{(\mathring{\bar{\underline{\underline{B}}}})}, \mathring{\bar{\underline{\underline{B}}}})$$

$$= 2\,(f_1^{[0]}(\underline{\underline{1}})\,[\underline{W}_1]^{(2)}, \mathring{\bar{\underline{\underline{B}}}})$$

$$= 2\sum_{pqst}\Big[\int d\underline{\underline{1}}\; f_1^{[0]}(\underline{\underline{1}})\,[\underline{W}_1]^{(2)}\,[\underline{W}_1]^{(p)}\,[\underline{\Omega}_1]^{(q)}$$

$$S^{(s)}_{p+\frac{1}{2}}(W_1^2)\; S^{(t)}_{q+\frac{1}{2}}(\Omega_1^2)\Big] \odot^{p+q} \underline{\underline{B}}^{pqst} \qquad (3.65)$$

where we have used Equations 3.35, 3.37 and 3.61 in these steps. Since the integral of Equation 3.65 is already partly in terms of $\underline{W}_1$ and $\underline{\Omega}_1$, we change variables of integration with the result that

$$\{\{\mathring{\bar{\underline{\underline{B}}}}, \mathring{\bar{\underline{\underline{B}}}}\}\} = \frac{2n}{\pi^3}\sum_{pqst}\Big[\int d\underline{W}_1 \int d\underline{\Omega}_1\; e^{-W_1^2-\Omega_1^2}\,[\underline{W}_1]^{(2)}\,[\underline{W}_1]^{(p)}$$

$$[\underline{\Omega}_1]^{(q)}\, S^{(s)}_{p+\frac{1}{2}}(W_1^2)\; S^{(t)}_{q+\frac{1}{2}}(\Omega_1^2)\Big] \odot^{p+q} \underline{\underline{B}}^{pqst}. \qquad (3.66)$$

The singly bracketed integral in Equation 3.66 is field independent and hence must be isotropic. From group theory (43), one knows that the only way for such an integral to be nonzero is for the direct product of the tensors in the integrand to be a basis for a representation which contains the totally symmetric irreducible representation. The direct product of two tensors of weights j_1 and j_2 (for instance $[\underline{W}_1]^{(2)} [\underline{W}_1]^{(p)}$, where the first tensor is of weight 2 and the second tensor is of weight p) is a basis for a representation which is the Kroneker product of the two original representations. The product representation can be decomposed into irreducible representations of weights $|j_1 - j_2| \ldots \ldots |j_1 + j_2|$. In order for the reducible product representation to contain the totally symmetric irreducible representation (of weight zero), j_1 must be equal to j_2 .

These group theoretical considerations require that for the singly bracketed integral of Equation 3.66 to be nonzero, p must equal two and q must equal zero. Thus Equation 3.66 becomes

$$\{\{ \overset{\circ}{\underline{\underline{B}}} , \overset{\circ}{\underline{\underline{B}}} \}\} = \frac{2n}{\pi^3} \sum_{st} \Big[\int d\underline{W}_1 \, [\underline{W}_1]^{(2)} [\underline{W}_1]^{(2)} e^{-W_1^2} \, S_{\frac{5}{2}}^{(s)}(W_1^2)$$

$$\int d\underline{\Omega}_1 \, S_{\frac{1}{2}}^{(t)} (\Omega_1^2) \, e^{-\Omega_1^2} \Big] \odot^{p+q} \underline{\underline{B}}^{pqst} \quad . \qquad (3.67)$$

The orthogonality properties of Sonine polynomials can be used in Equation 3.67 because the powers of $\underline{W}_1$ and $\underline{\Omega}_1$ which occur there can be written in terms of Sonine polynomials. The result is that the only nonzero terms in the summations over s and t are those for which $s = t = 0$. Equation 3.67 can thus be written as

$$\{\{ \overset{\circ}{\overline{\underline{\underline{B}}}} , \overset{\circ}{\overline{\underline{\underline{B}}}} \}\} = \frac{2n}{\pi^3} \Big[\int d\underline{W}_1 \; [\underline{W}_1]^{(2)} \, [W_1]^{(2)} \, e^{-W_1^2}$$

$$\int d\underline{\Omega}_1 \, e^{-\Omega_1^2} \; \Big] \odot^2 \underline{\underline{\underline{\underline{B}}}}^{2000} \qquad . \tag{3.68}$$

This singly bracketed tensor integral is proportional to the isotropic fourth rank tensor $\underline{\underline{\underline{\underline{\Delta}}}}$ which is traceless and symmetric on its first two and its last two indices and is given by (40)

$$\underline{\underline{\underline{\underline{\Delta}}}} = \underline{\underline{\underline{\underline{B}}}}_0^{a}(2) + \underline{\underline{\underline{\underline{B}}}}_1^{a}(2) + \underline{\underline{\underline{\underline{B}}}}_2^{a}(2) \qquad . \tag{3.69}$$

Performing the standard procedures of tensor algebra, we obtain

$$\{\{ \overset{\circ}{\overline{\underline{\underline{B}}}} , \overset{\circ}{\overline{\underline{\underline{B}}}} \}\} = n \, \underline{\underline{\underline{\underline{B}}}}^{2000} \tag{3.70}$$

and thus from Equation 3.63 we have that

$$\underline{\underline{\eta}} = \frac{nkT}{2} \; \underline{\underline{\underline{\underline{B}}}}^{2000} \qquad . \tag{3.71}$$

We solve for $\underline{\underline{B}}^{2000}$ by using that part of Equation 3.35 generated by terms linear in $\underline{\underline{S}}$, i.e.

$$2 f_1^{[0]}(\underline{I})\,[\underline{W}_1]^{(2)} = \hat{\Lambda} \sum_{pqst} \underline{\underline{\beta}}_1^{pqst} \odot^{p+q} \underline{\underline{B}}^{pqst} \tag{3.72}$$

where

$$\underline{\underline{\beta}}_1^{pqst} = [\underline{W}_1]^{(p)}\ [\underline{\Omega}_1]^{(q)}\ S_{p+\frac{1}{2}}^{(s)}(W_1^2)\ S_{q+\frac{1}{2}}^{(t)}(\Omega_1^2) \tag{3.73}$$

and where we employ the expansion of Equation 3.63. We now take integral moments of Equation 3.72 with the entire set of $\hat{T}\,\underline{\underline{\beta}}_1^{pqst}$. The result is the moments equations which are of the form

$$\left(\hat{T}\,\underline{\underline{\beta}}_1^{p'q's't'},\ 2 f_1^{[0]}(\underline{I})\,[\underline{W}_1]^{(2)}\right) = \sum_{pqst} \left(\hat{T}\,\underline{\underline{\beta}}_1^{p'q's't'},\right.$$
$$\left.\hat{\Lambda}\,\underline{\underline{\beta}}_1^{pqst}\right) \odot^{p+q} \underline{\underline{B}}^{pqst} \quad . \tag{3.74}$$

The reason that the time reversal operator is brought in here is that $\hat{\Lambda}$ becomes effectively self-adjoint. The proof of this is similar to that of Equations 3.61 and is

$$\left(\hat{T}\,\underline{\underline{\beta}}_1^{p'q's't'},\ \hat{\Lambda}\,\underline{\underline{\beta}}_1^{pqst}\right) = \left(\hat{\Lambda}^{+}\hat{T}\,\underline{\underline{\beta}}_1^{p'q's't'},\ \underline{\underline{\beta}}_1^{pqst}\right)$$
$$= \left(\hat{T}\hat{\Lambda}\,\underline{\underline{\beta}}_1^{p'q's't'},\ \underline{\underline{\beta}}_1^{pqst}\right) = \left(\hat{\Lambda}\,\underline{\underline{\beta}}_1^{p'q's't'},\ \hat{T}\,\underline{\underline{\beta}}_1^{pqst}\right)$$
$$= \left(\hat{T}\,\underline{\underline{\beta}}_1^{pqst},\ \hat{\Lambda}\,\underline{\underline{\beta}}_1^{p'q's't'}\right)^{T} \quad . \tag{3.75}$$

It is obviously impractical to include an infinite number of terms in the expansion of $\overset{\circ}{\underline{\underline{\underline{B}}}}$ and to create an infinite number of moments equations. The primary factor in deciding whether a tensor corresponding to a certain $pqst$ should be included in the expansion set is to determine its contribution to $\underline{\underline{\underline{B}}}^{2000}$. If $(\hat{T}\underline{B}^{pqst}, \Lambda \underline{B}^{2000}) = 0$, then the equations for the $pqst$ and 2000 coefficients do not directly couple and that $pqst$ can be assumed to give a small contribution to 2000. The possible reasons for which $(\hat{T}\underline{B}^{pqst}, \hat{\Lambda}\underline{B}^{2000})$ would be zero are either that there is no isotropic tensor of the form of the moment or that $\underline{B}^{pqst}$ and $\underline{B}^{2000}$ are of different parity. A linear dependence between the $\underline{B}^{pqst}$, originating from the subsidiary conditions of Equation 3.43, can also result in the elimination of various $pqst$ from the expansion. The result of these considerations as applied to Equation 3.74 leaves in the series $\underline{\underline{\underline{B}}}^{2000}$, $\underline{\underline{\underline{B}}}^{0200}$ and higher terms of even parity. We truncate our series at $\underline{\underline{\underline{B}}}^{2000}$ and $\underline{\underline{\underline{B}}}^{0200}$. Cooper and Hoffman (44) demonstrate that the magnetic field viscosity contribution of higher rank tensors and higher order polynomials is small. Thus our truncation is justified.

For this truncation the moments equations of Equation 3.74 are explicitly given by

$$(\overset{\circ}{\underline{W}_1\underline{W}_1}, 2f_1^{[0]}(\underline{I})\overset{\circ}{\underline{W}_1\underline{W}_1}) = (\overset{\circ}{\underline{W}_1\underline{W}_1}, \hat{\Lambda}\,\overset{\circ}{\underline{W}_1\underline{W}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{2000}$$

$$+ (\overset{\circ}{\underline{W}_1\underline{W}_1}, \hat{\Lambda}\,\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{0200}$$

$$(\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, 2f_1^{[0]}(\underline{I})\overset{\circ}{\underline{W}_1\underline{W}_1}) = (\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\Lambda}\,\overset{\circ}{\underline{W}_1\underline{W}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{2000}$$

$$+ (\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\Lambda}\,\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{0200} \qquad (3.76)$$

where we use the fact that $[\underline{a}]^{(2)} = \overset{\circ}{\underline{a}\underline{a}}$. The tensor integrals on the left hand side of Equations 3.76 can be performed to yield

$$n\underline{\underline{\underline{\underline{\Delta}}}} = n^2(\overset{\circ}{\underline{W}_1\underline{W}_1}, \hat{\beta}\,\overset{\circ}{\underline{W}_1\underline{W}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{2000} + n^2(\overset{\circ}{\underline{W}_1\underline{W}_1}, \hat{\beta}\,\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{0200}$$

$$0 = n^2(\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\beta}\,\overset{\circ}{\underline{W}_1\underline{W}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{2000} + n^2(\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\beta}\,\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{0200}$$

$$+ n(\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\Theta}\,\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}) \odot^2 \underline{\underline{\underline{\underline{B}}}}^{0200} \qquad (3.77)$$

where $\hat{\Lambda}$ is expanded by Equations 3.40 and $\hat{\Theta}$ terms which are zero are omitted.

The tensor coefficients $\underline{\underline{\underline{\underline{B}}}}^{2000}$ and $\underline{\underline{\underline{\underline{B}}}}^{0200}$ are fourth rank tensors which are traceless and symmetric on their first two and last two indices. In a field free situation these tensors are proportional to $\underline{\underline{\underline{\underline{\Delta}}}}$ and in the presence of a magnetic field they can be expanded linearly in terms of $\underline{\underline{\underline{B}}}{}^a_0(2)$, $\underline{\underline{\underline{B}}}{}^a_1(2)$, $\underline{\underline{\underline{B}}}{}^a_2(2)$, $\underline{\underline{\underline{B}}}{}^b_1(2)$ and $\underline{\underline{\underline{B}}}{}^b_2(2)$. In order to determine the value of the shear viscosity in the field free and field situations simultaneously, we expand $\underline{\underline{\underline{B}}}{}^{2000}$ and $\underline{\underline{\underline{B}}}{}^{0200}$ as follows:

$$\underline{\underline{\underline{B}}}{}^{2000} = b_{10}\,\underline{\underline{\underline{\Delta}}} + b_{11}\,\underline{\underline{\underline{B}}}{}^a_0(2) + b_{12}\,\underline{\underline{\underline{B}}}{}^a_1(2) + b_{13}\,\underline{\underline{\underline{B}}}{}^a_2(2) + b_{14}\,\underline{\underline{\underline{B}}}{}^b_1(2) + b_{15}\,\underline{\underline{\underline{B}}}{}^b_2(2)$$

$$\underline{\underline{\underline{B}}}{}^{0200} = b_{20}\,\underline{\underline{\underline{\Delta}}} + b_{21}\,\underline{\underline{\underline{B}}}{}^a_0(2) + b_{22}\,\underline{\underline{\underline{B}}}{}^a_1(2) + b_{23}\,\underline{\underline{\underline{B}}}{}^a_2(2) + b_{24}\,\underline{\underline{\underline{B}}}{}^b_1(2) + b_{25}\,\underline{\underline{\underline{B}}}{}^b_2(2) \quad . \tag{3.78}$$

In Equation 3.77 all of the integrals containing $\hat{\Pi}$ are proportional to $\underline{\underline{\underline{\Delta}}}$. The integral containing $\hat{\Theta}$ can be written as

$$n\,(\underline{\Omega}_1 \overset{\circ}{} \underline{\Omega}_1 , \hat{\Theta}\,(\underline{\Omega}_1 \overset{\circ}{} \underline{\Omega}_1) = \frac{nH}{\pi^3} \int d\underline{W}_1 \int d\underline{\Omega}_1\, e^{-W_1^2-\Omega_1^2}\, \underline{\Omega}_1 \overset{\circ}{} \underline{\Omega}_1\; \bar{\underline{m}}_1(\underline{1}) \times \hat{k}_s \cdot \frac{\partial}{\partial \underline{\underline{L}}_1}\, \underline{\Omega}_1 \overset{\circ}{} \underline{\Omega}_1 \quad . \tag{3.79}$$

The average magnetic dipole moment, $\bar{\underline{m}}_1$, has the property that

$$\bar{\underline{m}}_1 = \gamma\, \underline{\underline{L}}_1 \tag{3.80}$$

where γ is the gyromagnetic ratio. When we substitute this expression for $\underline{\bar{M}}_1$ into Equation 3.79 and perform the differentiation therein, we find that

$$n\left(\overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}, \hat{\Theta}\, \overset{\circ}{\underline{\Omega}\underline{\Omega}}\right) = \frac{nH\gamma}{\pi^3}\, \hat{k}_s\, \overline{\underline{X}}^2 \Big[\int d\underline{W}_1 \int d\underline{\Omega}_1$$

$$e^{-W_1^2-\Omega_1^2}\, \overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1}\ \overset{\circ}{\underline{\Omega}_1\underline{\Omega}_1} \Big] \tag{3.81}$$

where for any three vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$

$$\underline{a}\, \overline{\underline{X}}^2\, \underline{b}\, \underline{c} = \underline{a}\times\underline{b}\ \underline{c} + \underline{b}\ \underline{a}\times\underline{c} \quad . \tag{3.82}$$

The single bracketed integral in Equation 3.81 is also proportional to $\underline{\underline{\underline{\hat{A}}}}$. By the usual methods of tensor algebra, we find from these considerations that Equations 3.77 can be written as linear equations containing independent tensors. Coefficients of like tensors in Equations 3.77 can then be equated to form linear scalar equations. We must then calculate the coefficients in these equations which are scalar integrals containing $\hat{p}$ (called collision integrals) and solve these equations in the usual manner for the unknown b_{ij} .

The b_{ij} can be related to the coefficients in the scheme of deGroot and Mazur (45) in which appear η_0 , η_1' , η_2' , η_3' , η_4' and η_5' . These relations are

$$\begin{array}{ll} \eta_0 = b_{10}\, nkT/2 & \eta_3' = (b_{10} + b_{12})\, nkT/2 \\ \eta_1' = (b_{10} + b_{11})\, nkT/2 & \eta_4' = b_{15}\, nkT/2 \\ \eta_2' = (2b_{10} + b_{11} + b_{13})\, nkT/2 & \eta_5' = -b_{14}\, nkT/2 \, . \end{array} \tag{3.83}$$

Equations 3.83 are derived by identifying the components of $\underline{\underline{\underline{\eta}}}$ of Reference 45 with the components of $\underline{\underline{\underline{B}}}^{2000}$.

The steps which lead to the expressions for the magnetic field thermal conductivity in terms of collision integrals are parallel to those for viscosity. The macroscopic equation for the conductive kinetic energy flux, $\underline{Q}'$, is

$$\underline{Q}' = -\underline{\underline{\lambda}} \cdot \underline{\nabla}_1 T \tag{3.84}$$

where $\underline{\underline{\lambda}}$ is the thermal conductivity tensor. The macroscopic expression of Equation 3.84 can be compared to the appropriate microscopic expression of Equation 3.53 for the case of a pure substance in a magnetic field. The result of this comparison is that we can write that

$$\underline{\underline{\lambda}} = 2k^2T \,\{\{ \underline{A} , \underline{A} \}\} \, . \tag{3.85}$$

The vector $\underline{\underline{A}}$ can be expanded in the Kagan-Maksimov (41) series as follows:

$$\underline{A} = \sum_{pqst} [\underline{W}_1]^{(p)} [\underline{\Omega}_1]^{(q)} S^{(s)}_{p+\frac{1}{2}}(W_1^2)\, S^{(t)}_{q+\frac{1}{2}}(\Omega_1^2)$$

$$\odot^{p+q}\, \underline{\underline{A}}^{pqst} \tag{3.86}$$

where the $\underline{\underline{A}}^{pqst}$ are independent of the microscopic variables. The expansion of Equation 3.86 can be introduced into the expression for $\{\{\underline{A},\underline{A}\}\}$ and with the aid of Equations 3.35 and 3.36 we find that

$$\{\{\underline{A},\underline{A}\}\} = \frac{n\, m^{-3/2}}{\pi^3} \sum_{pqst} \int d\underline{W}_1 \int d\underline{\Omega}_1\, e^{-W_1^2-\Omega_1^2}\quad \underline{W}_1$$

$$(W_1^2+\Omega_1^2-4)\, [\underline{W}_1]^{(p)} [\underline{\Omega}_1]^{(q)}\, S^{(s)}_{p+\frac{1}{2}}(W_1^2)$$

$$S^{(t)}_{q+\frac{1}{2}}(\Omega_1^2)\, \odot^{p+q}\, \underline{\underline{A}}^{pqst} \quad . \tag{3.87}$$

Group theory and orthogonality of Sonine polynomials eliminate all but $\underline{\underline{A}}^{1010}$ and $\underline{\underline{A}}^{1001}$ from the series in Equation 3.87. When the remaining tensor integrals of Equation 3.87 are evaluated, the result is that

$$\{\{\underline{A},\underline{A}\}\} = \frac{n\, m^{-1/2}}{4}\left(5\, \underline{\underline{A}}^{1010} + 3\, \underline{\underline{A}}^{1001}\right) \quad . \tag{3.88}$$

We can now substitute the series of Equation 3.86 into the appropriate member of Equations 3.35. Then, as before, we take integral moments with the resulting equation. In considering which $pqst$ couple with $\underline{W}_1 S^{(1)}_{\frac{3}{2}}(W_1^2)$ and $\underline{W}_1 S^{(1)}_{\frac{1}{2}}(\Omega_1^2)$, we observe that parity requires that such p

be odd. The possibility of including $\underline{W}_1$ itself is eliminated by the fact that $\underline{\underline{A}}^{1000} = 0$ by virtue of the linear momentum contribution to the subsidiary conditions of Equation 3.43. The next two terms of the series in order of complexity are $\underline{W}_1 \underline{\Omega}_1$ and $\underline{W}_1 [\underline{\Omega}]^{(2)}$. For spherical tops all the moment equations' coefficients which would couple $\underline{W}_1 \underline{\Omega}_1$ to $\underline{W}_1 S_{\frac{3}{2}}^{(1)}(W_1^2)$ and $\underline{W}_1 S_{\frac{1}{2}}^{(1)}(\Omega_1^2)$ are zero. Therefore we take $\underline{W}_1 [\underline{\Omega}_1]^{(2)}$ as the third term and truncate the series there.

The function A then takes the form

$$\underline{A} = \underline{\Phi}_1 \cdot \underline{\underline{A}}^{1010} + \underline{\Phi}_2 \cdot \underline{\underline{A}}^{1001} + \underline{\underline{\underline{\Phi}}}_3 \odot^3 \underline{\underline{\underline{\underline{A}}}}^{1200} \tag{3.89}$$

with

$$\underline{\Phi}_1 = \underline{W}_1 \left(\tfrac{5}{2} - W_1^2 \right),$$

$$\underline{\Phi}_2 = \underline{W}_1 \left(\tfrac{3}{2} - \Omega_1^2 \right) \tag{3.90}$$

and

$$\underline{\underline{\underline{\Phi}}}_3 = \underline{W}_1 \underline{\Omega}_1^{\circ} \underline{\Omega}_1$$

These $\underline{\underline{A}}^{pqst}$ of Equation 3.89 can be expanded in $\underline{\underline{S}}^{(3)}$ and $\underline{\underline{\underline{\underline{\Delta}}}}$ for field off contributions and the appropriate tensors of Reference 27 for field on contributions as follows:

$$\underline{\underline{A}}^{1010} = a_{10}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3} a_{1i}\,\underline{\underline{J}}^{i} \quad ,$$

$$\underline{\underline{A}}^{1001} = a_{10}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3} a_{1i}\,\underline{\underline{J}}^{i} \tag{3.91}$$

and

$$\underline{\underline{\underline{A}}}^{1200} = a_{30}\,\underline{\underline{\underline{\Delta}}} + \sum_{i=1}^{9} a_{3i}\,\underline{\underline{\underline{I}}}^{i} \quad .$$

The expansions of Equations 3.91 can be substituted into the moments equations to give

$$-\tfrac{5}{4}\, n\, m^{-\frac{1}{2}}\, \underline{\underline{\delta}}^{(3)} = n^2\,(\hat{T}\,\underline{\Phi}_1\,,\,\hat{\mu}\,\underline{\Phi}_1)\cdot(a_{10}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3}\underline{\underline{J}}^{i}) + n^2\,(\hat{T}\,\underline{\Phi}_1\,,\hat{\mu}\,\underline{\Phi}_2)\cdot$$

$$(a_{20}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3} a_{2i}\,\underline{\underline{J}}^{i}) + n^2\,(\hat{T}\,\underline{\Phi}_1\,,\,\hat{\mu}\,\underline{\underline{\Phi}}_3)\odot^3\,(a_{30}\,\underline{\underline{\underline{\Delta}}} + \sum_{i=1}^{9} a_{3i}\,\underline{\underline{\underline{I}}}^{i})$$

$$-\tfrac{3}{4}\, n\, m^{-\frac{1}{2}}\, \underline{\underline{\delta}}^{(3)} = n^2\,(\hat{T}\,\underline{\Phi}_2\,,\,\hat{\mu}\,\underline{\Phi}_1)\cdot(a_{10}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3}\underline{\underline{J}}^{i}) + n^2\,(\hat{T}\,\underline{\Phi}_2\,,\hat{\mu}\,\underline{\Phi}_2)\cdot$$

$$(a_{20}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3} a_{2i}\,\underline{\underline{J}}^{i}) + n^2\,(\hat{T}\,\underline{\Phi}_2\,,\,\hat{\mu}\,\underline{\underline{\Phi}}_3)\odot^3(a_{30}\,\underline{\underline{\underline{\Delta}}} + \sum_{i=1}^{9} a_{3i}\,\underline{\underline{\underline{I}}}^{i})$$

$$0 = n^2\,(\hat{T}\,\underline{\underline{\Phi}}_3^{T}\,,\,\hat{\mu}\,\underline{\Phi}_1)\cdot(a_{10}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3}\underline{\underline{J}}^{i}) + n^2\,(\hat{T}\,\underline{\underline{\Phi}}_3^{T}\,,\hat{\mu}\,\underline{\Phi}_2)\cdot(a_{20}\,\underline{\underline{\delta}}^{(3)} + \sum_{i=1}^{3} a_{2i}$$

$$\underline{\underline{J}}^{i}) + (n\,(\hat{T}\,\underline{\underline{\Phi}}_3^{T}\,,\,\hat{\Theta}\,\underline{\underline{\Phi}}_3) + n^2\,(T\,\underline{\underline{\Phi}}_3^{T}\,,\,\hat{\mu}\,\underline{\underline{\Phi}}_3))\odot^3\,(a_{30}\,\underline{\underline{\underline{\Delta}}} + \sum_{i=1}^{9} a_{3i}\,\underline{\underline{\underline{I}}}^{i}). \tag{3.92}$$

The third moment equation of Equations 3.92 is formed with $\hat{T}\,\underline{\underline{\Phi}}_3^T$ instead of $\hat{T}\,\underline{\underline{\Phi}}_3$ for calculational convenience in constructing the isotropic tensors in which the resulting tensor integrals are to be expanded. In Equations 3.92 the single tensor integral containing $\hat{\Theta}$ can be written as

$$n\left(\hat{T}\,\underline{\underline{\Phi}}_3^T,\ \hat{\Theta}\ \underline{\underline{\Phi}}_3\right) = \frac{nH\gamma}{\pi^3}\ \hat{k}_\xi\ X^2 \int d\underline{W}_1 \int d\underline{\Omega}_1$$

$$e^{-W_1^2-\Omega_1^2}\ \overset{\circ}{\underline{\Omega}}_1\underline{\Omega}_1\ \underline{W}_1\underline{W}_1\,\overset{\circ}{\underline{\Omega}}_1\underline{\Omega}_1\ . \qquad (3.93)$$

The sixth rank tensor integrals of Equations 3.92 and 3.93 are isotropic and can be expanded linearly in terms of $T_1^{(6)}$, $T_2^{(6)}$ and $T_3^{(6)}$ given in Appendix C. The Equations 3.92 can now be reduced to scalar linear equations in the unknown a_{ij} whose coefficients contain collision integrals.

The a_{ij} can be related to the field changes in the thermal conductivity measured in References 10 and 11. Using Equations 3.85 and 3.88, we can write that

$$\Delta\lambda_1/\lambda_0 = (5a_{11} + 3a_{21})\,/\,(5a_{10} + 3a_{20})$$

$$\Delta\lambda_2/\lambda_0 = (5a_{12} + 3a_{22})\,/\,(5a_{10} + 3a_{20})$$

$$\Delta\lambda_3/\lambda_0 = (5a_{13} + 3a_{23})\,/\,(5a_{10} + 3a_{20}) \qquad (3.94)$$

where λ_0 is the field free thermal conductivity and $\Delta\lambda_1$, $\Delta\lambda_2$ and $\Delta\lambda_3$ are respectively the changes in λ_0 parallel, perpendicular and transverse to the magnetic field.

Solution of the Kinetic Equations for Thermal Conductivity, Diffusion and Thermal Diffusion in a Field Free Binary Isotopic Gas Mixture of Linear Molecules

In a field free gas mixture the macroscopic equations for the mass flux and conductive kinetic energy flux are (46)

$$(\underline{J})_i = -(D^T)_i \frac{\underline{\nabla}_1 T}{T} + (m_i n^2/\rho)\ (D)_{ij}(\underline{d}\, m)_j \tag{3.95}$$

$$\underline{Q}' = -\lambda' \underline{\nabla}_1 T - p\ (D^T)_i\ (\underline{d}/\rho)_i \tag{3.96}$$

where D_{ij} is the binary diffusion coefficient, D_i^T is the thermal diffusion coefficient of species i and λ' is the thermal conductivity of the mixture. As was previously mentioned, the $\underline{d}_j$ are linearly dependent. We can identify D_i^T through comparison of Equations 3.53 and 3.95. The diffusion coefficient is defined so that $D_{ii} = 0$ and therefore the implied summation over j in Equation 3.95 is effectively over $n_s - 1$ species (i.e., $j \neq i$) and thus the linear dependence is removed. We now write the diffusional contribution to $\underline{J}_i$ of Equation 3.53 also over all species $j \neq i$

as follows:

$$\underline{J}_i = \left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, \underline{\varsigma}^{(i)} \}\} - n \sum_{j \neq i} \underline{d}_j \cdot \left(\frac{1}{\rho_j} \{\{ \underline{\varsigma}^{(j)}, \underline{\varsigma}^{(i)} \}\} \right.$$

$$\left. - \{\{ \underline{\varsigma}^{(i)}, \underline{\varsigma}^{(i)} \}\} \right) \quad . \tag{3.97}$$

The identification of D_{ij} is then apparent. In particular, for the case of binary mixtures

$$\underline{J}_1 = \left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, \underline{\varsigma}^{(1)} \}\} - n \underline{d}_2 \cdot \{\{ \underline{\varsigma}^{(2)}, \underline{\varsigma}^{(1)} \}\} \quad . \tag{3.98}$$

The appropriate form of the microscopic equation for the conductive kinetic energy flux is

$$\underline{Q}' = - kT \, (2kT)^{1/2} \left[\left(\frac{2k}{T}\right)^{1/2} \underline{\nabla}_1 T \cdot \{\{ \underline{A}, \underline{A} \}\} - \right.$$

$$\left. n \underline{d}_1 \{\{ \underline{\varsigma}^{(1)}, \underline{A} \}\} \right] \, . \tag{3.99}$$

The second rank double bracketed tensors of Equations 3.98 and 3.99 are all proportional to $\underline{\underline{\xi}}^{(3)}$. The scalar coefficients of the macroscopic flux equations (Equations 3.95 and 3.96) can then be identified as

$$D_i^T = - \frac{(2kT)^{1/2}}{3} \{\{ \underline{A}, \underline{\varsigma}^{(i)} \}\} \, , \tag{3.100}$$

$$D_{12} = -\frac{\rho}{3 m_1 m_2 n} \{\{ \underline{\mathcal{G}}^{(2)} ; \underline{\mathcal{G}}^{(2)} \}\} \tag{3.101}$$

and

$$\lambda' = \frac{2k^2T}{3} \{\{ \underline{A} ; \underline{A} \}\} \quad . \tag{3.102}$$

The functions $\underline{A}_i$ and $\underline{\mathcal{G}}_i^{(j)}$ can be expanded in the Kagan-Maksimov (41) series

$$\underline{A}_i = \sum_{pqst} [\underline{W}_1]^{(p)} [\underline{\Omega}_1]^{(q)} S_{p+\frac{1}{2}}^{(s)} (W_1^2) \; S_q^{(t)} (\Omega_1^2) \odot^{p+q} \underline{\underline{A}}_i^{pqst} \tag{3.103}$$

$$\underline{\mathcal{G}}_i^{(j)} = \sum_{pqst} [\underline{W}_1]^{(p)} [\underline{\Omega}_1]^{(q)} S_{p+\frac{1}{2}}^{(s)} (W_1^2) \; S_q^{(t)} (\Omega_1^2) \odot^{p+q} \underline{\underline{\mathcal{G}}}_i^{(j)\,pqst} \tag{3.104}$$

When the expansions for $\underline{A}_i$ and $\underline{\mathcal{G}}_i^{(j)}$ are substituted into Equations 3.100-3.102 and the considerations of group theory, Sonine polynomial orthogonality and subsidiary conditions of Equations 3.43 are made, we find that

$$D_i^T = \frac{kT}{3} n_i m_i^{1/2} \; \underline{\underline{A}}_i^{1000} \odot^2 \underline{\underline{\delta}}^{(3)} \quad , \tag{3.105}$$

$$D_{12} = \frac{\rho n_1}{3n\, m_2} \left(\frac{kT}{2m_1} \right)^{1/2} \left\{ \frac{1}{\rho_2} \underline{\underline{C}}_1^{(2)\,1000} - \frac{1}{\rho_1} \underline{\underline{C}}_2^{(1)\,1000} \right\}$$

$$\odot^2 \; \underline{\underline{\delta}}^{(3)} \tag{3.106}$$

and

$$\lambda' = \frac{k^2 T}{3} \sum_i n_i m_i^{-1/2} \left\{ -\frac{5}{2} \underline{\underline{A}}_i^{1010} - \underline{\underline{A}}_i^{1001} \right\}$$

$$\odot^2 \; \underline{\underline{\delta}}^{(3)} \quad . \tag{3.107}$$

In order to form the moments equations, we truncate the expansions of Equations 3.103 and 3.104 so that they include only $\underline{W}_1$, $\underline{W}_1 (\frac{5}{2} - W_1^2)$, $\underline{W}_1 (1 - \Omega_1^2)$ and $\underline{W}_1 \underline{\Omega}_1^{\circ} \underline{\Omega}_1$. We justify this truncation by the fact that analogous work on spherical particles (46) indicates that for calculating isotopic thermal diffusion, which is of primary interest to us, higher order terms are not necessary. For the field free condition all of the $\underline{\underline{A}}_i^{pqst}$ and $\underline{\underline{C}}_i^{(j)\,pqst}$ are proportional to an isotropic tensor ($\underline{\underline{\delta}}^{(3)}$ or $\underline{\underline{\underline{\Delta}}}$) and as a result we can rewrite the truncated expansions of Equations 3.103 and 3.104 as

$$\underline{A}_i = \sum_{j=1}^{4} \underline{\Phi}_j'' \, a_{ji} \tag{3.108}$$

$$\underline{\varsigma}^{(j)}_i = \sum_{k=1}^{4} \underline{\Phi}''_k \, c_{ki} \tag{3.109}$$

where $\underline{\Phi}''_1 = \underline{W}_1$, $\underline{\Phi}''_2 = \underline{W}_1 (\frac{5}{2} - W_1^2)$, $\underline{\Phi}''_3 = \underline{W}_1 (1 - \Omega_1^2)$ and $\Phi''_4 = \underline{W}_1 \cdot \overset{\circ}{\Omega}_1 \Omega_1$. The moments equations in these terms are

$$(\underline{\Phi}''_1 , (\underline{D}^{(y)})_i) = n_1 n_2 (\underline{\Phi}''_1 , (\hat{\Pi})_{ij} \sum_{k=1}^{4} \underline{\Phi}''_k) (y_k)_j , \tag{3.110}$$

$$(\underline{\Phi}''_2 , (\underline{D}^{(y)})_i) = n_1 n_2 (\underline{\Phi}''_2 , (\hat{\Pi})_{ij} \sum_{k=1}^{4} \underline{\Phi}''_k) (y_k)_j , \tag{3.111}$$

$$(\underline{\Phi}''_3 , (\underline{D}^{(y)})_i) = n_1 n_2 (\underline{\Phi}''_3 , (\hat{\Pi})_{ij} \sum_{k=1}^{4} \underline{\Phi}''_k) (y_k)_j \tag{3.112}$$

and

$$(\underline{\Phi}''_4 , (\underline{D}^{(y)})_i) = n_1 n_2 (\underline{\Phi}''_4 , (\hat{\Pi})_{ij} \sum_{k=1}^{4} \underline{\Phi}''_k) (y_k)_j \tag{3.113}$$

where $(\underline{D}^{(y)})_i$ is $(\underline{D}^{(\underline{A})})_i$ or $(\underline{D}^{(\varsigma^{(j)})})_i$ when $(y_k)_j$ is respectively $(a_k)_j$ or $(c_k)_j$. The integrals which appear on the right hand side of Equations 3.110-3.113 are the same for either $\underline{A}_i$ or $\underline{\varsigma}^{(j)}_i$ terms because both are expanded in the same set. For the case that $(\underline{D}^{(y)})_i$ is $(\underline{D}^{(A)})_i$, the left hand sides of Equations 3.110 and 3.113 are zero and

$$(\underline{\Phi}''_2 , (\underline{D}^{(A)})_i) = -\frac{5}{4} n_i m_i^{-1/2} \underline{\underline{\delta}}^{(3)} \tag{3.114}$$

$$(\underline{\Phi}_3'' , (\underline{D}^{(A)})_i) = - \frac{1}{2} n_i m_i^{-1/2} \underline{\delta}^{(3)} . \tag{3.115}$$

For the case that $(\underline{D}^{(4)})_i$ is $(\underline{D}^{(\varsigma^{(0)})})_i$, the right hand sides of Equations 3.111-3.113 are zero and

$$(\underline{\Phi}_1'' , (\underline{D}^{(\varsigma^{(0)})})_i) = - \frac{\rho_1 \rho_2}{\rho} \left(\frac{2kT}{m_i} \right)^{1/2} \left(\frac{1}{2} \right) \underline{\delta}^{(3)} . \tag{3.116}$$

These moments equations contain second rank tensors all of which are proportional to $\underline{\delta}^{(3)}$. From the coefficients of the tensors in the moments equations, we can form scalar equations which can easily be solved. In terms of the scalar unknowns a_{ij} and α_{ij} , Equations 3.105-3.107 are given by

$$D_i^T = kT \, n_i \, m_i^{-1/2} \, a_{1i} \quad , \tag{3.117}$$

$$D_{12} = \frac{\rho n_1}{n m_2} \left(\frac{kT}{2m_1} \right)^{1/2} \left(\frac{\alpha_{11}}{\rho_2} - \frac{\alpha_{12}}{\rho_1} \right) \tag{3.118}$$

and

$$\lambda' = k^2 T \sum_i n_i m_i^{-1/2} \left[\frac{5}{2} a_{2i} - a_{3i} \right] . \tag{3.119}$$

Thus we have derived the kinetic equations for the cases of interest. These equations contain the notorious collision integrals. The next chapter will be devoted to the evaluation of these integrals for nonspherical molecular models.

CHAPTER 4. EVALUATION OF COLLISION INTEGRALS FOR NONSPHERICAL MOLECULAR MODELS

The collision integral coefficients in the moments equations (Equations 3.78, 3.92 and 3.110-3.113) are tensors which can be written as a linear combination of a basis set of isotropic tensors with scalar integral coefficients. A scalar collision integral between a function $\underline{\underline{\Phi}}_i$ of tensor rank u and $\underline{\underline{\Psi}}_j$ of tensor rank v is of the form

$$\underline{\underline{\mathcal{A}}} \odot^{u+v} (\underline{\underline{\Phi}}_i, \hat{P}_{ij}\, \underline{\underline{\Psi}}_j) = \underline{\underline{\mathcal{A}}} \odot^{u+v} \int d\underline{\bar{1}} \int d\underline{\bar{2}} \int d\underline{\bar{1}}' \int d\underline{\bar{2}}'$$

$$\frac{f^{[0]}_{1i}(\underline{\bar{1}})}{n_i} \frac{f^{[0]}_{2j}(\underline{\bar{2}})}{n_j} W_F(\underline{\bar{1}}\, \underline{\bar{2}} \mid \underline{\bar{1}}'\, \underline{\bar{2}}')$$

$$\underline{\underline{\Phi}} \left(\underline{\underline{\Psi}}(\underline{\bar{1}}) - \underline{\underline{\Psi}}(\underline{\bar{1}}') + \underline{\underline{\Psi}}(\underline{\bar{2}}) - \underline{\underline{\Psi}}(\underline{\bar{2}}') \right) \tag{4.1}$$

where $\underline{\underline{\mathcal{A}}}$ is some isotropic tensor of rank $u+v$. We can make the division of terms such that

$$\underline{\underline{\mathcal{A}}} \odot^{u+v} (\underline{\underline{\Phi}}_i, \hat{P}_{ij}\, \underline{\underline{\Psi}}_j) = \underline{\underline{\mathcal{A}}} \odot^{u+v} \Big([\underline{\underline{\Phi}}_i, \underline{\underline{\Psi}}]^{1,1}_{i,j}$$

$$+ [\underline{\underline{\Phi}}_i, \underline{\underline{\Psi}}]^{1,2}_{i,j} \Big) \tag{4.2}$$

where

$$\underline{\underline{g}} \odot^{u+v} [\, \underline{\underline{\phi}}_{i} , \underline{\underline{\Psi}} \,]^{1,k}_{i,j} = \underline{\underline{g}} \odot^{u+v} \int d\bar{\underline{1}} \int d\bar{\underline{2}} \int d\bar{\underline{1}}' \int d\bar{\underline{2}}'$$

$$\frac{f^{[0]}_{1i}(\bar{\underline{1}})}{n_i} \; \frac{f^{[0]}_{1j}(\bar{\underline{2}})}{n_j} \; W_F(\bar{\underline{1}}\,\bar{\underline{2}} \mid \bar{\underline{1}}'\,\bar{\underline{2}}')$$

$$\underline{\underline{\phi}}(\bar{\underline{1}}) \; (\underline{\underline{\Psi}}(\bar{\underline{k}}) \cdot \underline{\underline{\Psi}}(\bar{\underline{k}}')) . \qquad (4.3)$$

From this point, we refer only expressions of the form of Equation 4.3 as collision integrals.

From the Kagan-Maksimov expansions (Equations 3.66, 3.87, 3.103 and 3.104), the functions $\underline{\underline{\phi}}_i$ and $\underline{\underline{\Psi}}_j$ can be taken to be polyads in $\underline{w}$ and $\underline{\Omega}$, the reduced linear momentum and reduced angular momentum respectively. These momenta of colliding molecules are conveniently taken to be the components of a generalized 12-D momentum vector $\underset{\sim}{\eta} = (\underline{\Omega}_1, \underline{\Omega}_2, \underline{w}_1, \underline{w}_2)$, where the curved underscore signifies a vector in the 12-D space as opposed to a straight underscore for a vector in the 3-D space. When writing a tensor $\underset{\sim}{P}$ in this space in component form, we write $(P)_{\alpha i, \beta j}$. The Greek indices run from one to four, indicating whether we are in the $\underline{\Omega}_1$, $\underline{\Omega}_2$, $\underline{w}_1$ or $\underline{w}_2$ subspace, and the Latin indices run from one to three. We define the following projection operators:

$$\underset{\approx}{P}_{\Omega_1} = \begin{pmatrix} \underline{\underline{\delta}}^{(3)} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \end{pmatrix} \qquad \underset{\approx}{P}_{\Omega_2} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\delta}}^{(3)} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \end{pmatrix}$$

$$\underset{\approx}{P}_{W_1} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{\delta}}^{(3)} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \end{pmatrix} \qquad \underset{\approx}{P}_{W_2} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{\delta}}^{(3)} \end{pmatrix} \tag{4.4}$$

which are second rank tensors in the 12-D space. For any j from one to four, $\underline{M}_j$ ($\underline{M}_1 = \underline{\Omega}_1$, $\underline{M}_2 = \underline{\Omega}_2$, $\underline{M}_3 = \underline{W}_1$ and $\underline{M}_4 = \underline{W}_2$) are such that we can define a quantity $\underset{\sim}{M}_j = (M_j)_{\alpha i} = \sum_{\beta k} (P_{M_j})_{\alpha i, \beta k} \, (\eta)_{\beta k}$. The operations $\odot_3$ and $\odot_{12}$ in the 12-D space of concern here are defined by

$$(\underline{\underline{I}} \odot_3 \underset{\sim}{M}_j)_i = \sum_{\alpha k} (I)_{ik} \, (M_j)_{\alpha k}$$

and

$$\underset{\sim}{M}_j \odot_{12} \underset{\sim}{M}_k = \sum_{\alpha} \sum_{i} (M_j)_{\alpha i} \, (M_k)_{\alpha i}$$

where $\underline{\underline{I}}$ is a second rank tensor in the 3-D space. These operations can be carried out more than once within a single expression. In the case of $\odot_3^{a}$ $(a \geq 1)$ we imply that the operations are carried out a times according to the nested convention of indicial collapse of Chapman and Cowling (42).

The polyad $\underline{\underline{\phi}}_i \, \underline{\underline{\psi}}_j$ can be written as

$$\underline{\underline{\phi}}_i \, \underline{\underline{\psi}}_j = \underline{\mathfrak{m}}_{i_1} \cdots \underline{\mathfrak{m}}_{i_u} \, \underline{\mathfrak{m}}_{j_1} \cdots \underline{\mathfrak{m}}_{j_v} \quad .$$

Likewise a 12-D analogue of this polyad, $\underset{\approx}{\phi}_i \, \underset{\approx}{\psi}_j$, is given by

$$\underset{\approx}{\phi}_i \, \underset{\approx}{\psi}_j \equiv \sum_{\beta l} \cdots \sum_{\delta n} \left(P_{m_{i_1}} \right)_{\alpha k, \beta l} \cdots \left(P_{m_{j_v}} \right)_{\gamma m, \delta l} (\eta)_{\beta l} \cdots (\eta)_{\delta n}$$

$$\equiv \underset{\approx}{P}_{m_{i_1}} \cdots \underset{\approx}{P}_{m_{j_v}} \; \odot_{12}^{u+v} \; (\underset{\sim}{\eta})^{u+v}$$

$$\equiv \underset{\approx}{\mathcal{P}}_{\phi_i \psi_j} \; \odot_{12}^{u+v} \; (\underset{\sim}{\eta})^{u+v} .$$

As a consequence of these definitions, we have that

$$\underline{\underline{\mathcal{J}}} \odot^{u+v} \underline{\underline{\phi}}_i \, \underline{\underline{\psi}}_j = \underline{\underline{\mathcal{J}}} \odot_3^{u+v} \underset{\approx}{\mathcal{P}}_{\phi_i \psi_j} \; \odot_{12}^{u+v} \; (\underset{\sim}{\eta})^{u+v} \tag{4.5}$$

The identification of Equation 4.5 can be used to rewrite Equation 4.3 as

$$\underline{\underline{\mathcal{J}}} \odot^{u+v} \left[\underline{\underline{\phi}}_i , \underline{\underline{\psi}} \right]^{1,k}_{i,j} = \pi^{-l} \, \underline{\underline{\mathcal{J}}} \odot_3^{u+v} \underset{\approx}{\mathcal{P}}_{\phi_i \psi_l} \; \odot_{12}^{u+v}$$

$$\int d\underline{\eta} \int d\underline{\eta}' \, e^{-\eta^2} \, w_E(\underline{\eta}|\underline{\eta}')(\underline{\eta})^u ((\underline{\eta})^v - (\underline{\eta}')^v) \qquad (4.6)$$

where $\ell = i$ if $k = 1$ and $\ell = j$ if $k = 2$. Thus, without loss of generality, we can restrict our attention to a tensor integral of the form

$$\underset{=}{A}_{uv} = \pi^{-6} \int d\underline{\eta} \int d\underline{\eta}' \, e^{-\eta^2} \, W_E(\underline{\eta}|\underline{\eta}') (\underline{\eta})^u ((\underline{\eta})^v - (\underline{\eta}')^v). \qquad (4.7)$$

The collisions do not depend on the momentum of the center of mass of the two particles and it is therefore advantageous to transform the 12-D momentum to a frame such that $\underline{\eta}^{com} = (\underline{\Omega}_1, \underline{\Omega}_2, \underline{P}, \underline{\gamma})$; where $\underline{P}$; the reduced linear momentum of the center of mass, and $\underline{\gamma}$, the reduced relative linear momentum of the colliding particles, are defined respectively by

$$\underline{P} = \xi^{(2)} \underline{W}_1 + \xi^{(1)} \underline{W}_2$$

and

$$\underline{\gamma} = -\xi^{(1)} \underline{W}_1 + \xi^{(2)} \underline{W}_2 \qquad (4.8)$$

with $\xi^{(i)} = (\mu/m_i)^{1/2}$ and μ equal to the reduced mass. The superscript com refers to the center of mass coordinates. The unitary transformation, $\underset{\approx}{S}$, which transforms the generalized momentum from $(\underline{\Omega}_1, \underline{\Omega}_2, \underline{w}_1, \underline{w}_2)$ to $(\underline{\Omega}_1, \underline{\Omega}_2, \underline{\beta}, \underline{\gamma})$ is given by

$$\underset{\approx}{S} = \begin{pmatrix} \underline{\underline{\delta}}^{(3)} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{\delta}}^{(3)} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \xi^{(2)}\underline{\underline{\delta}}^{(3)} & \xi^{(1)}\underline{\underline{\delta}}^{(3)} \\ \underline{\underline{0}} & \underline{\underline{0}} & -\xi^{(1)}\underline{\underline{\delta}}^{(3)} & \xi^{(2)}\underline{\underline{\delta}}^{(3)} \end{pmatrix} \tag{4.9}$$

Any projection operator $\underset{\approx}{P}_{m_j}$ can be converted to and from center of mass frame using $\underset{\approx}{S}$ as follows:

$$\underset{\approx}{P}^{com}_{m_j} = \underset{\approx}{S} \odot_{12} \underset{\approx}{P}_{m_j} \odot_{12} \underset{\approx}{S}^{-1}$$

$$\underset{\approx}{P}_{m_j} = \underset{\approx}{S}^{-1} \odot_{12} \underset{\approx}{P}^{com}_{m_j} \odot_{12} \underset{\approx}{S} \tag{4.9a}$$

As an illustration of Equation 4.9a, we note that

$$\underset{\approx}{P}^{com}_{w_1} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & (\xi^{(2)})^2\,\underline{\underline{\delta}}^{(3)} & -\xi^{(1)}\xi^{(2)}\underline{\underline{\delta}}^{(3)} \\ \underline{\underline{0}} & \underline{\underline{0}} & -\xi^{(1)}\xi^{(2)}\underline{\underline{\delta}}^{(3)} & (\xi^{(1)})^2\,\underline{\underline{\delta}}^{(3)} \end{pmatrix}$$

$$\underset{\approx}{P}{}^{com}_{w_2} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & (\xi^{(1)})^2 \, \underline{\underline{\delta}}^{(3)} & \xi^{(1)} \xi^{(2)} \, \underline{\underline{\delta}}^{(3)} \\ \underline{\underline{0}} & \underline{\underline{0}} & \xi^{(1)} \xi^{(2)} \, \underline{\underline{\delta}}^{(3} & (\xi^{(2)})^2 \, \underline{\underline{\delta}}^{(3)} \end{pmatrix}$$

$$\underset{\approx}{P}_p = \underset{\approx}{P}{}^{com}_{w_1} \qquad \underset{\approx}{P}_\gamma = \underset{\approx}{P}{}^{com}_{w_2} \quad . \tag{4.10}$$

Because of the collisional invariance of $\underset{\sim}{p}$, it is convenient in the evaluation of Equation 4.7 to work in the center of mass frame; but, in the actual process of performing projections on the tensor resulting from the integrations in that equation, it is easier to stay in the laboratory frame because of the simple form of the projection operators.

Let $\underset{\sim}{\eta}^*$ be the precollision momentum vector corresponding to the postcollision momentum $\underset{\sim}{\eta}$ on a given trajectory in a binary collision. We can define an apse vector $\hat{\kappa}$ for the collision in the 12-D space by the relation

$$\hat{\kappa} = (\underset{\sim}{\eta} - \underset{\sim}{\eta}^*) \; / \; |\underset{\sim}{\eta} - \underset{\sim}{\eta}^*| \quad . \tag{4.11}$$

As a trivial consequence of this definition and the fact that total kinetic energy is conserved in collision (i.e. $\eta^{*2} = \eta^2$), we have that

$$\underset{\sim}{\eta} \cdot \hat{\kappa} \geqslant 0 \quad , \tag{4.12}$$

$$\underset{\sim}{\eta}^{*} \cdot \hat{\kappa} = - \underset{\sim}{\eta} \cdot \hat{\kappa} \tag{4.13}$$

and

$$\underset{\sim}{\eta} - (\underset{\sim}{\eta} \cdot \hat{\kappa}) \hat{\kappa} = \underset{\sim}{\eta}^{*} - (\underset{\sim}{\eta}^{*} \cdot \hat{\kappa}) \hat{\kappa} . \tag{4.14}$$

Thus the net effect of the collision is to change the sign of the component of the momentum along the apse vector while leaving the other momentum components unchanged. It is then natural to think of $\hat{\kappa}$ as a unit vector along the "reaction coordinate".

The components of $\hat{\kappa}$ in the center of mass frame are given by

$$\hat{\kappa}^{com} = \frac{1}{D} (- \underset{\sim}{a}_1 , - \underset{\sim}{a}_2 , 0 , \hat{\underset{\sim}{k}}_a) \tag{4.15}$$

where $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$ and $\hat{\underset{\sim}{k}}_a$ are defined by this equation, $D = (1 + a_1^2 + a_2^2)^{1/2}$ and the invariance of the center of mass momentum component is reflected in the fact that $\underset{\approx}{P}_p \cdot \hat{\kappa} = (\underset{\sim}{0} , \underset{\sim}{0} , \underset{\sim}{0} , \underset{\sim}{0})$. In the laboratory frame, $\hat{\kappa}$ is given by

$$\hat{\kappa} = D^{-1} (- \underset{\sim}{a}_1 , - \underset{\sim}{a}_2 , - \xi^{(1)} \hat{\underset{\sim}{k}}_a , \xi^{(2)} \hat{\underset{\sim}{k}}_a) . \tag{4.16}$$

For spherical potentials there are no collisionally active rotational degrees of freedom and hence $\hat{k}^{com} = (\underline{0}, \underline{0}, \underline{0}, \hat{k}_a)$.

Since the component of the generalized momentum along the apse vector changes sign upon collision, it follows that for an odd number of times during the collision the generalized momentum is orthogonal to the apse vector. The temporally central point of perpendicularity we term the apse point.

The specific transition rate $w_F(\eta | \eta')$ from the η' to the η states can be expressed in the form

$$w_F(\eta | \eta') = \left(\frac{2kT}{\mu}\right)^{1/2} \frac{1}{\Delta_1 \Delta_2} \int_{\hat{k} \odot_2 \eta > 0} d\hat{k} \, (\hat{k} \cdot \eta) \, \mathcal{J}(\hat{k}, \eta) \, \delta(\eta' - \eta^*) \qquad (4.17)$$

where the integral restriction $\hat{k} \odot_2 \eta > 0$ assures that η is a postcollisional momentum. This equation defines $\mathcal{J}(\hat{k}, \eta)$ which we call the generalized cross section and whose explicit functional form depends on the nature of the interaction potential. Since $\hat{k}$ is a unit vector in the 12-D space of η , it is specified by 11 generalized Eulerian angles. However, since $\underset{\approx}{P}_{\beta} \cdot \hat{k} = \underset{\sim}{0}$, $\hat{k}$ has a nontrivial dependence of only eight generalized Eulerian angles which fix it in the $\underset{\approx}{P}_{\Omega_1} + \underset{\approx}{P}_{\Omega_2} + \underset{\approx}{P}_{\gamma}$ subspace. Substituting Equation 4.17 into Equation 4.7 yields

$$\underset{=}{\Lambda}_{uv} = \frac{\pi^{-6}}{\Delta_1 \Delta_2} \left(\frac{2kT}{\mu}\right)^{1/2} \int d\hat{k} \;\; (\underline{u}, \underline{v}) \qquad (4.18)$$

where

$$(\underline{u},\underline{v}) = \int_{\hat{k}\odot_{12}\eta>0} d\eta \; e^{-\eta^2} \; (\hat{k}\cdot\eta) \; \mathcal{J}(\hat{k},\eta)$$

$$(\eta)^u \left((\eta)^v - (\eta^*)^v\right) \quad . \tag{4.19}$$

Further evaluation of $\underline{\underline{\Lambda}}_{uv}$ requires specific knowledge of the generalized cross section, $\mathcal{J}(\hat{k},\eta)$.

The form of $\mathcal{J}$ is known for the limiting cases of rigid ovaloids and central soft potentials. For rigid ovaloids it is known that (26)

$$\mathcal{J} = \bar{\mathcal{J}}_{r_0}(\hat{k})\, Q_{r_1 r_2} = D \left| \frac{\partial(\underline{\alpha}_1, \underline{\alpha}_2, \hat{k}_e)}{\partial \hat{k}} \right| S \, Q_{r_1 r_2} \tag{4.20}$$

where $\left| \frac{\partial(\underline{\alpha}_1, \underline{\alpha}_2, \hat{k}_e)}{\partial \hat{k}} \right|$ is the Jacobian of transformation from the coordinates $(\underline{\alpha}_1, \underline{\alpha}_2, \hat{k}_e)$ to $\hat{k}$. Here S is the surface area per unit solid angle of $\hat{k}_e$ on the volume excluded to the center of mass of molecule 2 by the presence of molecule 1 at fixed $\underline{\alpha}_1$ and $\underline{\alpha}_2$. The unit vector $\hat{k}_e$ is the normal to the excluded volume surface at the position of the center of mass of molecule 2 during the instant of contact. The factor $Q_{r_1 r_2}$ (r_1 and r_2 being the number of collisionally active rotational degrees of freedom of molecules 1 and 2 respectively) is unity for r_1 and r_2 equal to zero or three and is a product of delta functions otherwise. For instance, for a collision between rigid ellipsoids $r_1 = r_2 = 2$ and $Q_{r_1 r_2} = \delta(\underline{\Omega}_1 \cdot \hat{e}_1)\,\delta(\underline{\Omega}_2 \cdot \hat{e}_2)$ to account for the fact that the angular momentum does not change along the major axes of bodies 1 and 2 which are respectively $\hat{e}_1$ and $\hat{e}_2$. As previously mentioned $D = (1 + a_1^2 + a_2^2)^{1/2}$. We note that the factor $\bar{g}_{ro}(\hat{k})$ is momentum independent. The subscript ro signifies that a quantity is evaluated using the rigid ovaloid model.

For a central soft potential $g = g_{sp}(\hat{k}\odot_{12}\eta, \gamma_\perp^2)$ where $\gamma_\perp^2 = \gamma^2 - (\hat{k}_a \cdot \underline{\gamma})^2$ and $\hat{k}\odot_{12}\eta = \hat{k}_a \cdot \underline{\gamma}$. That is, the cross section depends on the component of the generalized momentum along the reaction coordinate and the magnitude of the relative velocity normal to $\hat{k}_a$. The latter quantity governs the "fly by" time and hence, in part, the time of duration of contact.

For a general soft potential it seems physically reasonable to expect that g will sensitively depend on $\hat{k}\odot_{12}\eta$ and $\gamma_\perp^2$ (or perhaps some other appropriately chosen speed which determines the "fly by" time) as in the case of soft spheres. We first assume that g can be factored into $g = \bar{g}\, Q_{r_1 r_2}$ where the delta functions in $Q_{r_1 r_2}$ depend on the apse geometry. Then we assume that $\bar{g}$ is only a function of the momentum through $\hat{k}\odot_{12}\eta$ and $\gamma_\perp^2$

(i.e. that $\bar{j} = \bar{j}(\hat{k}, \hat{k}\odot_{12}\eta, \gamma_1^2)$). The $(\underline{u}, \underline{v})$ tensors of Equation 4.19 then can be greatly simplified. In this approximation

$$(\underline{u}, \underline{v}) = \int_{\hat{k}\odot_{12}\eta > 0} d\bar{\eta}\; e^{-\bar{\eta}^2}\; \hat{k}\odot_{12}\eta\;\; \bar{j}(\hat{k}, \hat{k}\odot_{12}\bar{\eta}, \gamma_1^2)$$

$$(\bar{\eta})^{u}\left((\bar{\eta})^{v} - (\bar{\eta}^{*})^{v}\right) \qquad (4.21)$$

where

$$\int d\eta\;\; \eta\;\; Q_{r_1 r_2} = \int d\bar{\eta}\;\; \bar{\eta}$$

and $\bar{\eta}$ is a vector in the $n_\lambda (= r_1 + r_2 + 6)$ -D subspace of the 12-D space. From symmetry considerations, it is evident that the tensorial character of $(\underline{u}, \underline{v})$ can be expressed in terms of the unit vector $\hat{k}$, the projection operator $\underset{\approx}{U}^{(2)} = \underset{\approx}{P}_{\delta} - \underset{\approx}{P}_{k_a k_a}$ where

$$\underset{\approx}{P}^{com}_{k_a k_a} = \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} \\ \underline{\underline{0}} & \underline{\underline{0}} & \underline{\underline{0}} & \hat{k}_a \hat{k}_a \end{pmatrix}$$

and the unit tensor in the $n_\perp$-D subspace, $\underset{\approx}{\delta}^{(n_\perp)}$.

In order to proceed we rotate the vector η, by some unitary transformation $\underset{\approx}{R}$, into a frame such that $\hat{k}$ is along the last axis. From Reference 47 we see that we can construct this transformation such that it does not mix the $\underset{\sim}{p}$ and $\gamma_\perp$ subspaces with any other components. In the transformed space, Equation 4.21 becomes

$$(\underline{y},\underline{v}) = \int d\bar{\eta}_\perp \; e^{-\bar{\eta}_\perp^2} \int\limits_{\gamma_n>0} d\bar{\underset{\sim}{\gamma}} \; \gamma_n \; \bar{J}(\hat{k},\gamma_n,\bar{\gamma}_\perp^2)$$

$$e^{-\bar{\gamma}^2}(\bar{\eta}_\perp+\bar{\underset{\sim}{\gamma}})^u \left[(\bar{\eta}_\perp+\bar{\underset{\sim}{\gamma}})^v-(\bar{\eta}_\perp+\bar{\underset{\sim}{\gamma}}^{*})^v\right] \qquad (4.22)$$

where

$$\bar{\eta}_\perp = \underset{\approx}{R}\odot_{12}\eta - \underset{\approx}{P}_\gamma\odot_{12}(\underset{\approx}{R}\odot_{12}\eta) \qquad (4.23)$$

and

$$\bar{\underset{\sim}{\gamma}} \equiv \underset{\sim}{\gamma}_\perp + (\hat{k}\odot_{12}\bar{\eta})\,\underset{\approx}{R}\odot_{12}\hat{k} \equiv \underset{\sim}{\gamma}_\perp + \gamma_n(\underset{\approx}{R}\odot_{12}\hat{k}). \qquad (4.24)$$

The integrand of Equation 4.22 can be separated into a sum of polyads in $\bar{\eta}$ (by means of the tensorial equivalent of the binomial theorem) as follows:

$$(\bar{\eta}_\perp+\bar{\gamma}) = \sum_{a=0}^{u}\sum_{p}(\bar{\underset{\sim}{\gamma}})^a(\bar{\eta}_\perp)^{u-a} \qquad (4.25)$$

and

$$(\bar{\eta}_\perp + \bar{\underset{\sim}{\gamma}})^{v} = \sum_{b=0}^{v} \sum_{p} (\bar{\eta}_\perp)^{v-b} (\bar{\underset{\sim}{\gamma}})^{b} \quad . \tag{4.26}$$

We adopt the convention that p below a summation symbol indicates the sum over all possible unique permutations of the indices of the tensor to its right. When Equations 4.25 and 4.26 are substituted into Equation 4.22, we find that

$$(\underline{u},\underline{v}) = \underset{[(-1)^{u+v} = (-1)^{a+b}]}{\sum_{a=0}^{u} \sum_{b=0}^{v}} \sum_{p_{u,v}} \int_{\gamma_n > 0} d\bar{\underset{\sim}{\gamma}} \; \bar{g}(\hat{K}, \gamma_n, \bar{\gamma}_\perp^2) \, e^{-\bar{\gamma}^2} (\bar{\underset{\sim}{\gamma}})^{a}$$

$$\int d\bar{\underset{\sim}{\eta}}_\perp \, e^{-\bar{\eta}_\perp^2} (\bar{\eta}_\perp)^{u+v-a-b} \left((\bar{\underset{\sim}{\gamma}})^{b} - (\bar{\underset{\sim}{\gamma}}^{*})^{b} \right) \tag{4.27}$$

where we indicate in the brackets the parity constraints on the summations. The symbol $p_{a,b}$ indicates the restricted sum over all possible unique permutations over the first a and the last b indices of the tensor. It is convenient in Equation 4.27 to change the indices of summation from a,b to j,k where $j=a$ and $k=a+b$ with the result that

$$(\underset{\sim}{u},\underset{\sim}{v}) = \sum_{j=0}^{u} \sum_{\substack{k=j+1 \\ [(-1)^{u+v} = (-1)^{k}]}}^{v+j} \sum_{P_{u,v}} \int_{\gamma_n>0} d\underset{\sim}{\gamma}\, \ddot{J}\, \gamma_n e^{-\gamma^2} (\underset{\sim}{\gamma})^{j}$$

$$\left\{ \int d\bar{\eta}_\perp e^{-\bar{\eta}_\perp^2} (\bar{\eta}_\perp)^{u+v-k} \right\} \left((\underset{\sim}{\bar{\gamma}})^{k-j} - (\underset{\sim}{\bar{\gamma}}^{*})^{k-j} \right). \quad (4.28)$$

The tensor integral over $\bar{\eta}_\perp$ is proportional to an isotropic cartesian tensor of rank $u+v-k$. Because of the complete symmetry with respect to indical interchange, this tensor is

$$\underset{\approx}{J}^{(n_d-3)}_{u+v-k} = \sum_{P} \left(\underset{\approx}{\delta}^{(n_d-3)} \right)^{\frac{u+v-k}{2}} \quad (4.29)$$

We define the coefficient of proportionality between

$$\int d\bar{\eta}_\perp e^{-\bar{\eta}_\perp^2} (\bar{\eta}_\perp)^{u+v-k}$$

and

$$\underset{\approx}{J}^{(n_d-3)}_{u+v-k}$$

by α. By the usual methods of tensor algebra, we can show that

$$\alpha = \left(\Gamma\left((n_d-3)/2 \right) \Big/ \left(\Gamma\left((u+v-k+n_d-3)/2 \right) 2^{\frac{u+v-k}{2}} \right) \right)$$

$$\int d\bar{\eta}_\perp \, e^{-\bar{\eta}_\perp^2} \, (\bar{\eta}_\perp)^{u+v-k} \tag{4.30}$$

The remaining scaler integral of Equation 4.30 can be evaluated by transforming $\bar{\eta}_\perp$ to $(n_d - 3)$ -D spherical polar coordinates as follows:

$$\int d\bar{\eta}_\perp \, \bar{\eta}_\perp^{\,u+v-k} \, e^{-\bar{\eta}_\perp^2} = \int dA^{(n_d-3)} \int d\bar{\eta}_\perp \, \bar{\eta}_\perp^{\,u+v-k+n_d-4} \, e^{-\bar{\eta}_\perp^2}$$

$$= \pi^{(\frac{n_d-3}{2})} \, \Gamma\left((u+v-k+n_d-3)/2\right) /$$

$$\Gamma\left((n_d-3)/2\right) \tag{4.31}$$

where $\int dA^{(b)}$ signifies the angular integrations in a b -D spherical polar frame and is given by

$$\int dA^{(b)} = 2\pi^{b/2} / \Gamma(b/2) \quad . \tag{4.32}$$

Combining the results of Equations 4.30 and 4.31, we can rewrite Equation 4.28 as

$$(\underset{\sim}{u}, \underset{\sim}{v}) = \pi^{(\frac{n_d-3}{2})} \sum_{\substack{j=0 \\ [(-1)^{u+v}=(-1)^k]}}^{u} \; \sum_{k=j+1}^{v+j} \; \sum_{P_{u,v}} \; \int_{\gamma_n>0} d\bar{\underset{\sim}{\gamma}} \; \gamma_n \, \bar{\gamma} \, e^{-\bar{\gamma}^2} \; 2^{-(\frac{u+v-k}{2})}$$

$$(\bar{\underset{\sim}{\gamma}})^j \quad \underset{\approx}{J}{}^{(n_d-3)}_{u+v-k} \; \left((\bar{\underset{\sim}{\zeta}})^{k-j} - (\bar{\underset{\sim}{\zeta}}^*)^{k-j} \right) \quad . \tag{4.33}$$

The remaining tensor integrals can be linearly expanded in terms of appropriate tensors formed from polyads of $\underset{\approx}{U}^{(2)}$ and $\hat{k}$. When this expansion is carried out and when $\underset{\approx}{\delta}^{(n_A-3)}$ is written as

$$\underset{\approx}{\delta}^{(n_A-3)} = \underset{\approx}{\delta}^{(n_A)} - \underset{\approx}{U}^{(2)} - \hat{k}\hat{k} \quad , \qquad (4.34)$$

we find that for the important cases in which μ and ν range from one to three

$$(\underline{1}, \underline{1}) = 2 \langle y^2 \rangle \hat{k}\hat{k} \quad , \qquad (4.35)$$

$$(\underline{1}, \underline{3}) = \langle y^2 \rangle \Big(\sum_{P_{1,3}} (\hat{k} \underset{\approx}{\delta}^{(n_A)} \hat{k} - \hat{k} \underset{\approx}{U}^{(2)} \hat{k}) - 3 \hat{k}\hat{k}\hat{k}\hat{k} \Big)$$
$$+ \langle y^2 z \rangle \sum_{P_{1,3}} \hat{k} \underset{\approx}{U}^{(2)} \hat{k} + 2 \langle y^4 \rangle \hat{k}\hat{k}\hat{k}\hat{k} \quad , \qquad (4.36)$$

$$(\underline{2}, \underline{2}) = \langle y^2 \rangle \Big(\sum_{P_{2,2}} (\hat{k} \underset{\approx}{\delta}^{(n_A)} \hat{k} - \hat{k} \underset{\approx}{U}^{(2)} \hat{k}) - 4 \hat{k}\hat{k}\hat{k}\hat{k} \Big)$$
$$+ \langle y^2 z \rangle \sum_{P_{2,2}} \hat{k} \underset{\approx}{U}^{(2)} \hat{k} \quad , \qquad (4.37)$$

$$(\underline{3}, \underline{3}) = (\langle y^2 \rangle / 2) \Big[\sum_{P_{3,3}} (\hat{k} \underset{\approx}{J}_4^{(n_A)} \hat{k} - \hat{k} \underset{\approx}{J}_4^{(n_A,2)} \hat{k}$$

$$- \hat{K}\, \underset{\approx}{J}_4^{(2,n_d)}\, \hat{K} + \hat{K}\, \underset{\approx}{J}_4^{(2)}\, \hat{K} \Big) - 3 \sum_{P_{3,3}} \Big(\hat{K}\, \underset{\approx}{\delta}^{(n_d)}\, \hat{K}\hat{K}\hat{K}$$

$$+ \hat{K}\hat{K}\hat{K}\, \underset{\approx}{\delta}^{(n_d)}\, \hat{K} - \hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K}\hat{K} - \hat{K}\hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K} \Big)$$

$$- 4 \sum_{P_{3,3}} \Big(\hat{K}\hat{K}\, \underset{\approx}{\delta}^{(n_d)}\, \hat{K}\hat{K} + \hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K} \Big) + 27\, \hat{K}\hat{K}\hat{K}\hat{K}\hat{K}\hat{K} \Big]$$

$$+ \left(\frac{\langle y^2 z \rangle}{2} \right) \Big[\sum_{P_{3,3}} \Big(\hat{K}\, \underset{\approx}{J}_4^{(n_d,2)}\, \hat{K} + \hat{K}\, \underset{\approx}{J}_4^{(2,n_d)}\, \hat{K} - 2\, \hat{K}\, \underset{\approx}{J}_4^{(2)}\, \hat{K} \Big)$$

$$- 4 \sum_{P_{3,3}} \hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K} - 3 \sum_{P_{3,3}} \Big(\hat{K}\hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K} + \hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K}\hat{K} \Big) \Big]$$

$$+ \langle y^4 \rangle \Big[\sum_{P_{3,3}} \Big(\hat{K}\hat{K}\hat{K}\, \underset{\approx}{\delta}^{(n_d)}\, \hat{K} + \hat{K}\, \underset{\approx}{\delta}^{(n_d)}\, \hat{K}\hat{K}\hat{K} - \hat{K}\hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}$$

$$- \hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K}\hat{K} \Big) - 6\, \hat{K}\hat{K}\hat{K}\hat{K}\hat{K}\hat{K} \Big] + \left(\frac{\langle y^2 z^2 \rangle}{4} \right) \sum_{P_{3,3}} \hat{K}\, \underset{\approx}{J}_4^{(2)}\, \hat{K}$$

$$+ \langle y^4 z \rangle \sum_{P_{3,3}} \Big(\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K}\hat{K}\hat{K} + \hat{K}\hat{K}\hat{K}\, \underset{\approx}{\sqcup}^{(2)}\, \hat{K} \Big) + 2 \langle y^6 \rangle\, \hat{K}\hat{K}\hat{K}\hat{K}\hat{K}\hat{K}, \qquad (4.38)$$

$$(\underline{1}, \underline{2}) = \langle y \rangle \sum_{P_{2,2}} \underset{\approx}{\delta}^{(n_d)}\, \hat{K} + \langle yz - y \rangle \sum_{P_{2,2}} \underset{\approx}{\sqcup}^{(2)}\, \hat{K} - 2 \langle y \rangle\, \hat{K}\hat{K}\hat{K}, \qquad (4.39)$$

$$(\underline{2}, \underline{1}) = \langle y \rangle \underset{\approx}{\delta}^{(n_d)} \hat{k} + \langle yz - y \rangle \underset{\approx}{U}^{(2)} \hat{k} + \langle 2y^3 - y \rangle \hat{k}\hat{k}\hat{k} \tag{4.40}$$

$$(\underline{2}, \underline{3}) = \left(\frac{\langle y \rangle}{2}\right) \Big[\sum_{P_{2,3}} \Big(\underset{\approx}{J}_4^{(n_d)} \hat{k} - \underset{\approx}{J}_4^{(n_d,2)} \hat{k} - \underset{\approx}{J}_4^{(2,n_d)} \hat{k} - \underset{\approx}{J}_4^{(2)} \hat{k} \Big)$$

$$- 2 \sum_{P_{2,3}} \Big(\hat{k} \underset{\approx}{\delta}^{(n_d)} \hat{k}\hat{k} - \hat{k} \underset{\approx}{U}^{(2)} \hat{k} \Big) - \sum_{P_{2,3}} \Big(\hat{k}\hat{k} \underset{\approx}{\delta}^{(n_d)} \hat{k}$$

$$- \hat{k}\hat{k} \underset{\approx}{U}^{(2)} \hat{k} \Big) - 3 \Big(\underset{\approx}{\delta}^{(n_d)} \hat{k}\hat{k}\hat{k} - \underset{\approx}{U}^{(2)} \hat{k}\hat{k}\hat{k} \Big)$$

$$+ 9 \hat{k}\hat{k}\hat{k}\hat{k}\hat{k} \Big] + \left(\frac{\langle y z \rangle}{2}\right) \Big[\sum_{P_{2,3}} \Big(\underset{\approx}{J}_4^{(n_d,2)} \hat{k}$$

$$+ \underset{\approx}{J}_4^{(2,n_d)} - 2 \underset{\approx}{J}_4^{(2)} \hat{k} - \hat{k}\hat{k} \underset{\approx}{U}^{(2)} \hat{k} \Big) + \sum_{P_{2,3}} \hat{k} \underset{\approx}{U}^{(2)} \hat{k}\hat{k}$$

$$- 3 \underset{\approx}{U}^{(2)} \hat{k}\hat{k}\hat{k} \Big] + \langle y^3 \rangle \Big[\underset{\approx}{\delta}^{(n_d)} \hat{k}\hat{k}\hat{k} - \underset{\approx}{U}^{(2)} \hat{k}\hat{k}\hat{k}$$

$$+ \sum_{P_{2,3}} \Big(\hat{k}\hat{k} \underset{\approx}{\delta}^{(n_d)} \hat{k} - \hat{k}\hat{k} \underset{\approx}{U}^{(2)} \hat{k} \Big) - 4 \hat{k}\hat{k}\hat{k}\hat{k}\hat{k} \Big]$$

$$+ \left(\frac{\langle y z^2 \rangle}{4}\right) \sum_{P_{2,3}} \underset{\approx}{J}_4^{(2)} \hat{k} + \langle y^3 z \rangle \Big[\sum_{P_{2,3}} \Big(\hat{k}\hat{k}\hat{k} \underset{\approx}{U}^{(2)} \Big) + \underset{\approx}{U}^{(2)} \hat{k}\hat{k}\hat{k} \Big]$$

$$+ 2 \langle y^5 \rangle \hat{k}\hat{k}\hat{k}\hat{k}\hat{k} \tag{4.41}$$

and

$$(\underline{3},\underline{2}) = \left(\frac{\langle y\rangle}{2}\right) \Big[\sum_{P_{3,2}} \Big(\underset{\approx}{J}_4^{(n_d)} \hat{K} - \underset{\approx}{J}_4^{(n_d,2)} \hat{K} - \underset{\approx}{J}_4^{(2,n_d)} \hat{K}$$

$$+ \underset{\approx}{J}_4^{(2)} \hat{K} \Big) - \sum_{P_{3,2}} \Big(\hat{K} \hat{K} \underset{\approx}{\delta}^{(n_d)} \hat{K} - \hat{K} \hat{K} \underset{\approx}{U}^{(2)} \hat{K} \Big)$$

$$- 2 \sum_{P_{3,2}} \Big(\underset{\approx}{\delta}^{(n_d)} \hat{K} \hat{K} \hat{K} + \underset{\approx}{U}^{(2)} \hat{K} \hat{K} \hat{K} \Big) + 6 \hat{K} \hat{K} \hat{K} \hat{K} \hat{K} \Big]$$

$$+ \langle y z\rangle \Big[\sum_{P_{3,2}} \Big(\underset{\approx}{J}_4^{(n_d,2)} \hat{K} + \underset{\approx}{J}_4^{(2,n_d)} \hat{K} - 2 \underset{\approx}{J}_4^{(2)} \hat{K} \Big)$$

$$- \sum_{P_{3,2}} \hat{K} \hat{K} \underset{\approx}{U}^{(2)} \hat{K} - 2 \sum_{P_{3,2}} \underset{\approx}{U}^{(2)} \hat{K} \hat{K} \hat{K} \Big] + \langle y^3\rangle \Big[\sum_{P_{3,2}} \Big(\hat{K} \hat{K} \underset{\approx}{\delta}^{(n_d)} \hat{K}$$

$$- \hat{K} \hat{K} \underset{\approx}{U}^{(2)} \hat{K} \Big) - 6 \hat{K} \hat{K} \hat{K} \hat{K} \hat{K} \Big] + \left(\frac{\langle y z^2\rangle}{4}\right) \sum_{P_{3,2}} \underset{\approx}{J}_4^{(2)} \hat{K}$$

$$+ \langle y^3 z\rangle \sum_{P_{3,2}} \hat{K} \hat{K} \underset{\approx}{U}^{(2)} \hat{K} \qquad (4.42)$$

with

$$\langle a\rangle = \pi^{\left(\frac{n_d-3}{2}\right)} \int_{\gamma_n>0} d\underset{\sim}{\gamma}\, \gamma_n \bar{J}\, e^{-\gamma^2} a \quad , \qquad (4.43)$$

$$y = \gamma_n \tag{4.44}$$

$$z = \underset{\approx}{U}^{(2)} \odot^2_{12} \quad \underset{\sim}{\bar{\gamma}}\,\underset{\sim}{\bar{\gamma}} \tag{4.45}$$

$$\underset{\approx}{J}^{(2)}_{a} = \sum_{p} \left(\underset{\approx}{U}^{(2)} \right)^{a/2} \tag{4.46}$$

and

$$\underset{\approx}{J}^{(a_1; \cdots a_{b/2})}_{b} = \sum_{p}{}' \left(\delta(a_1 - 2)\, \underset{\approx}{U}^{(2)} + \delta(a_1 - n_\lambda)\, \underset{\approx}{\delta}^{(n_\lambda)} \right) \cdots$$

$$\left(\delta(a_{b/2} - 2)\, \underset{\approx}{U}^{(2)} + \delta(a_{b/2} - n_\lambda)\, \underset{\approx}{\delta}^{(n_\lambda)} \right). \tag{4.47}$$

In Equation 4.47 $\sum'_p$ means a sum over all permutations of only right hand indices of the constituent second rank tensors $\underset{\approx}{U}^{(2)}$ and $\underset{\approx}{\delta}^{(n_\lambda)}$. In Equations 4.35-4.42 we have grouped together terms with equal numbers of distinct $\sum_{p_{u,v}}$ permutations.

The tensor $(\underline{3}, \underline{1})$ is the same form as $(\underline{1}, \underline{3})$ except that $\sum_{p_{3,1}}$ replaces $\sum_{p_{1,3}}$ everywhere. From the moments equations of Chapter 3, we can see that the $(\underline{1}, \underline{1})$, $(\underline{1}, \underline{3})$, $(\underline{3}, \underline{1})$ and $(\underline{3}, \underline{3})$ integrals are necessary for the calculation of thermal conductivity (field on and field off), binary diffusion coefficient and thermal diffusion coefficient and the $(\underline{2},\underline{2})$ integral is necessary for the calculation of viscosity. The development of an expression for $(\underline{u},\underline{v})$ of Equation 4.33 still leaves the problem of deriving a specific formula for the generalized cross section for a nonspherical soft potential. We return to this problem after first describing a convenient form for $(\underline{u},\underline{v})_{ro}$.

Reduction of the $(\underline{u},\underline{v})$ Tensors in the Case of Rigid Ovaloids

The division of $\underset{\approx}{R}\odot_{12}\bar{\eta}$ of Equation 4.22, which was adopted in order to perform outright the integrations over momentum variables of which $\mathcal{J}$ is independent, is needlessly awkward in the case of rigid ovaloids. For rigid ovaloids $\bar{\mathcal{J}}_{ro} = \bar{\mathcal{J}}_{ro}(\hat{k})$ is independent of $\bar{\underset{\sim}{\gamma}}_1$ so that a more judicious division of $\underset{\approx}{R}\odot_{12}\bar{\eta}$ is given by

$$\underset{\approx}{R}\odot_{12}\bar{\eta} \equiv (\bar{\eta}_1)_{ro} + \gamma_n\hat{k} \quad . \tag{4.48}$$

If the division of Equation 4.48 is applied to Equation 4.21, we can show that

$$(\underline{u},\underline{v})_{ro} = \bar{\mathcal{J}}_{ro}(\hat{k})\,\pi^{\left(\frac{n_1-1}{2}\right)} \sum_{j=1}^{u}\sum_{k=j}^{v+j} \frac{2}{P_{u,v}}\left(\frac{k}{2}\right) B\left(\frac{k}{2}\right) 2^{-\left(\frac{u+v-k}{2}\right)}$$

$$\left[(-1)^{k} = (-1)^{u+v}\ ;\ (-1)^{j} = -1\right]$$

$$(\hat{K})^{k-j} \; \underset{\approx}{J}^{(n_d-1)}_{u+v-k} \; (\hat{K})^{j} \qquad (4.49)$$

where the additional factors $\frac{k}{2}\,\beta(\frac{k}{2})$ originate from the integration over γ_n. The expression of Equation 4.49 differs from that of Hoffman (35) because the collision integrals to which they pertain differ by one being the time reversal of the other, i.e. we can write Hoffman's "$(\underline{u},\underline{v})$" in terms of $(\underline{u},\underline{v})_{ro}$ as follows:

$$"(\underline{u},\underline{v})" = \hat{T}\,(\underline{u},\underline{v})_{ro} = \bar{g}_{ro}(\hat{K}) \; \pi^{\left(\frac{n_d-1}{2}\right)} \; (-1)^{u+v}$$

$$\sum_{j=1}^{u} \; \sum_{k=j}^{v+j} \; \sum_{P_{v,u}} \; \frac{k}{2}\,\beta\left(\frac{k}{2}\right) \; (\hat{K})^{j} \; \underset{\approx}{J}^{(n_d-1)}_{u+v-k} \; (\hat{K})^{k-j} \, . \qquad (4.50)$$

$$[(-1)^{u} = -1 \, ; \; (-1)^{u+v} = (-1)^{k}]$$

It is convenient for purposes of checking with other work to complete the reduction of the tensor in the "$(\underline{u},\underline{v})$" form.

The projection operators can be applied more easily to "$(\underline{u},\underline{v})$" if the tensors $\underset{\approx}{\delta}^{(n_d-1)}$ contained in $\underset{\approx}{J}^{(n_d-1)}_{u+v-k}$ are expanded in terms of $\underset{\approx}{\delta}^{(n_d)}$ and $\hat{K}\hat{K}$. Accordingly we expand $\underset{\approx}{J}^{(n_d-1)}_{\ell}$ $(\ell \equiv u+v-k)$ into

$$\underset{\approx}{J}_{\ell}^{(n_d-1)} = \sum_{m=0}^{\ell/2} S_m \sum_{p} (\hat{k})^{2m} \underset{\approx}{J}_{\ell-2m}^{(n_d)} \qquad (4.51)$$

where $S_m = (-1)^m \, \Gamma(m+\tfrac{1}{2}) \, 2^m \, \pi^{-\frac{1}{2}}$. When Equation 4.51 is inserted into Equation 4.50, we derive after rearrangement of the sums

$$"(\underline{u},\underline{v})" = \bar{j}_{r0}(\hat{k}) \, \pi^{\left(\frac{n_d-1}{2}\right)} (-1)^{u+v} \sum_{b'=0}^{v} \sum_{j'=0}^{u} \sum_{P_{v,u}} (\hat{k})^{j'} \underset{\approx}{J}_{u+v-b'-j'}^{(n_d)}$$

$$(\hat{k})^{b'} \Big\{ \sum_{j=0}^{j'} \sum_{b=0}^{b'} x_{b+j} \, S_{((b'+j'-b-j)/2)} \, B_j \, B_{u+v-b}$$

$$((j'! \; b'!)/(j! \; b! \; (j-j')! \; (b-b')!)\,\Big\} \qquad (4.52)$$

where B_j is zero when j is even and unity when j is odd and where

$$x_{b+j} = (b+j)\,\Gamma\left(\tfrac{b+j}{2}\right) 2^{-((u+v-b-j)/2)} \quad . \qquad (4.53)$$

The bracketed quantity in Equation 4.52 can be evaluated separately for a whole series of b' and j' for even or odd rank collision integrals. Thus we have derived an expression of only slightly greater complexity than Equation 4.50 and one to which it is much easier to apply projections. We could not proceed to list the $"(\underline{u},\underline{v})"$ quantities needed in the rigid ovaloid calculations.

Instead we show below how they can easily be derived as rigid limits of more general expressions.

Further Reduction of the $(\underline{u},\underline{v})$ Tensors in the General Potential Using the Kihara Model

Kihara (34) has introduced a molecular interaction potential which assumes that the molecules consist of impenetrable hard cores which interact via a potential which is a function of the shortest distance between the cores. This model leads to molecular forces which are directed along the vector connecting the points of closest approach of the cores and to torques which can be thought of as arising from application of the force on a given molecule at the closest approach point on its core. Thus the direction of the forces and the "lever arms" for the torques are independent of the magnitude of the separation and instead depend only on the orientations of the molecules and a unit vector along the distance of closest approach. Two obvious examples of this model are spherical, soft molecules and rigid ovaloids.

If we define the generalized force by $d\eta/dt = \underline{\bar{\xi}}$, then averaging over the collision time leads to the average force $\langle \underline{\bar{\xi}} \rangle = \hat{k}\bar{F}$, where $\bar{F}$ is a constant of the motion. Thus the average generalized force is directed along $\hat{k}$. For rigid ovaloids and for soft, spherical molecules, the generalized force at the apse point is directed along the apse vector. In the first case this results from the fact that the collision is instantaneous, and in the second case from the fact that the collision trajectory is symmetric about the apse vector. This is not generally true for all interaction potentials.

Our object now is to reduce the expressions of Equation 4.43 to the same functional form as for spherical potentials (i.e., to reduce the collision integrals to a linear combination of the so-called Ω^* integrals (46)). These are dimensionless, two-fold integrals which are relatively easy to compute for any central potential and which have been extensively tabulated for the Lennard-Jones model (46, 48). To obtain this reduction we make two assumptions. We first assume that the apse vector (i.e. the unit vector along the average generalized force) is along the generalized force at the apse point. It follows from our previous discussion of the Kihara model that in this approximation $\hat{k}$ is solely a function of $\hat{k}_a$ and the Eulerian angle sets $\underline{\alpha}_1$ and $\underline{\alpha}_2$. Finally we assume a generalized cross section of the form

$$\bar{\mathcal{I}}(\hat{k}, \gamma_n, \bar{\gamma}_\perp^2) = D \left| \frac{\partial(\underline{\alpha}_1, \underline{\alpha}_2, \hat{k}_a)}{\partial \hat{k}} \right| S\, \mathcal{I}_{sp}(\gamma_n, \bar{\gamma}_\perp^2) / \sigma^2 \qquad (4.54)$$

where $\mathcal{I}_{sp}$ is the spherical differential cross section for a potential with zero interaction energy at the separation distance, σ. The differential area $S d\hat{k}_a$ is that swept out by molecule a for a differential solid angle change $d\hat{k}_a$ at zero interaction energy holding the Eulerian angles $\underline{\alpha}_1$ and $\underline{\alpha}_2$ fixed. This form for $\bar{\mathcal{I}}$ reduces to the exact expression for the cross section for rigid ovaloids and for soft spherical potentials in the appropriate limits. Physically, the assumed momentum dependence is that for a spherical potential but with a sphere radius and a sphere center which vary as a function of $\hat{k}_a$ and the Eulerian angle sets $\underline{\alpha}_1$ and $\underline{\alpha}_2$. It should be emphasized that although $\mathcal{I}_{sp}$ is the spherical cross section, Equation 4.54 is not a spherical approximation since, in general, $\hat{k}_a \neq \hat{k}$.

The functional form of the generalized cross section of Equation 4.54 is the same as that of Equation 4.33 and hence leads to the $(\underline{u},\underline{v})$ integrals of Equations 4.35-4.42. When Equation 4.54 is substituted into Equation 4.43, the scalar integrals are of the spherical form. Thos with integrands even in $\bar{\underline{\gamma}}$ can be reduced to a linear combination of Ω^* integrals. Those with integrands odd in $\bar{\underline{\gamma}}$ can be expressed in terms of integrals which differ only slightly from the Ω^* integrals. These modified integrals do not arise in the case of soft spheres (or any other interaction model for which inverse collisions exist).

The (μ,ν) integrals $(\underline{1},\underline{1})$, $(\underline{1},\underline{3})$, $(\underline{3},\underline{1})$, $(\underline{2},\underline{2})$ and $(\underline{3},\underline{3})$ (all of which are even in $\underset{\sim}{\bar{\gamma}}$) are given by

$$(\underline{1},\underline{1}) = C'' \Omega^{(1,1)*} \hat{k}\hat{k} \quad , \tag{4.55}$$

$$(\underline{1},\underline{3}) = \left(\frac{C''}{2}\right) \Big[\Omega^{(1,1)*} \sum_{P_{1,3}} \hat{k}\, \underset{\approx}{\delta}^{(n_4)} \hat{k} + \left(\Omega^{(2,2)*} - \Omega^{(1,1)*}\right)$$

$$\sum_{P_{1,3}} \hat{k}\, \underset{\approx}{U}^{(2)} \hat{k} + \left(6\,\Omega^{(1,2)*} - 2\,\Omega^{(2,2)*} - 3\,\Omega^{(1,1)*}\right) \hat{k}\hat{k}\hat{k}\hat{k} \Big], \tag{4.56}$$

$$(\underline{2},\underline{2}) = \left(\frac{C''}{2}\right) \Big[\Omega^{(1,1)*} \sum_{P_{2,2}} \hat{k}\, \underset{\approx}{\delta}^{(n_4)} \hat{k} + \left(\Omega^{(2,2)*} - \Omega^{(1,1)*}\right)$$

$$\sum_{P_{2,2}} \hat{k}\, \underset{\approx}{U}^{(2)} \hat{k} - 4\,\Omega^{(1,1)*} \hat{k}\hat{k}\hat{k}\hat{k} \Big] \tag{4.57}$$

and

$$(\underline{3},\underline{3}) = C'' \Big[\left(\frac{\Omega^{(1,1)*}}{2}\right) \sum_{P_{3,3}} \hat{k}\, \underset{\approx}{J}_4^{(n_4)} \hat{k} + \frac{1}{4}\Big(6\,\Omega^{(1,2)*}$$

$$-2\,\Omega^{(2,2)*} - 3\,\Omega^{(1,1)*}\Big)\Big(\sum_{P_{3,3}} \big(\hat{k}\hat{k}\hat{k}\, \underset{\approx}{\delta}^{(n_4)} \hat{k} + \hat{k}\, \underset{\approx}{\delta}^{(n_4)} \hat{k}\hat{k}\hat{k}\big)\Big)$$

$$-\Omega^{(1,1)*} \sum_{P_{3,3}} \hat{k}\,\hat{k}\,\underset{\approx}{\delta}^{(n_1)}\,\hat{k}\,\hat{k} - \frac{1}{4}\left(\Omega^{(1,1)*} - \Omega^{(2,2)*}\right)$$

$$\Big(\sum_{P_{3,3}} \big(\hat{k}\,\underset{\approx}{J}_4^{(n_1,2)}\,\hat{k} + \hat{k}\,\underset{\approx}{J}_4^{(2,n_1)}\,\hat{k}\big)\Big) + \Big(\frac{1}{8}\big(-3\,\Omega^{(1,3)*}$$

$$+ 2\,\Omega^{(2,3)*} + 3\,\Omega^{(3,3)*}\big) + \frac{1}{4}\,\Omega^{(1,1)*} - \frac{1}{2}\,\Omega^{(2,2)*}\Big) \sum_{P_{3,3}} \hat{k}\,\underset{\approx}{J}_4^{(2)}\,\hat{k}$$

$$+ \Big(\frac{1}{2}\big(3\,\Omega^{(1,3)*} + 2\,\Omega^{(2,3)*} - 3\,\Omega^{(3,3)*}\big) + \frac{3}{4}\,\Omega^{(1,1)*} - \frac{1}{4}\,\Omega^{(2,2)*}$$

$$-\frac{3}{2}\,\Omega^{(1,2)*}\Big)\Big(\sum_{P_{3,3}}\big(\hat{k}\,\underset{\approx}{U}^{(2)}\,\hat{k}\,\hat{k}\,\hat{k} + \hat{k}\,\hat{k}\,\hat{k}\,\underset{\approx}{U}^{(2)}\,\hat{k}\big)\Big)$$

$$+ \left(\Omega^{(1,1)*} - \Omega^{(2,2)*}\right) \sum_{P_{3,3}} \hat{k}\,\hat{k}\,\underset{\approx}{U}^{(2)}\,\hat{k}\,\hat{k}$$

$$+ \Big(\big(9\,\Omega^{(1,3)*} - 6\,\Omega^{(2,3)*} + 3\,\Omega^{(3,3)*}\big) - \frac{27}{4}\,\Omega^{(1,1)*}$$

$$- 9\,\Omega^{(1,2)*} + 3\,\Omega^{(2,2)*}\Big)\,\hat{k}\,\hat{k}\,\hat{k}\,\hat{k}\,\hat{k}\,\hat{k} \tag{4.58}$$

where $(\underline{2},\underline{1})$ is again of the same form as $(\underline{1},\underline{3})$ with P_{31} replacing P_{13} and where

$$c'' = \pi^{\left(\frac{n_d - 1}{2}\right)} \quad D \quad S \quad \left| \frac{\partial\,(\underline{\alpha}_1, \underline{\alpha}_2, \hat{k}_a)}{\partial\,\hat{\underline{k}}} \right| \quad . \qquad (4.59)$$

For this general soft model, completion of the evaluation of the collision integrals requires projection on the tensors $(\underline{u}, \underline{v})$ by $\underset{\approx}{\mathcal{P}}_{\phi_i \psi_i}$, contraction of these tensors with $\underline{\underline{g}}$ and integration of the resulting scalars over $\hat{\underline{k}}$. In Appendix D we show for even rank tensors how these first two steps can be expeditiously carried out. From the assumed form of $\bar{g}$ of Equation 4.54, the integration over κ is equivalent to the usual integration over $\hat{k}_a$, $\underline{\alpha}_1$ and $\underline{\alpha}_2$.

CHAPTER 5. RIGID CONVEX TETRAHEDRAL MODEL AS APPLIED TO THE SENFTLEBEN-BEENAKKER EFFECT IN GASES COMPOSED OF CX_4 MOLECULES

In References 10 and 11 the changes of the components of the thermal conductivity tensor induced by an external, static magnetic field were measured. In the case of the measurement of $\Delta\lambda_1$ and $\Delta\lambda_2$, the apparatus consisted of two identical cylindrical cells placed between two brass plates which were held at the same constant temperature. A thin steadily powered hot plate of slightly smaller diameter than the cylinders was placed in the center of each cylinder parallel to the end plates. One cylinder was filled with a noble gas, which exhibits no field effect, and one cylinder was filled with the polyatomic gas under study. The field was applied first parallel to the axis of the cylinder and then perpendicular to it. The quantities $\Delta\lambda_1$ and $\Delta\lambda_2$ were related to temperature readings in the hot plate in the polyatomic gas cylinder relative to simultaneous readings in the noble gas cylinder. In the case of the measurement of λ_3, a cylinder was mounted between a hot plate and a cold plate and was filled with a polyatomic gas. Then the field was applied perpendicular to the axis of the cylinder and the temperature difference was measured in a direction perpendicular to both the axis of the cylinder and the direction of the field. After calibration with noble gases, the measured temperature difference was related to λ_3.

In Reference 12 the magnetic field's changes of the components of the viscosity tensor were measured in the combinations $(\eta_3' - \eta_0)/\eta_0$ and $(2\eta_2' - \eta_1' - \eta_3')/\eta_0$. These measurements were made by running a gas at constant flow rate through a set of four identical capillaries lined up in parallel two by two. The magnetic field is placed across one or two of the capillaries and the pressure drop is measured across different points of the system. These pressure drops are related to the above component combinations for certain field configurations.

In Reference 13 the magnetic field's changes of the viscosity tensor components (η_4'/η_0) and (η_5'/η_0) were measured. These measurements were made by applying a magnetic field across a capillary of rectangular cross section and relating the pressure drop across the long side of the rectangle to these viscosity components.

Of the gases studied in References 10-13, we concentrate on those with tetrahedral symmetry, namely CH_4, CD_4 and CF_4. The model that we use is a rigid convex body of tetrahedral symmetry. The supporting function of such a body labeled i is by Appendix A $h^{(i)}(\hat{k}^{(i)} \cdot \hat{e}_1^{(i)} \ldots \hat{k}^{(i)} \cdot \hat{e}_4^{(i)})$ where the four unit vectors $\hat{e}_j^{(i)}$ extend from the origin (which is taken to be the mass center) in the direction of the vertices of an imaginary regular tetrahedron. The simplest nontrivial supporting function of this form is

$$h^{(i)} = A^{(i)} + B^{(i)} \sum_{j=1}^{4} (\hat{k}^{(i)} \cdot \hat{e}_j^{(i)})^3 \tag{5.1}$$

where $A^{(i)}$ and $B^{(i)}$ are constants.

We parameterize this model by $\langle \sigma^{(i)} \rangle$, the average cross sectional area described in Appendix A, and $R^{(i)}$, the ratio of the largest $|\tilde{\xi}^{(i)}|$ (where $\tilde{\xi}^{(i)}$ is a vector from the origin to a point on the surface of i) to the smallest. The average cross sectional area determines the size of a figure. The parameter $R^{(i)}$ for a body specified by the supporting function of Equation 5.1 can be shown to be

$$R^{(i)} = ((A^{(i)}/B^{(i)}) + (8/9))/((A^{(i)}/B^{(i)}) - (8/9)) \tag{5.2}$$

For a regular tetrahedron $R=3$. As was mentioned in Appendix A, the differential surface area of a convex body must be positive over the entire body. The resulting condition of convexity for a figure described by Equation 5.1 is that $R^{(i)}$ can range from unity to 1.42. We plot the contours of a convex tetrahedral model in Figures 5.1 and 5.2 for a typical value of $R^{(i)}$.

Now that a model is specified, we are left with the

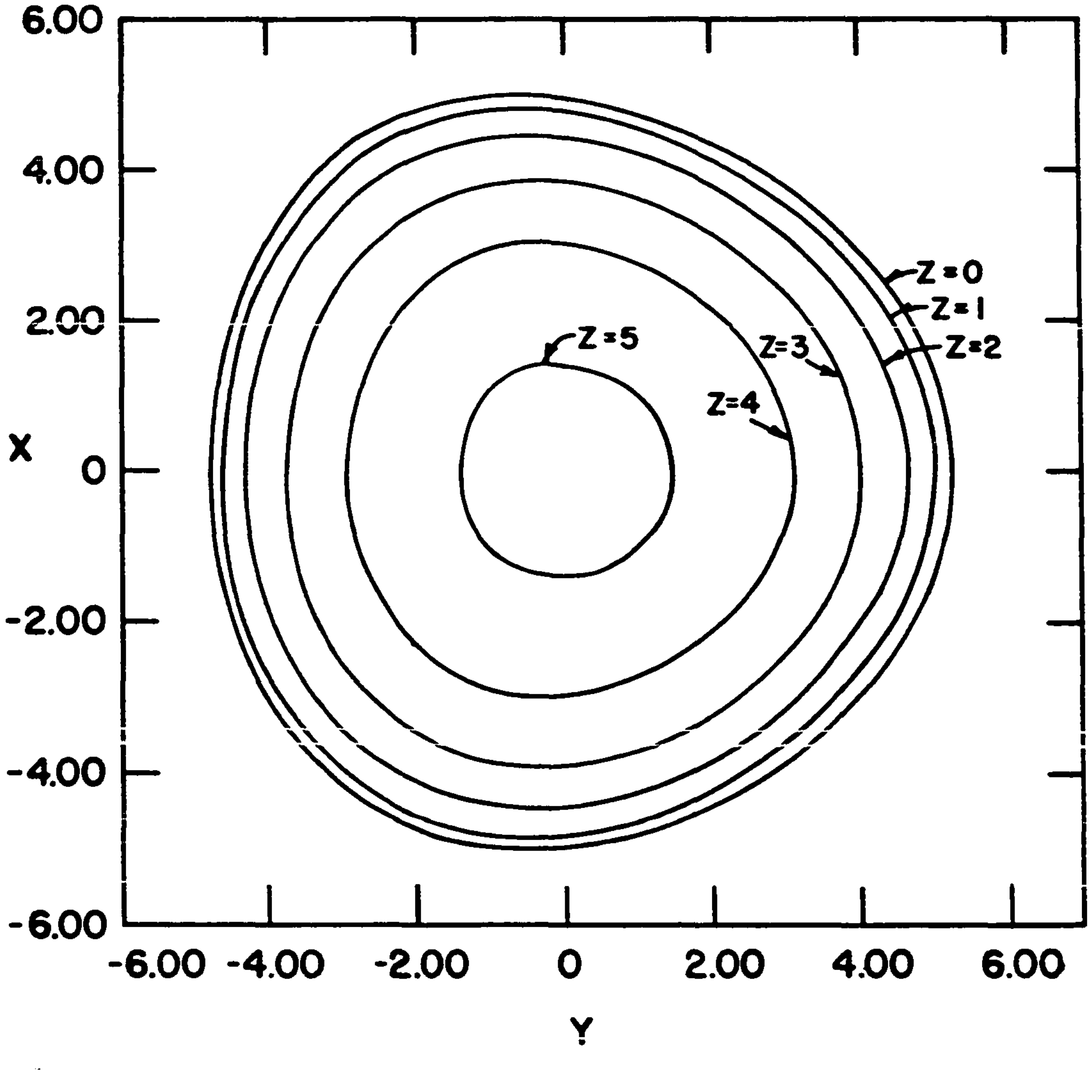


Figure 5.1. Upper surface contours ($Z \geq 0$) formed by passing planes through a tetrahedral model with R = 1.19 and its z-axis (origin at the geometric center) passing through one vertex, are shown. These planes are perpendicular to the z-axis and are taken at unit intervals along the z-axis

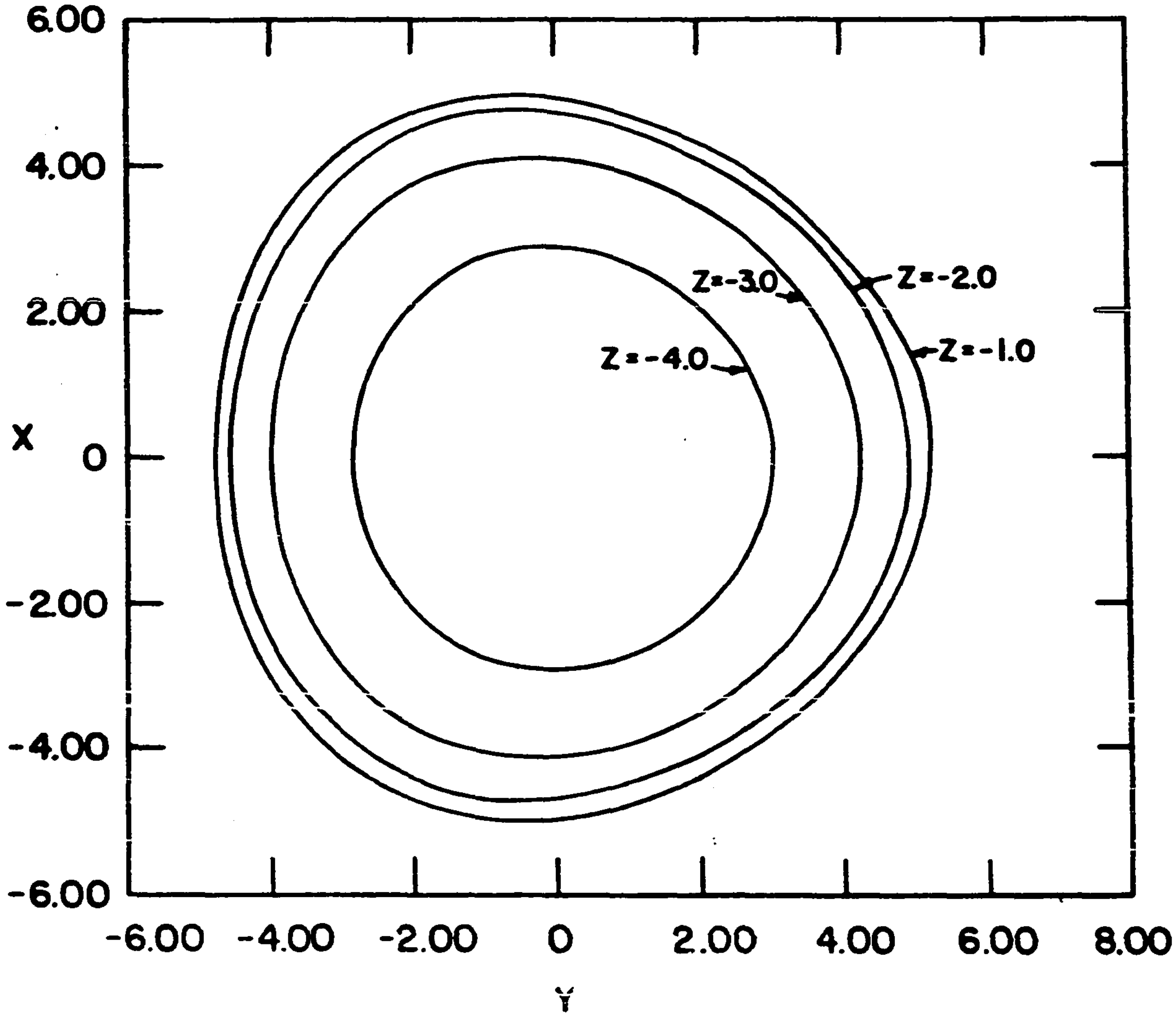


Figure 5.2. Here we show the lower ($Z < 0$) surface contours for a tetrahedral model (see Figure 5.1)

task of performing the scalar collision integrals which appear in the moments equations. These integrals are, by Equations 4.6 and 4.20, of the form

$$\underline{\underline{\ell}}\ \odot^{u+v}\ [\,\underline{\Phi}_i\,,\ \underline{\underline{\Psi}}_j\,] = \frac{\pi^{-6}}{\Delta_1\Delta_2}\left(\frac{2kT}{m}\right)^{1/2}\int d\underline{\alpha}_1 \int d\underline{\alpha}_2 \int d\hat{k}$$

$$\underline{\underline{\ell}}\ \odot_3^{u+v}\ \underset{\approx}{\rho}_{\phi_i\psi_j}\ \odot_{12}^{u+v}\ (\underline{u}\,,\underline{v})''_{ro} \qquad (5.3)$$

where

$$(\underline{u}\,,\underline{v})''_{ro} = (u,v)_{ro}\ \Big/ \left(\left|\frac{\partial(\underline{\alpha}_1,\underline{\alpha}_2,\hat{k})}{\partial\hat{k}}\right|\right)$$

and where we have rearranged the order of integration. The integrations over the orientations of body 1 and body 2 constitute a four-fold multiple integration (one angle integration in each body is trivial if $\hat{k}$ is held fixed). It would be a substantial time-saver if we could write the integrands of Equation 5.3 as a sum of terms each of which is a product of factors: one factor being a function of the orientation of body 1 and the other of body 2 . The result of this time-saver is that we only have to evaluate two-fold integrals. We illustrate how this separation can be achieved using the integrands necessary for the determination of the collision integrals used in the analysis of the Senftleben-Beenakker effects in spherical top molecules.

However the method is of general utility.

The integrands investigated are $S_{ro}D^{-\nu}$, $(S_{ro}\, a_1^2)/D^{\nu}$, $(S_{ro}\, a_1^4)/D^{\nu}$, $(S_{ro}\, a_1^2 a_2^2)/D^{\nu}$ and $(S_{ro}\, (a_1 \cdot a_2)^2/D^{\nu})$. The quantity $D^{-\nu}$ can be written as

$$D^{-\nu} = (1+a_1^2)^{-\frac{\nu}{2}} \, (1+a_2^2)^{-\frac{\nu}{2}} \left[1 - \left(\frac{a_1^2}{1+a_1^2}\right)\left(\frac{a_2^2}{1+a_2^2}\right)\right]^{-\frac{\nu}{2}} \qquad (5.4)$$

where the last factor of this equation can be expanded in the convergent series

$$\left(1 - \frac{a_1^2 \, a_2^2}{(1+a_1^2)(1+a_2^2)}\right)^{-\frac{\nu}{2}} = \sum_{r=0}^{\infty} \frac{\Gamma(\frac{\nu}{2}+r)}{\Gamma(\frac{\nu}{2})\, r!}$$

$$\left(\frac{a_1^2 \, a_2^2}{(1+a_1^2)(1+a_2^2)}\right)^{r} \quad . \qquad (5.5)$$

The integrands in question can therefore be written as

$$\frac{S_{ro}}{D^{\nu}} \begin{bmatrix} 1 \\ a_1^2 \\ a_1^4 \\ a_1^2 a_2^2 \end{bmatrix} = \sum_{r=0}^{\infty} \begin{bmatrix} 1 \\ a_1^2 \\ a_1^4 \\ a_1^2 a_2^2 \end{bmatrix} \frac{\Gamma(\frac{\nu}{2}+r)}{\Gamma(\frac{\nu}{2}) \quad r!} \; \frac{a_1^{2r} \, a_2^{2r}}{((1+a_1^2)(1+a_2^2))^{r+(\frac{\nu}{2})}}$$

$$\left[-\tfrac{1}{2} \left(\underline{\underline{G}}^{(1)} : \underline{\underline{G}}^{(1)} + \underline{\underline{G}}^{(2)} : \underline{\underline{G}}^{(2)} - 2\, \underline{\underline{G}}^{(1)} : \underline{\underline{G}}^{(2)} \right) \right] \qquad (5.6)$$

$$\frac{S_{ro}}{D^{\nu}} \; (\underline{a}_1 \cdot \underline{a}_2)^2 = \sum_{r=0}^{\infty} \frac{\Gamma(\frac{\nu}{2}+r)}{\Gamma(\frac{\nu}{2})\, r!} \; \frac{a_1^{2r} \; a_2^{2r}}{((1+a_1^2)(1+a_2^2))^{r+(\frac{\nu}{2})}}$$

$$\underline{a}_1 \underline{a}_1 : \underline{a}_2 a_2 \; [-\tfrac{1}{2} (\underline{\underline{G}}^{(1)} : \underline{\underline{G}}^{(1)} + \underline{\underline{G}}^{(2)} : \underline{\underline{G}}^{(2)} - 2\, \underline{\underline{G}}^{(1)} : \underline{\underline{G}}^{(2)})] \qquad (5.7)$$

where we have used Equation A.16 to evaluate S_{ro} . Orientation integration of the expressions of Equation 5.6 leads immediately to single molecule scalar integrals of the form

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} \; b^{(i)}$$

and tensor integrals of the form

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} \; b^{(i)}$$

where $b^{(i)}$ represents some scalar function of the orientation angles of body i . Since it can be shown that $\underline{\underline{G}}^{(i)}$ is proportional to $\underline{\underline{V}}^{(i)}$ ($= \hat{k}^{(i)} \times \underline{\underline{\delta}}^{(3)}$), we derive that

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} \; b^{(i)} = -\tfrac{1}{2} \underline{\underline{V}}^{(i)} \int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{V}}^{(i)} \; b^{(i)} . \qquad (5.8)$$

Orientation integration of the expression in Equation 5.7 results in the single molecule tensor integrals of the forms

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} \; \underline{a}_i \; a_i \; b^{(i)}$$

and

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} \, \underline{a}_i \, \underline{a}_i \; b^{(i)} \quad .$$

The first of these two integrals is proportional to $\underline{\underline{\sqcup}}^{(2)}_{\hat{k}}$ ($= \underline{\underline{\delta}}^{(3)} - \hat{k}\hat{k}$) and hence we can write that

$$\int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} \, \underline{a}_i \, \underline{a}_i \; b^{(i)} = \frac{1}{2} \, \underline{\underline{\sqcup}}^{(2)}_{\hat{k}} \int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} \, a_i^2 \; b^{(i)} . \tag{5.9}$$

The second of these integral forms can be expanded linearly as follows:

$$\int d\underline{a}_i \; \underline{\underline{G}}^{(i)} \, \underline{a}_i \, \underline{a}_i \; b^{(i)} = \hat{\alpha}^{(i)} \underline{\underline{V}}^{(i)} \, \underline{\underline{\sqcup}}^{(2)}_{\hat{k}} + \hat{\beta}^{(i)} \left(\underline{\underline{V}}^{(i)}\!\!\underline{\underline{\sqcup}}^{(2)} + \overset{\underline{\underline{\sqcup}}^{(2)}_{\hat{k}}}{\underline{\underline{V}}}{}^{(i)} \right)$$

$$+ \hat{\gamma}^{(i)} \left(\underline{\underline{\left\lfloor \underline{\underline{\sqcup}}^{(2)}_{\hat{k}} \right\rfloor}}{}^{(2)}_{\hat{k}} + \underline{\underline{\left\lfloor \underline{\underline{\sqcup}}\!\!\sqcup^{(2)}_{\hat{k}} \right\rfloor}}{}^{(2)}_{\hat{k}} - \underline{\underline{\sqcup}}^{(2)}_{\hat{k}} \; \underline{\underline{\sqcup}}^{(2)}_{\hat{k}} \right) \tag{5.10}$$

where

$$\hat{\alpha}^{(i)} = \frac{1}{2} \left(3\hat{A}^{(i)} - \hat{B}^{(i)} \right) \quad , \tag{5.11}$$

$$\hat{\beta}^{(i)} = \frac{1}{2} \left(\hat{B}^{(i)} - \hat{A}^{(i)} \right) \tag{5.12}$$

and

$$\hat{\gamma}^{(i)} = \frac{1}{4} \int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{a}_i \, \underline{a}_i \; b^{(i)} \tag{5.13}$$

with

$$\hat{A}^{(i)} = -\frac{1}{4} \int d\underline{\alpha}_i \; \underline{\underline{G}}^{(i)} : \underline{\underline{V}}^{(i)} \tag{5.14}$$

and

$$\hat{B}^{(i)} = -\frac{1}{2} \int d\underline{\alpha}_i \; (\underline{\underline{G}}^{(i)} \cdot \underline{a}_i \underline{a}_i) : \underline{\underline{V}}^{(i)} \, b^{(i)} \; . \tag{5.15}$$

Therefore we can write any integral in the form of a sum of products of integrals over the orientations of a single molecule. In practice we truncate the series of Equations 5.6 and 5.7 at ten terms. The orientation integrations are performed numerically.

We now show the comparison between the Senftleben-Beenakker effect data on CX_4 molecules of References 10-13 and the best fits of that data. These fits are achieved by using the rigid tetrahedral convex model and by optimizing the values of that model's parameters, R and $\langle\sigma\rangle$. The measurements of $\Delta\lambda_1$ and $\Delta\lambda_2$ were made at room temperature and of $\Delta\lambda_3$ at 85°K for CH_4 and CD_4 and at 93°K for CF_4. Therefore we fit $\Delta\lambda_1$ and $\Delta\lambda_2$ with one set of parameters and $\Delta\lambda_3$ with another. We use a single set of parameters per species to fit all the room temperature viscosity measurements. Different parameters are used for viscosity and thermal conductivity. For a certain species at a given temperature, relations between the components of $\underline{\lambda}$ are fixed theoretically. The same is true for $\underline{\underline{\eta}}$.

Therefore we need only fit one component of each of these tensors with a single parameter set. The properties are all plotted as a function of a dimensionless field strength magnitude, β , which is given by

$$\beta = \left(\frac{m k T}{\pi}\right)^{1/2} \left(\frac{\mu_N g_r}{d^2 \hbar}\right)\left(\frac{H}{p}\right) \tag{5.16}$$

where μ_N is the nuclear magneton, g_r is the rotational g factor found from other measurements and d is the bond length.

The procedure for obtaining the optimum fit is to choose a reasonable value for $\langle\sigma\rangle$. Then B of Equation 5.1 is varied to reproduce the property's characteristic value (either its nonzero saturation ($H = \infty$) value as in the case of $(\Delta\lambda_1/\lambda_0)_{sat}$ or its maximum value as in the case of $-((2\eta_2' - \eta_1' - \eta_3')/\eta_0)_{max}$. We find that if B is held fixed while $\langle\sigma\rangle$ is varied, the property's characteristic value does not change. Therefore the value of $\langle\sigma\rangle$ can be varied to fit the remaining features: the field off value of the property and the β value at which a characteristic value occurs. For the properties which saturate at high field strengths we fit the value of the field strength, $\beta_{1/2}$, at which the property achieves half of its saturation value. We indicate $\beta_{1/2}$ for $\Delta\lambda_1/\lambda_0$ as $\beta^{(1)}_{1/2}$, for $\Delta\lambda_2/\lambda_0$ as $\beta^{(2)}_{1/2}$ and for $\Delta\eta_3'/\eta_0$ as $\beta^{(3)}_{1/2}$. For the properties which have a maximum value we fit the dimensionless field strength, β_{max} , at that maximum. We indicate β_{max} for $\Delta\lambda_3/\lambda_0$ as $\beta^{(3)}_{max}$, for $-((2\eta'_2-\eta'_1-\eta'_3)/\eta_0)$ as β_{max}, for η'_4/η_0 as $\beta^{(4)}_{max}$ and for η'_5/η_0 as $\beta^{(5)}_{max}$.

In Figure 5.3 we demonstrate the graphical method employed to determine the optimum value of $\langle\sigma\rangle$ once B has been fixed by matching the characteristic value. The property used in this demonstration is $\Delta\lambda_2/\lambda_0$ of CH_4. If we assume that experimental measurements of λ_0 and $\beta^{(2)}_{1/2}$ are both equally trustworthy, then we would take a value of $\langle\sigma\rangle \approx 15$ (where their ratio curves intersect). If we assume that λ_0 is a much more reliable measurement, we would take $\langle\sigma\rangle \approx 11$ where λ_0 experimental is equal to the calculated value of λ_0 .

In Figures 5.4-5.6 we show the results from fitting $\Delta\lambda_1/\lambda_0$ and $\Delta\lambda_2/\lambda_0$ at 300°K (10) for CH_4, CD_4 and CF_4 respectively. The parameters which were used are those given in Table 5.1 for which the measurements of both λ_0 and $\beta^{(1)}_{1/2}$ and $\beta^{(2)}_{1/2}$ are considered equally trustworthy. In Table 5.1 we also compare the experimental values for these species of λ_0 , $-(\Delta\lambda_1/\lambda_0)$, $-(\Delta\lambda_2/\lambda_0)$, $\beta^{(1)}_{1/2}$ and $\beta^{(2)}_{1/2}$ with values calculated from the parameters which fit λ_0 and $\beta_{1/2}$ equally, and those which fit λ_0 exactly. The agreement with experiment is not quite as good as that

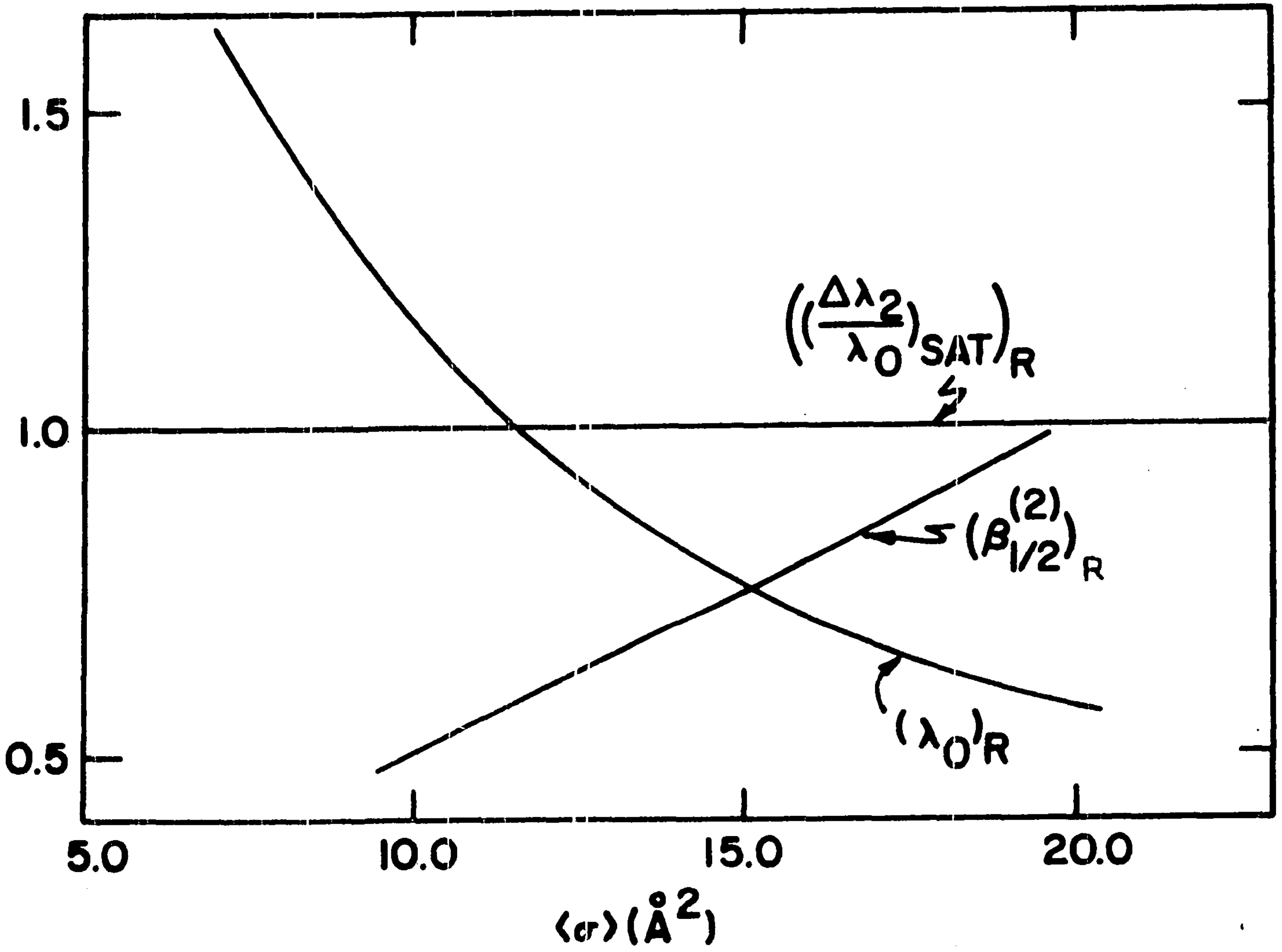


Figure 5.3. A plot of $(\alpha)_R = \alpha_{calc}/\alpha_{exp}$ where $\alpha = \Delta\lambda_2/\lambda_o$, $\beta^{(2)}_{1/2}$, λ_o vs. $\langle\sigma\rangle$ $\mathring{A}^2$ for CH_4 where B (Equation 5.1) is held fixed

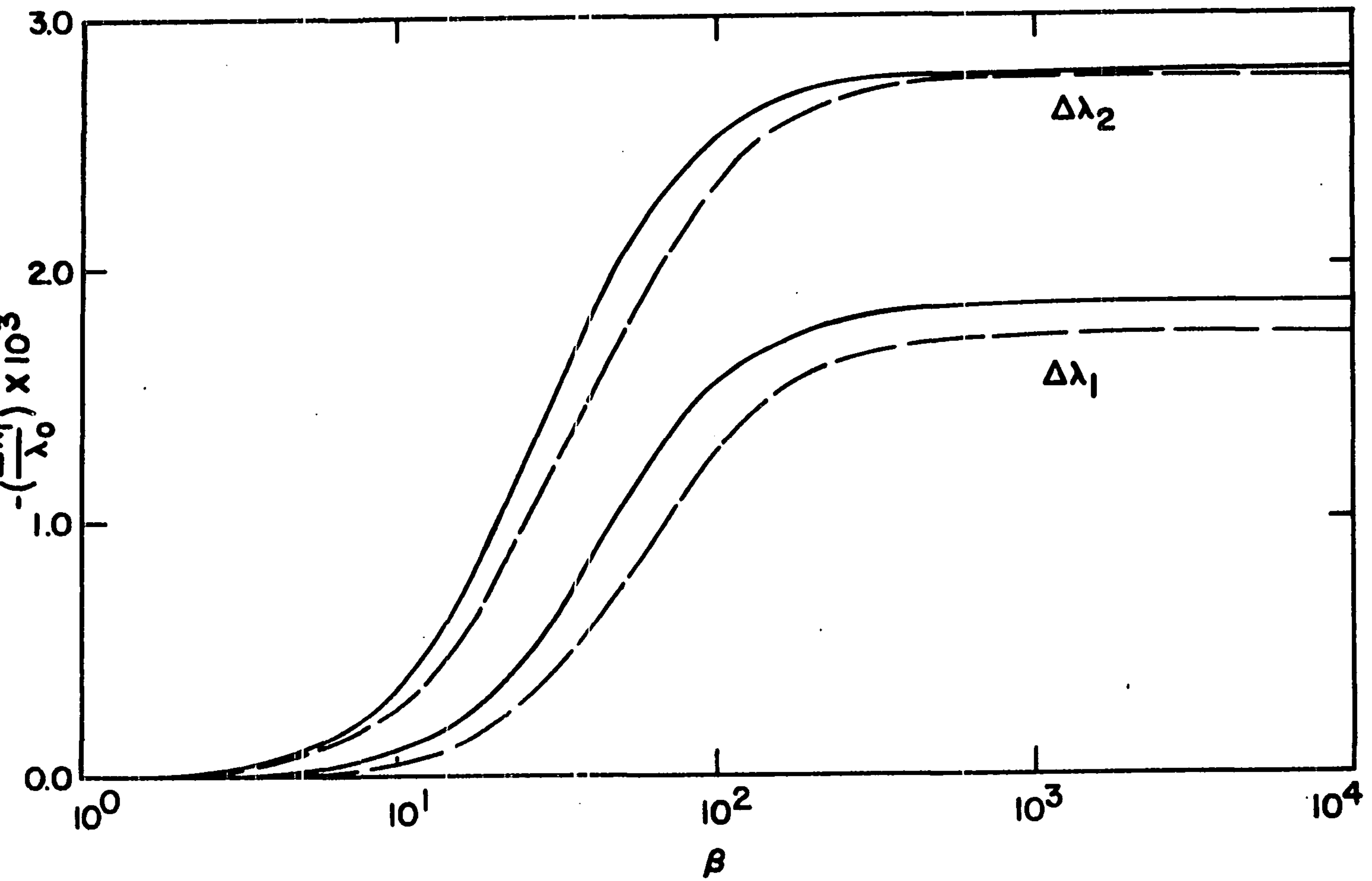


Figure 5.4. A plot of $(\Delta\lambda_1/\lambda_o)$, $(\Delta\lambda_2/\lambda_o)$ vs. β (see Equation 5.16) for CH_4. The solid lines are the calculated results and the dashed lines are the experimental results

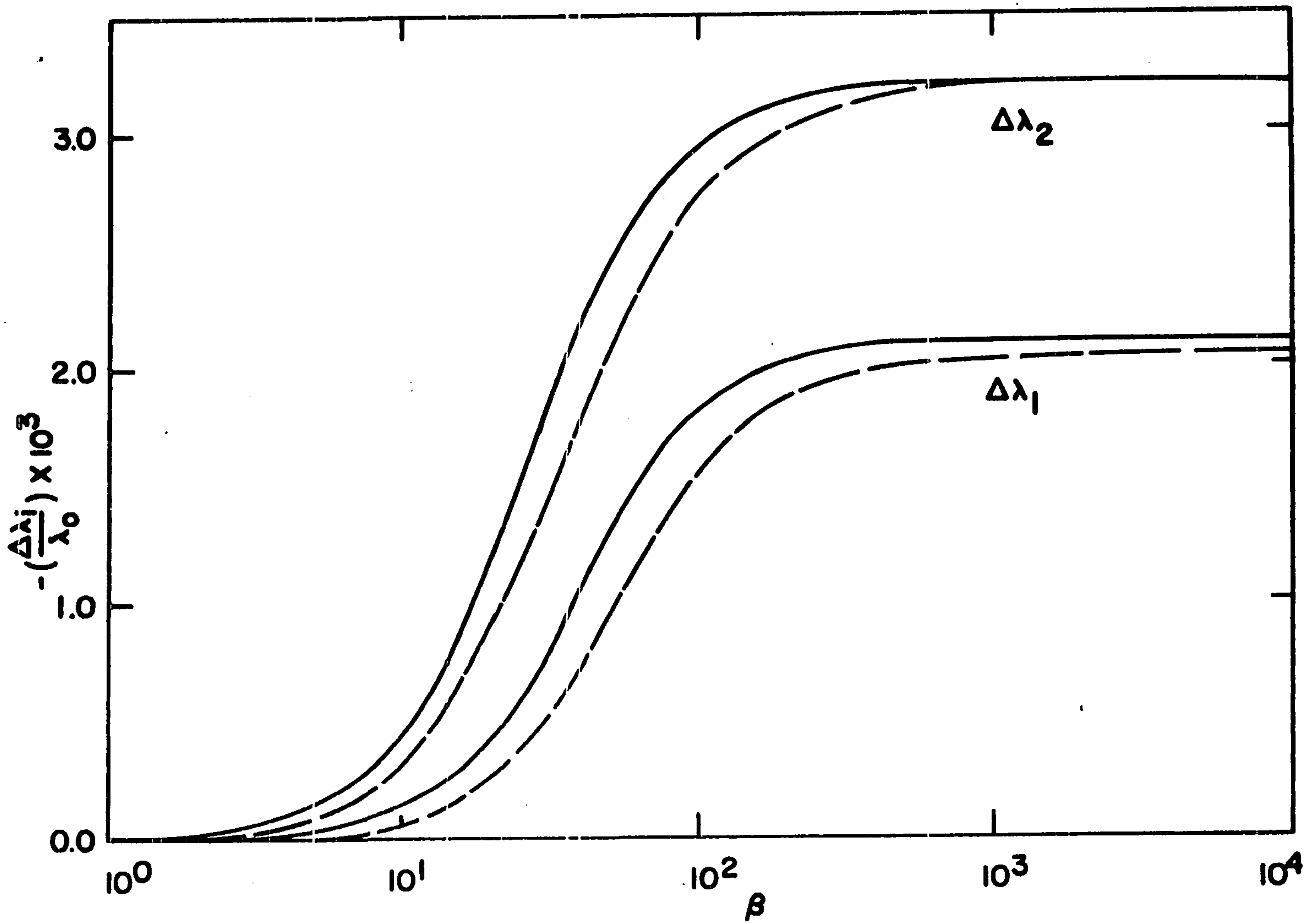


Figure 5.5. Symbols are as in Figure 5.4 for CD_4

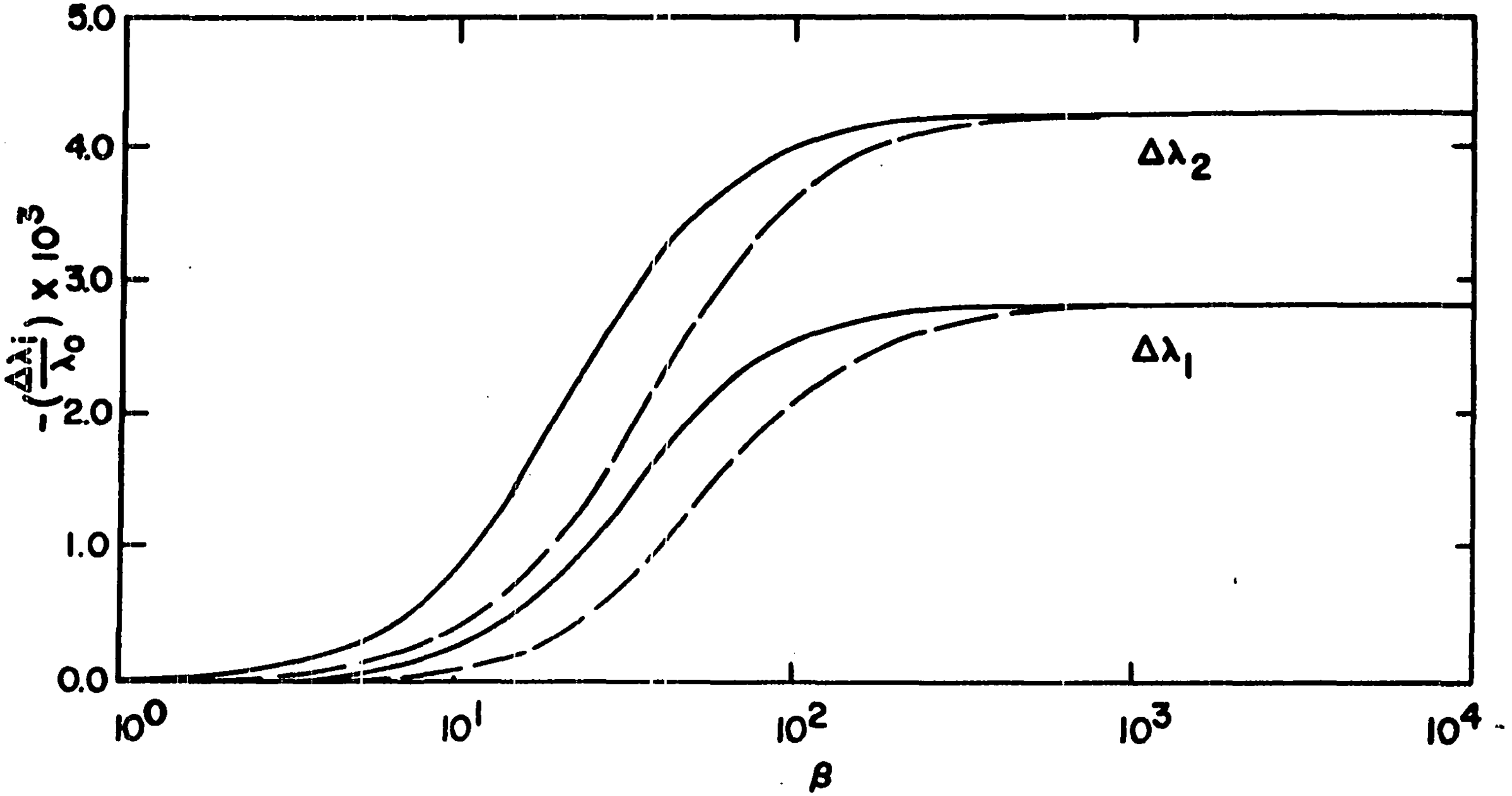


Figure 5.6. Symbols are as in Figure 5.4 for CF_4

Table 5.1. Comparison of experimental (10) (in parentheses) and theoretical values for λ_0 in calories per centimeter second degree, $(\Delta\lambda_1/\lambda_0)_{sat}$, $\beta_{1/2}^{(1)}$, $(\Delta\lambda_2/\lambda_0)_{sat}$, and $\beta_{1/2}^{(2)}$. In the top line for each molecule R and $\langle\sigma\rangle$ are determined by optimally fitting λ_0 and $\beta_{1/2}$, whereas in the second line only λ_0 is fitted

Gas	R	$\langle\sigma\rangle(\text{Å}^2)$	$\lambda_0 \times 10^5$	$-(\Delta\lambda_1/\lambda_0)_{sat} \times 10^3$	$\beta_{1/2}^{(1)}$	$-(\Delta\lambda_2/\lambda_0)_{sat} \times 10^3$	$\beta_{1/2}^{(2)}$
CH_4	1.0844	15.1021	6.59	1.84	41.5	2.78	29.0
	1.0968	11.6097	8.75	1.84	34.2	2.78	21.8
			(8.75)	(1.72)	(58.5)	(2.75)	(37.8)
CD_4	1.1187	13.7311	6.48	2.12	40.0	3.19	26.5
	1.1392	10.1781	8.77	2.12	29.9	3.2	20.0
			(8.77)	(2.05)	(55)	(3.2)	(35.8)
CF_4	1.2227	16.9798	2.50	2.81	33	4.24	22.0
	1.2902	10.5293	4.01	2.815	20.5	4.24	14.0
			(4.01)	(2.18)	(54.3)	(4.3)	(36.0)

obtained for the application of the rigid ellipsoid model to diatomic molecules (31).

In Figures 5.7-5.9 we show the results of fitting the experimental (11) magnetic field dependence of $(\Delta\lambda_3/\lambda_0)$ for CH_4, CD_4 and CF_4. The fit is about the same as for the other components of thermal conductivity. The model parameters used in these figures are listed in Table 5.2 and are derived assuming all measurements equally reliable. Also listed in Table 5.2 are the comparisons of calculated versus experimental data for λ_0, $(\lambda_3/\lambda_0)_{max}$ and $\beta^{(3)}_{max}$ for these species.

We plot the experimental (12) and calculated field behavior of $(\Delta\eta'_3/\eta_0)$ and $((2\eta'_2-\eta'_1-\eta'_3)/\eta_0)$ for CH_4 and CF_4 in Figures 5.10-5.11 respectively. For CH_4 we plot the calculated and experimental (13) field behavior of (η'_4/η_0) and (η'_5/η_0) in Figure 5.12. The parameters used in all viscosity cases are given in Table 5.3. These parameters were found by fitting B in the usual way and by fitting $\langle\sigma\rangle$ to match only the experimental η_0 because the calculated β features are not really improved by reasonable changes in $\langle\sigma\rangle$. Also listed in Table 5.3 are the experimental and calculated values for η_0, $(\Delta\eta'_3/\eta_0)_{sat}$, $\beta^{(3)}_{1/2}$, $-((2\eta'_2-\eta'_1-\eta'_3)/\eta_0)_{max}$, β_{max}, $(\eta'_4/\eta_0)_{max}$, $\beta^{(4)}_{max}$, $(\eta'_5/\eta_0)_{max}$ and $\beta^{(5)}_{max}$. The agreement with experiment of the β values is

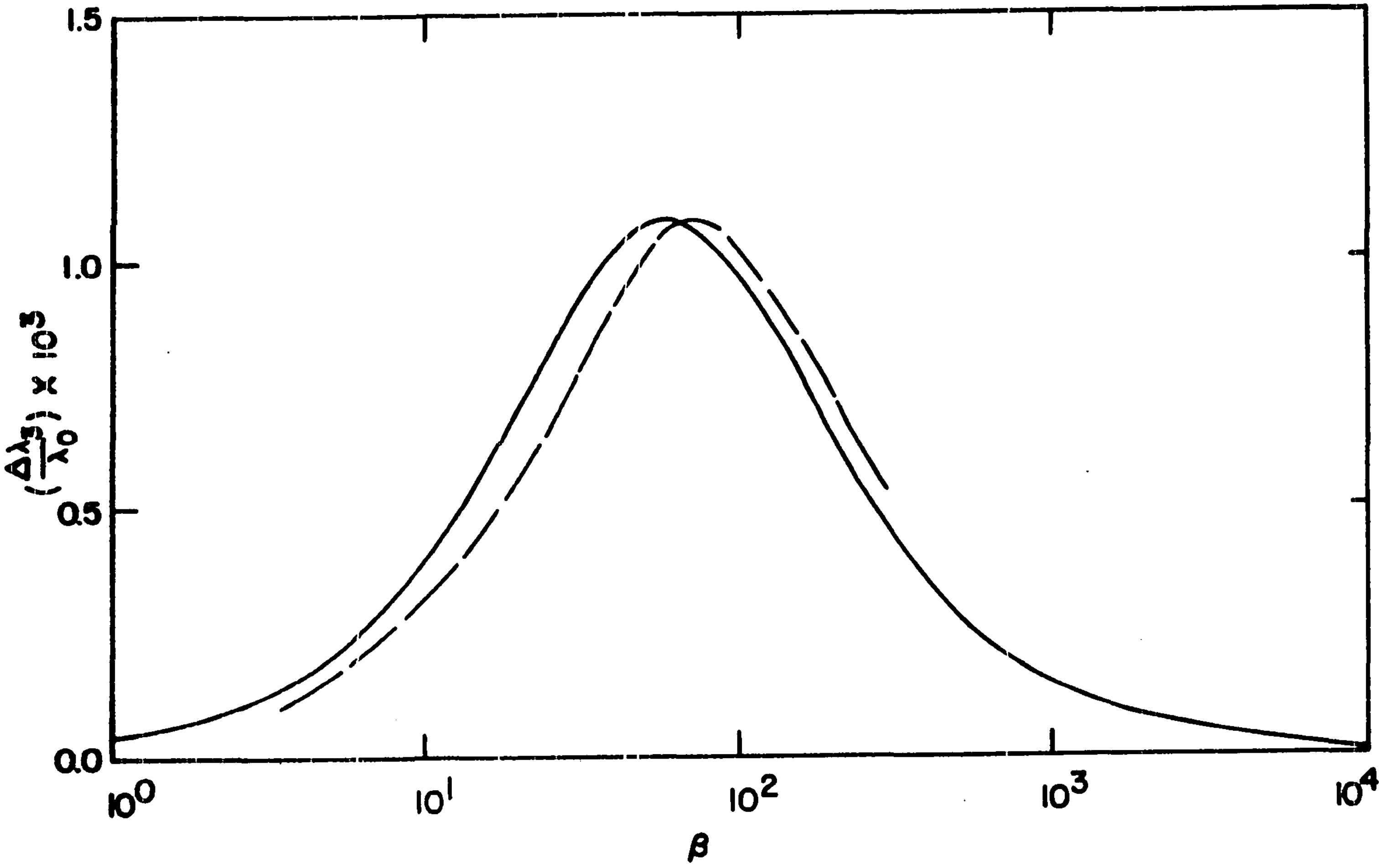


Figure 5.7. A plot of $\Delta\lambda_3/\lambda_0$ vs. β (see Equation 5.16) for CH_4. The solid line is the calculated result and the dashed line is the experimental result

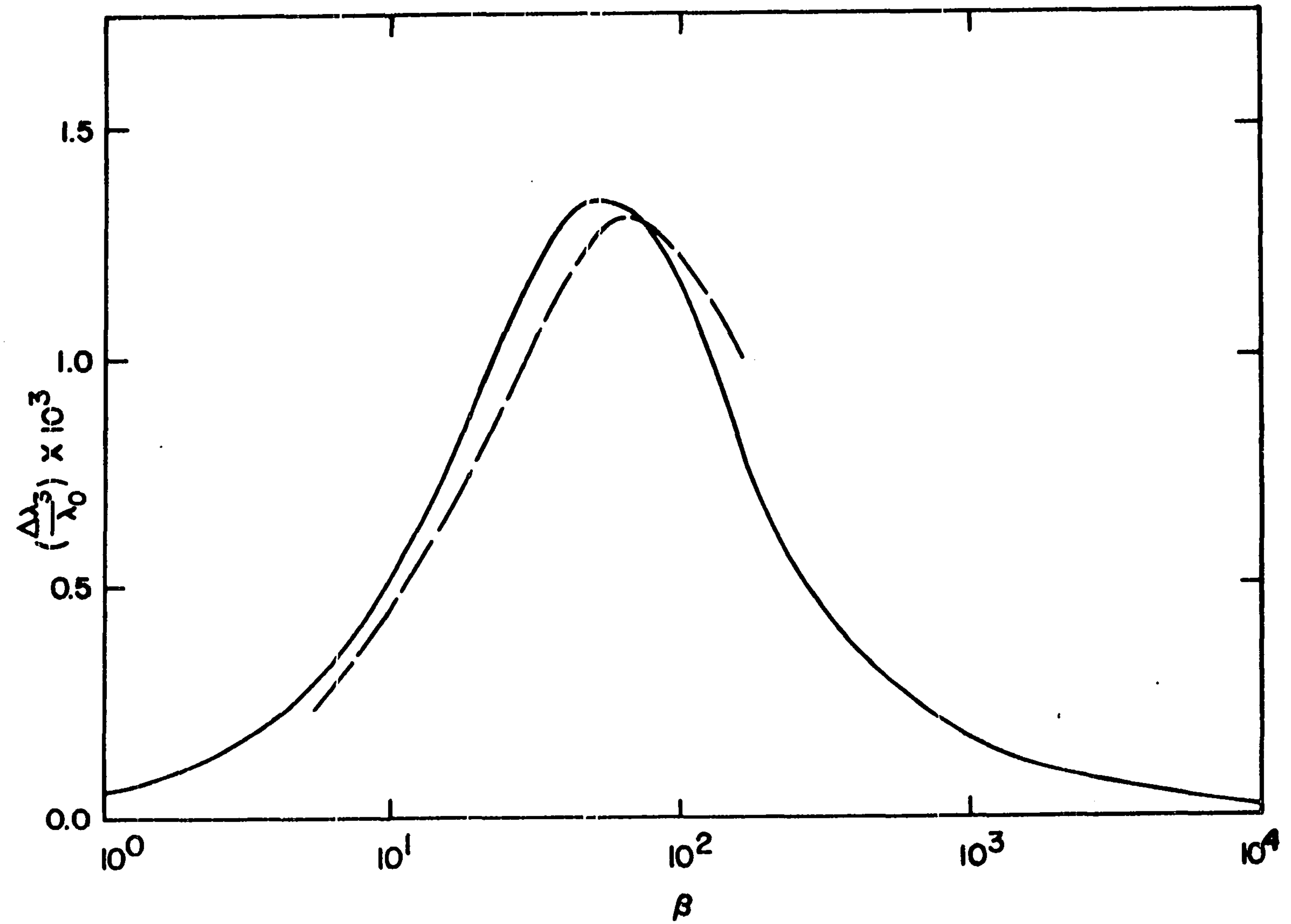


Figure 5.8. Symbols are as in Figure 5.7 for CD_4

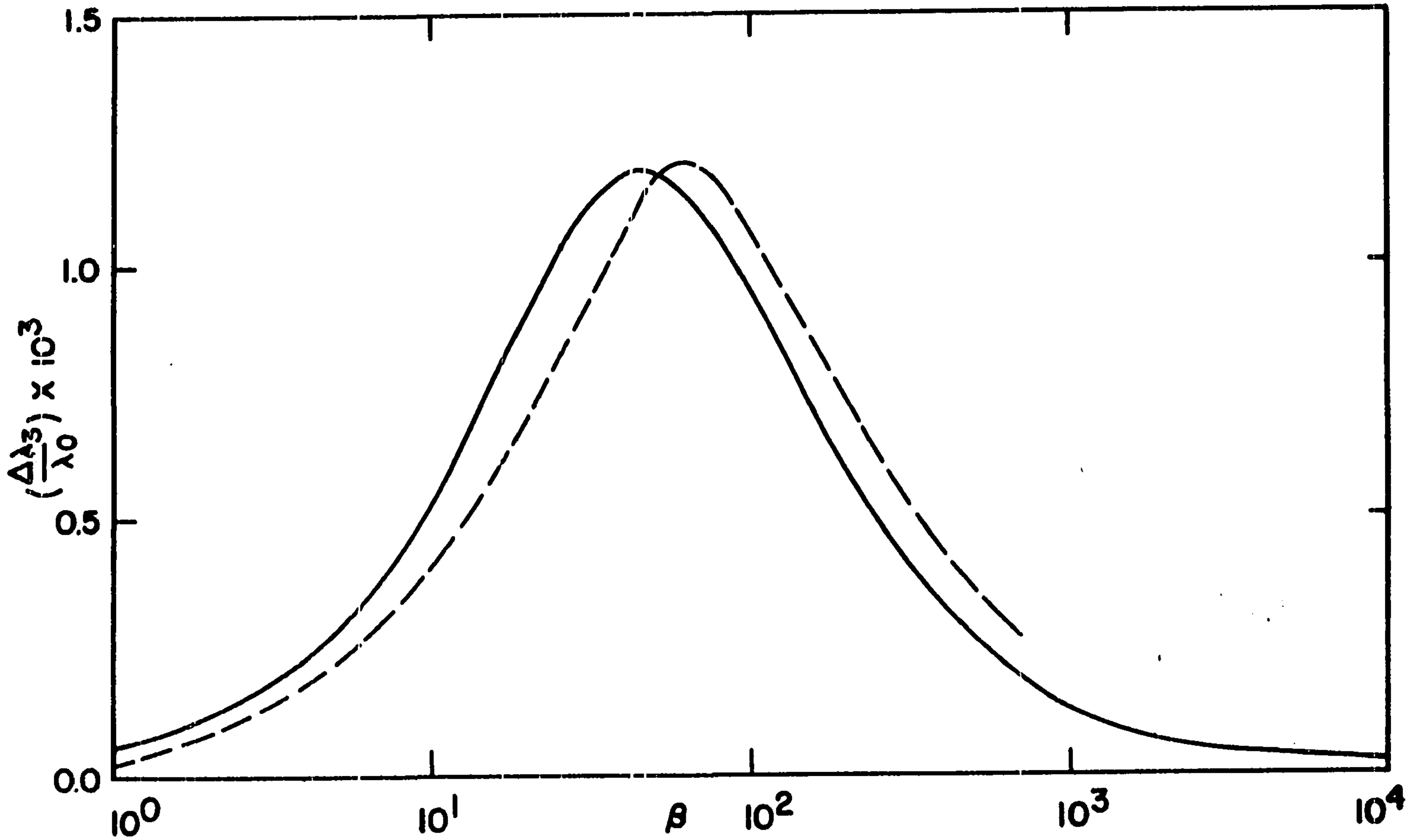


Figure 5.9. Symbols are as in Figure 5.7 for CF_4

Table 5.2. Comparison of experimental (11) (in parentheses) and theoretical values of λ_0 in calories per centimeter second degree, $(\lambda_3/\lambda_0)_{max}$ and $\beta^{(3)}_{max}$

Gas	R	$<\sigma>(\mathring{A}^2)$	$\lambda_0 x10^5$	$(\lambda_3/\lambda_0)_{max} x10^3$	$\beta^{(3)}_{max}$
CH_4	1.0542	31.6380	1.675	1.08	58
			(2.14)[a]	(1.08)	(74)
CD_4	1.0781	28.2195	1.680	1.33	52
			(2.14)[a]	(1.30)	(66)
CF_4	1.1200	38.3241	0.617	1.19	46
			(0.753)[b]	(1.2)	(58)

[a] Source: Reference 49.

[b] Source: Reference 50.

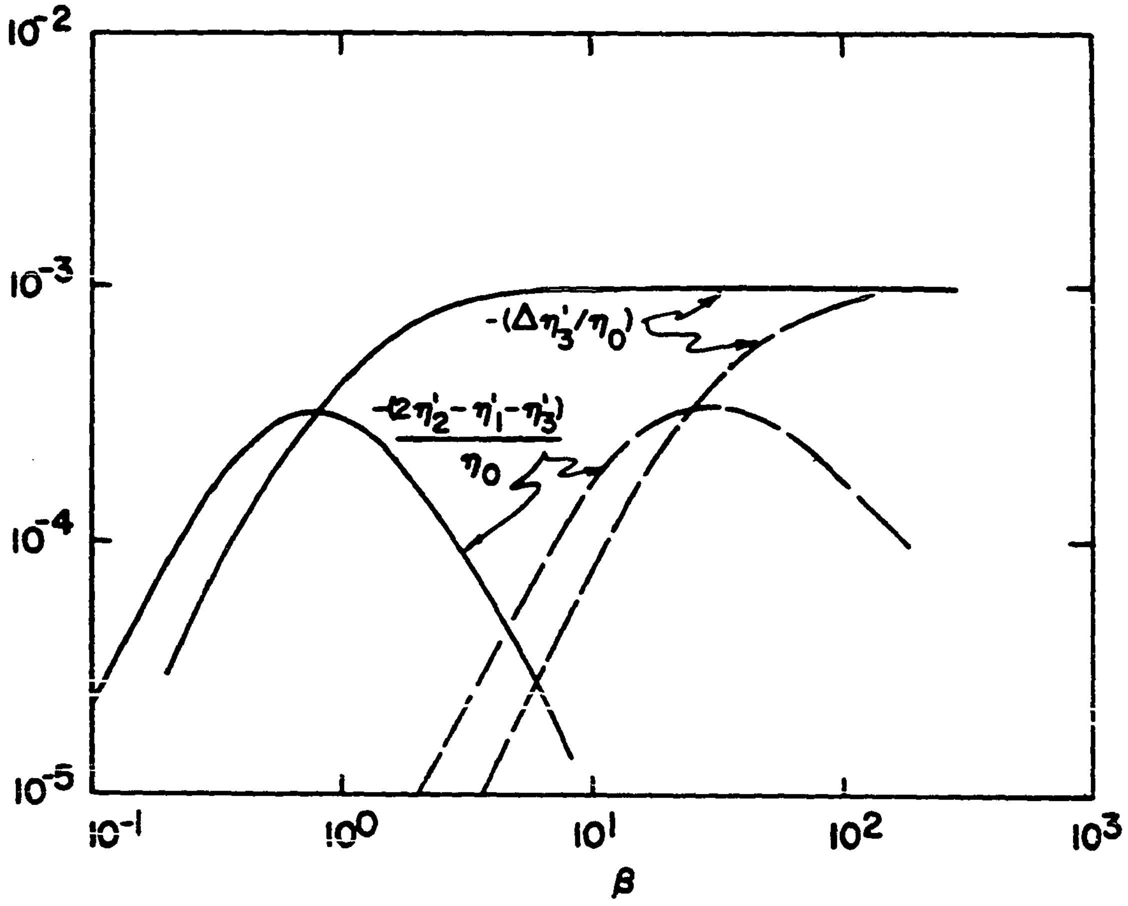


Figure 5.10. A plot of $\Delta\eta_3'/\eta_0$, $\frac{-(2\eta_2'-\eta_1'-\eta_3')}{\eta_0}$ vs. β (see Equation 5.16) for CH_4. The solid lines are the calculated results and the dashed lines are the experimental results

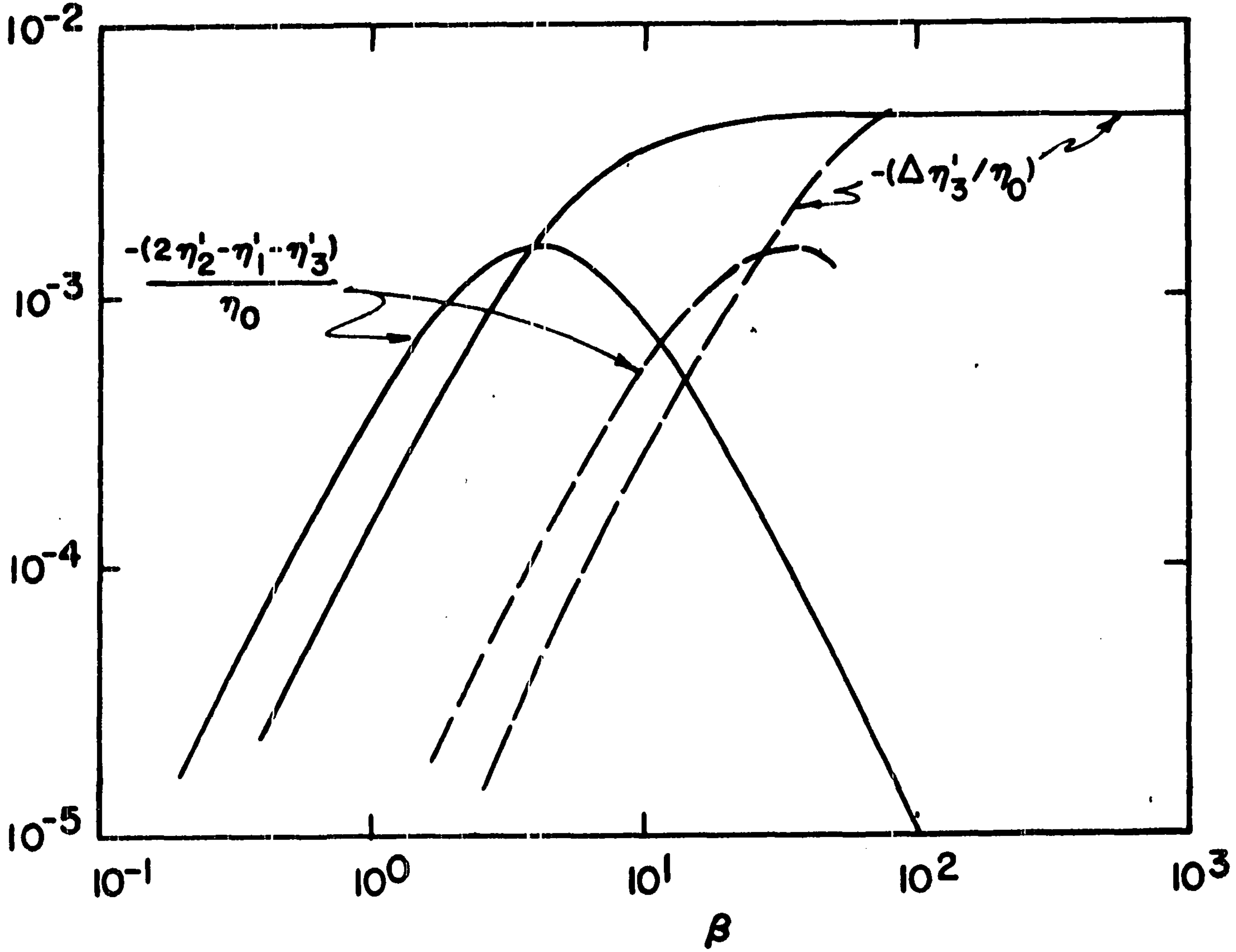


Figure 5.11. Symbols are as in Figure 5.10 for CF_4

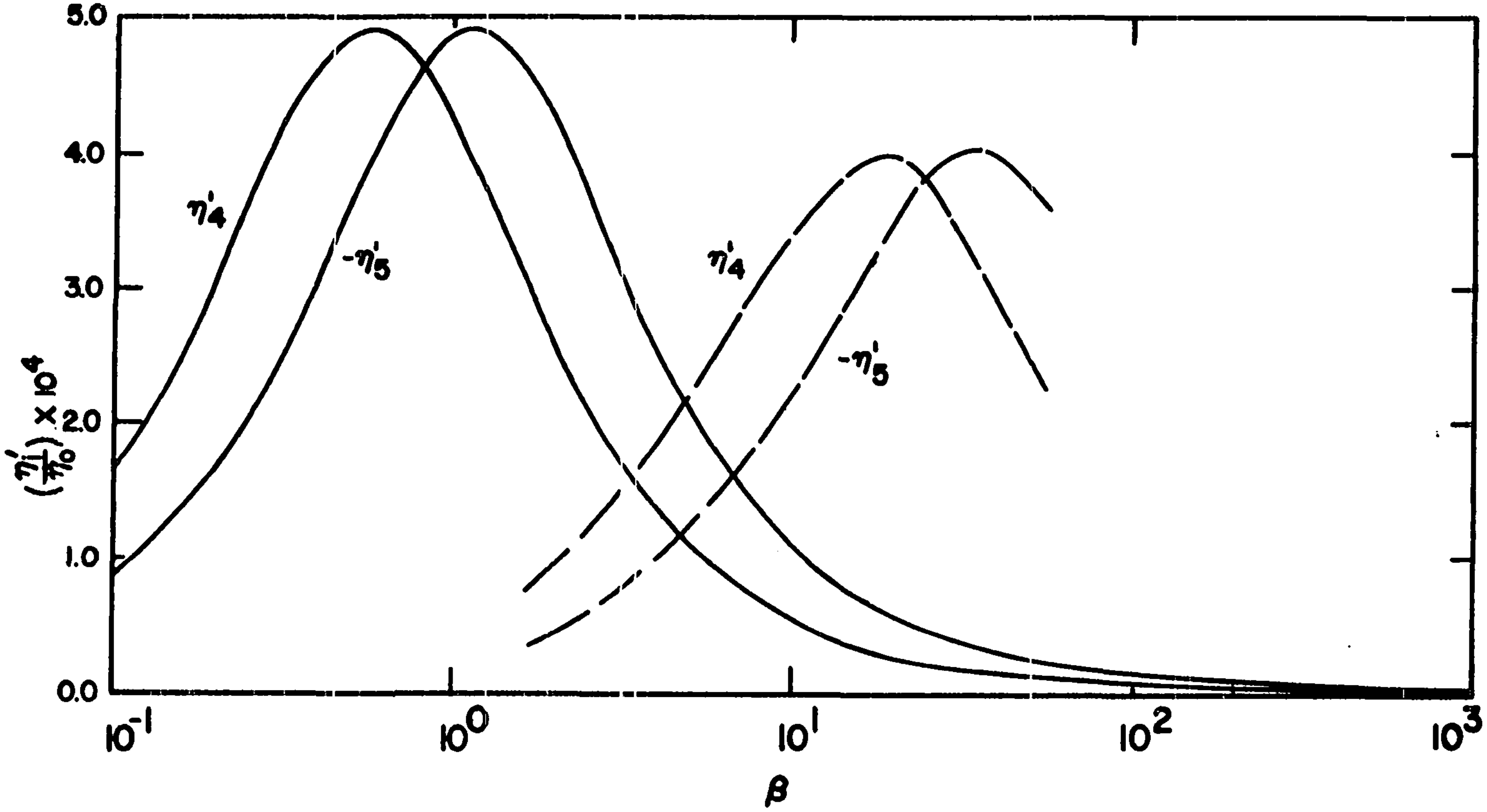


Figure 5.12. A plot of η_4'/η_0, η_5'/η_0 vs. β (see Equation 5.16) for CH_4. The solid lines are the calculated results and the dashed lines are the experimental results

Table 5.3. Comparison of experimental (12, 13) (in parentheses) and theoretical values of η_0 in g per centimeter second, $(\Delta\eta'_3/\eta_0)_{sat}$ $\beta_{1/2}^{(3)}$, $(2\eta'_2 - \eta'_1 - \eta'_3/\eta_0)_{max}$, β_{max}, $(\eta'_4/\eta_0)_{max}$, $\beta^{(4)}_{max}$, $(\eta'_5/\eta_0)_{max}$, and $\beta^{(5)}_{max}$

Gas	CH_4	CF_4
R	1.0311	1.1460
$<\sigma>(Å^2)$	13.3905	19.6721
$\eta_0 x10^4$	1.084 (1.09)	1.717 (1.709)
$-(\frac{\Delta\eta'_3}{\eta_0})_{sat} x10^3$	1.0 (0.99)	4.6 (4.6)
$\beta_{1/2}^{(3)}$	1.2 (37.3)	5.8 (38)
$-(\frac{2\eta'_2-\eta'_1-\eta'_3}{\eta_0})_{max} x10^3$	0.32 (0.34)	1.5 (1.5)
β_{max}	0.8 (29.4)	4 (37.6)
$(\frac{\eta'_4}{\eta_0})_{max} x10^3$	0.49 (0.40)	2.27 --
$\beta^{(4)}_{max}$	0.58 (19)	2.75 --

Table 5.3 (Continued)

Gas	CH_4	CF_4
$(-\frac{\eta'_5}{\eta_0})_{max} x10^3$	0.49 (0.40)	2.27 --
$\beta^{(5)}_{max}$	1.15 (35)	5.75 --

not as good as for thermal conductivity. This was also observed in the case of diatomic molecules (31).

In Table 5.4 we show the results for CH_4 and CF_4 of fitting $(\Delta\lambda_2/\lambda_0)_{sat}$, $\beta^{(2)}_{1/2}$, $(\Delta\eta'_3/\eta_0)_{sat}$ and $\beta^{(3)}_{1/2}$ using a fixed $\langle\sigma\rangle$ and varying R . We do not show any R value to fit $\beta^{(2)}_{1/2}$ and $\beta^{(3)}_{1/2}$ for CF_4 because the R value needed is so large as to be beyond the limits of meaning for our model. We can conclude from this that a model of much higher nonsphericity (greater R) is necessary to fit the field strengths at which the field effects occur than to fit the magnitudes of the field effects themselves.

For viscosity the crucial collision integral determining β values at which changes in the transport coefficients occur vanishes in the spherical limit ($R = 1$); but this is

Table 5.4. List of R values that fit (for fixed $<\sigma>$) experimental values of $(\Delta\lambda_2/\lambda_0)_{sat}$, $\beta_{1/2}^{(2)}$, $(\Delta\eta_3'/\eta_0)_{sat}$, and $\beta_{1/2}^{(3)}$, for CH_4 and CF_4

	$R_{CH_4}(<\sigma>=13.4614\ Å^2)$	$R_{CF_4}(<\sigma>=19.9293\ Å^2)$
$(\Delta\lambda_2/\lambda_0)_{sat}$	1.085	1.158
$\beta_{1/2}^{(2)}$	1.30	--
$(\Delta\eta_3'/\eta_0)_{sat}$	1.031	1.06
$\beta_{1/2}^{(3)}$	1.236	--

not the case for thermal conductivity. As a consequence only the magnitudes of the field effects are extremely sensitive to the nonsphericity (degree to which $R>1$) for the thermal conductivity; whereas both the magnitudes and the field strength values are sensitive to the non-sphericity in the case of viscosity. Hence the fact that substantially smaller R values are required to fit magnitudes than are needed to fit field strength values is of numerical importance in the case of viscosity but not in the case of thermal conductivity. This accounts for the better agreement with experiment in the latter case.

In summary we conclude that the rigid models give comparable results for linear molecules and those with tetrahedral symmetry. In both cases agreement is less satisfactory for viscosity than for thermal conductivity.

CHAPTER 6. THE GENERAL SOFT POTENTIAL

The Limitations of the Rigid Ovaloid and Soft Sphere Models

Though the rigid ovaloid model has been shown to be capable of reproducing the major features of the magnetic field changes of thermal conductivity and viscosity, it cannot be used to calculate temperature dependence of these effects. The reason is that there is no way to parameterize the temperature dependence with this model since the cross section, $\bar{\delta}_{ro}(\hat{k})$, is energy independent. A phenomenon in which temperature dependence is particularly important is the thermal diffusion ratio in isotopic binary mixtures. The thermal diffusion ratio, α^T, is defined by

$$\alpha^T \equiv (\rho D_i^T) / (n^2 n_i m_j x_i x_j D_{ij}) \quad . \tag{6.1}$$

Matzen et al. (31) have found that the rigid ovaloid model gives reasonable estimates to the effects of rotational degrees of freedom on α^T on binary isotopic mixtures of CO at a single high temperature. However the predicted α^T is temperature independent. As a consequence the important phenomenon of temperature inversion of α^T (a reversal of the direction of thermal diffusion at low temperatures which causes the sign of α^T to change) is completely missed. The attractive part of the true interaction plays a central role in determining this last property; and, of course, rigid ovaloid molecule models suffer only repulsive collisions. A related difficulty with the rigid ovaloid model is that the spherical part of the collision cross section is unrealistic. As a result, if there is an important spherical contribution to the property of interest (as in the case of thermal diffusion in a binary mixture whose components have different masses) the rigid ovaloid model is again unsatisfactory.

The soft sphere model has no collisionally active rotational degrees of freedom and hence cannot be used to predict magnetic field effects. Although this model predicts a temperature dependence for α_T , there is no way of indicating differences in mass distribution with it. Thus, contrary to experiment, the soft sphere model predicts no thermal diffusion effect for a mixture composed of components of the same total mass but different mass distribution.

An attempt was made by Cooper et al. (51) to correct the deficiencies of the rigid ovaloid model calculations of thermal diffusion ratio in a simplistic way. The method used was to add the rigid ovaloid results for D_{ij} and D_i^T to the difference for these respective properties as calculated using the Lennard-Jones spherical model and the rigid sphere model. The results obtained using these corrections were not a satisfactory improvement. Thus it is necessary to employ a general soft potential for this problem.

The General Soft Model Applied to Thermal Diffusion in Binary Isotopic Mixtures of CO

We now apply the general soft model, based on the collision integral formulation of Chapter 4, to the analysis of the temperature dependence of α^T in binary isotopic CO mixtures. The temperature span studied is from 80°K to 300°K and includes the reported (15) inversion temperatures for all mixtures under investigation. In addition we decompose the calculated thermal diffusion coefficients into their additive contributions arising from the mixture components' differences in mass, moment of inertia and load (center of bond displacement from the center of mass). To test the model we calculate, using the same parameters, the thermal conductivity and diffusion coefficients over the same temperature range. These latter transport properties are largely determined by the spherical contribution to the cross section. In the present work we use the thermal conductivity to fix the parameters which govern the spherical part of the interaction. This procedure has the advantage of widening the range of applicability of the model and at the same time leaving only the nonsphericity parameters to be determined from the thermal diffusion data. Following the Born-Oppenheimer approximation, we use the same model parameters for all CO isotopes.

The importance of quantum effects (which might be important at the lower range of the temperature span) is not rigorously assessed. We note, however, that the characteristic rotational temperature of CO is 2.8°K and hence the maximum contribution to equilibrium thermodynamic properties from these effects is of the order of one percent at 80°K. Unless the effect on thermal diffusion is several times greater, it will not be significant.

The moments equations and the equations relating their solutions to the transport properties (thermal diffusion, thermal conductivity and diffusion) of linear molecules are given in Chapter 3. The collision integrals required in the moments equations can be calculated from projections and orientation integrations over the $(\underline{u},\underline{v})$ expressions of Equations 4.55, 4.56 and 4.58. The integrands of these orientation integrals depend on four interaction parameters. These parameters can be related in a nonrigorous way to the Kihara type model of Chapter 4 which assumes that the molecules are surrounded by body fixed ellipsoidal (in this case) cores. The potential energy of interaction is a function of the shortest distance between cores (if the cores overlap, a distance of analogous significance can be defined). The functionality of the interaction is taken to be the Lennard-Jones potential. When the cores are in contact at only a point the interaction energy is zero. The parameter which determines the value of the Ω^* integrals is (ϵ/k) , the depth of the well of the Lennard-Jones potential. The three geometric parameters, which determine the differential surface area of the cores' excluded volume, are $\langle\sigma\rangle$, the average cross sectional area of the core, $\hat{R}$, the ratio of the major to minor axis of the core, and S_s , the displacement of the center of the ellipsoidal core from its bond center (measured in units of the minor axis). A positive value of S_s means that the ellipsoid surface is nearer to the carbon atom than to the oxygen atom in CO. The parameters (ϵ/k) and $\langle\sigma\rangle$ basically govern the spherical part of the interaction whereas $\hat{R}$ and S_s characterize the nonsphericity. In order to perform the orientation integrations we must specify the dependence of the integrands on the above parameters.

The model geometry determines the functional form of $S\,d\hat{k}_a$, the differential surface element of the volume which is equivalent to the excluded volume formed by considering the zero potential cores as rigid ovaloids. Therefore the methods of Appendix A used to form S_{r_0} can be used in the same way to form S .

In the case at hand, the supporting function of an ellipsoidal model, in the coordinates of the center of mass systems of body i, is given by

$$h^{(i)} = a^{(i)} \left[1 + (\hat{k}^{(i)} \cdot \hat{e}^{(i)})((\hat{R}^{(i)})^2 - 1)\right]^{1/2}$$

$$- (c_m^{(i)} + S_s^{(i)}) \, (\hat{k}^{(i)} \cdot \hat{e}^{(i)}) \qquad (6.2)$$

where $a^{(i)}$ is the length of minor axis, $\hat{e}^{(i)}$ is a unit vector along the carbon-oxygen axis and points from oxygen to carbon and $c_m^{(i)}$ is the displacement of the center of the bond from the center of mass. A positive value of $c_m^{(i)}$ and $S_s^{(i)}$ cause displacements in the same direction. The parameter $S_s^{(i)}$ accounts for the difference in the repulsive qualities of the oxygen and carbon ends of the molecule. The supporting function of Equation 6.4 can be inserted into Equation A.8 with the result that

$$\langle \sigma^{(i)} \rangle = \frac{a^{(i)\,2}\pi}{2} \left\{ 1 + \left(\frac{(\hat{R}^{(i)})^2}{2((\hat{R}^{(i)})^2 - 1)} \right) \left(\tan^{-1}((\hat{R}^{(i)})^2 - 1)^{1/2} \right.\right.$$

$$\left.\left. - \tan^{-1}\left(-((\hat{R}^{(i)})^2 - 1)^{1/2}\right) \right) \right\} . \qquad (6.3)$$

Therefore the specification of $\langle \sigma^{(i)} \rangle$ and $\hat{R}^{(i)}$ gives $a^{(i)}$.

Because of the symmetry of the ellipsoids ($h^{(i)} = h^{(i)}(\hat{k}^{(i)} \cdot \hat{e}^{(i)})$), the only nontrivial orientation integrations are over $(\hat{k}^{(i)} \cdot \hat{e}^{(i)})$ and $(\hat{k}^{(j)} \cdot \hat{e}^{(j)})$. The integrals are therefore of the tractable two-fold variety which can be performed directly without the expansions required for tetrahedral shapes.

The spherical, Lennard-Jones parameters (ϵ/k) and $\langle\sigma\rangle$ are fixed by fitting the calculated thermal conductivity of pure $^{12}C^{16}O$ to the experimental data (52) over the temperature range from 100°K to 300°K. Since the thermal conductivity is a "mean free path" type transport property it is fairly insensitive to small variations in $\hat{R}$ and S_s and can independently fix (ϵ/k) and $\langle\sigma\rangle$. It is found that for a reasonable range of $\hat{R}$ and S_s values, the thermal conductivity is fit within experimental error by the parameters $(\epsilon/k) = 144.3$°K and $\langle\sigma\rangle = (1.78)^2\pi\text{Å}^2$ (see Figure 6.1). The calculated self-diffusion coefficient, which is also dominated by the spherical part of the interaction, is compared with experiment (53, 54) in Figure 6.2. It is seen that different (ϵ/k) and $\langle\sigma\rangle$ values (primarily those of $\langle\sigma\rangle$) are required in this case. This discrepancy in potential parameters between different transport properties is observed also for monatomic gases and hence can be at least partially ascribed to the approximate nature of the Lennard-Jones potential.

Boersma-Klein and deVries (15) have measured thermal diffusion ratios of CO and N_2. The device they used was an eight tube swing separator which consists of eight enclosed

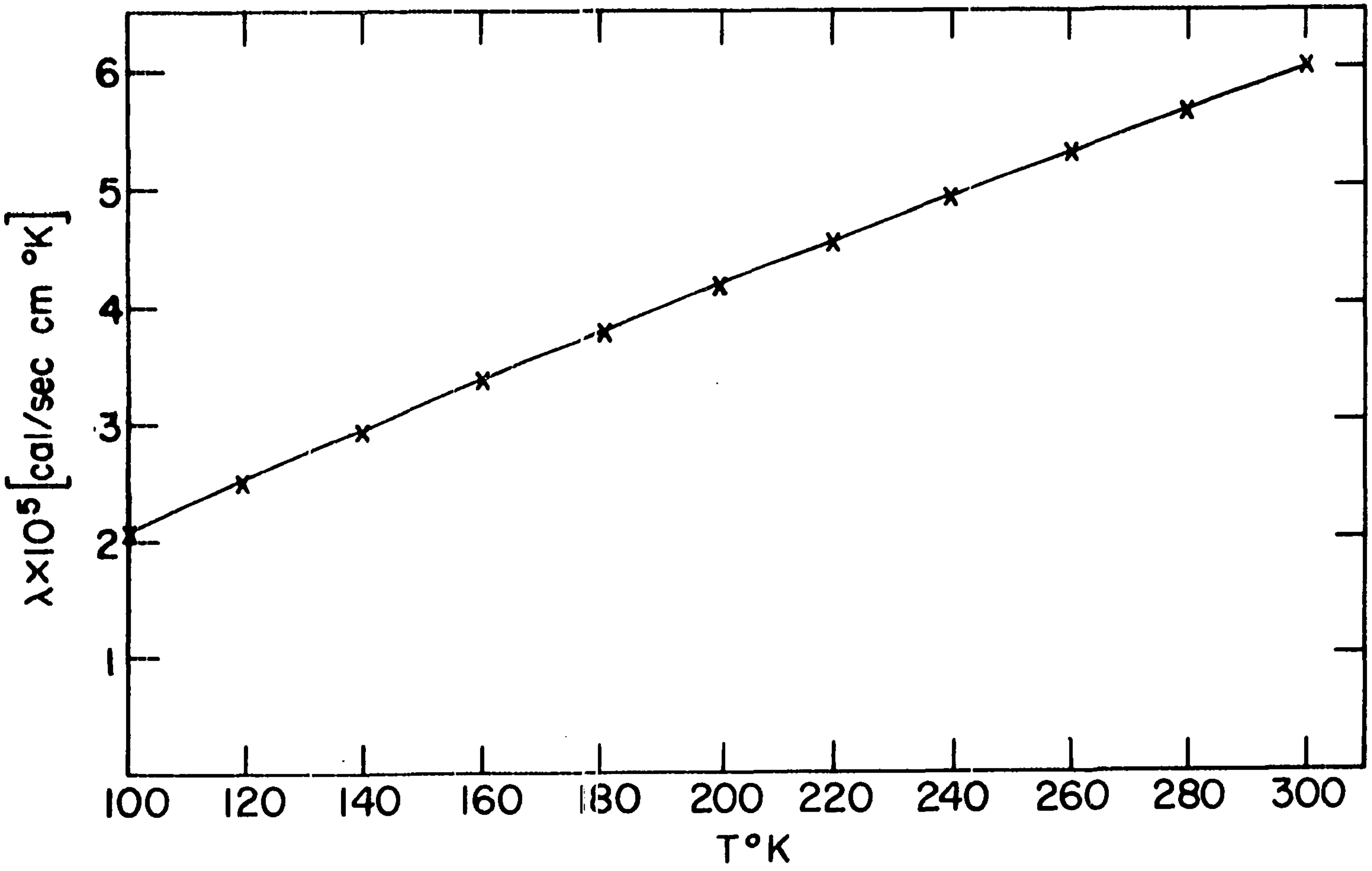


Figure 6.1. Thermal conductivity of $^{12}C^{16}O$ for the temperature range 100°K-300°K. Experimental data (Reference 52) denoted by X, and solid line denotes theoretical curve calculated using $(\epsilon/k) = 144.3$°K, $\langle\sigma\rangle = (1.78)^2\pi\hat{R}^2$, $\hat{R} = 1.06$ and $S_s = 0.057$

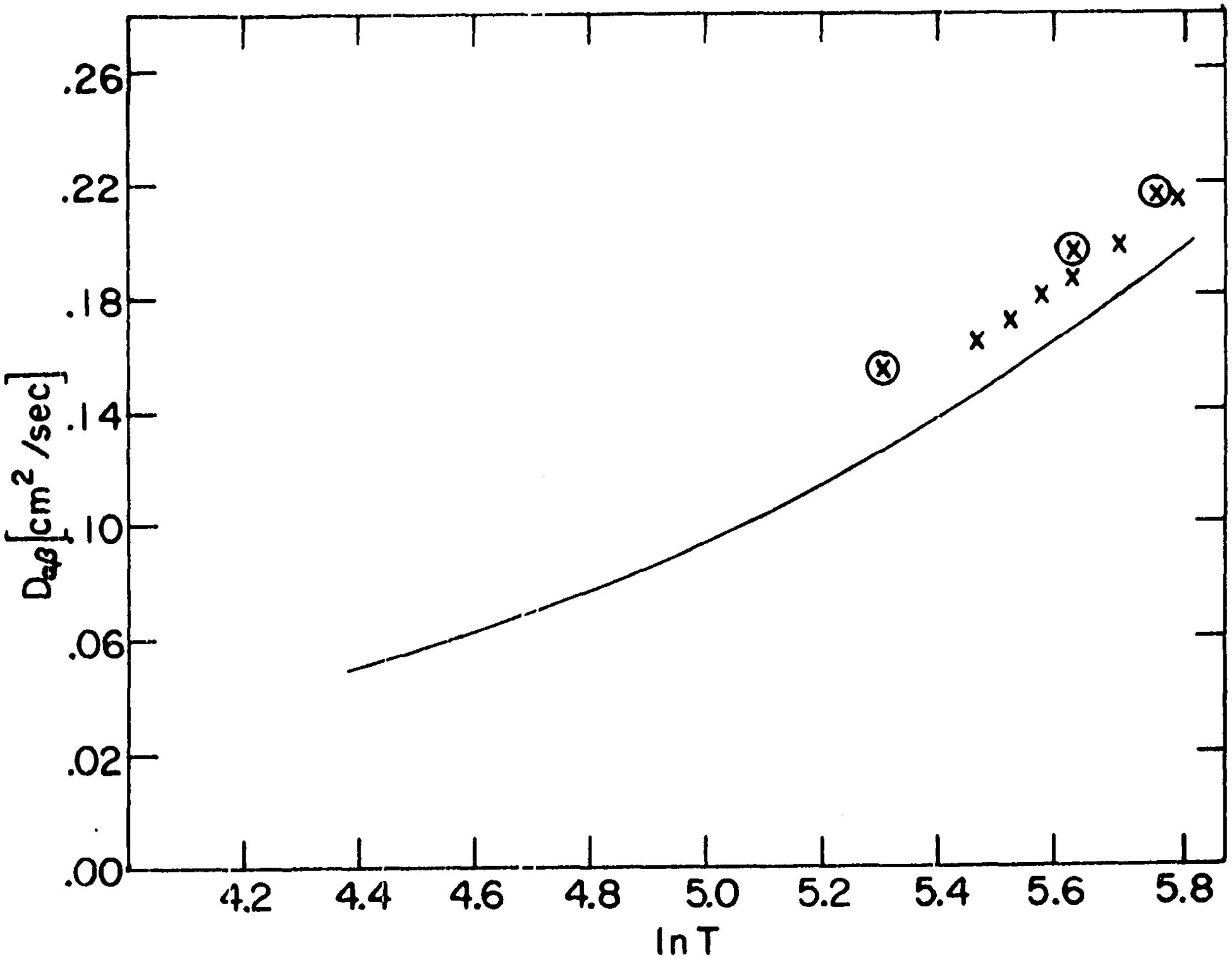


Figure 6.2. Diffusion coefficient for $^{14}C^{16}O$-$^{12}C^{16}O$ vs. ln T. Experimental data of Reference 53 denoted by ⊗ and experimental data of Reference 54 (for $^{12}C^{18}O$-$^{12}C^{16}O$) by X. (Theoretical curves for the two mixtures are nearly identical)

copper tubes mounted between two copper blocks. The top block (hot end) is kept at 303°K and the bottom block (cold end) is varied from 260°K to 80°K. The top end of the first tube is connected by a capillary to the bottom end of the second tube and so on until the top end of the seventh tube is connected to the bottom end of the eighth. The equality of concentration at both ends of each capillary is maintained by a pump. A binary mixture of a certain concentration is entered into all the tubes at the start of the experiment. Then after a steady state is reached, the concentration is measured in the bottom of the first tube and in the top of the eighth. The measured quantity, q, which is called the separation factor is defined by

$$q \equiv [x/(1-x)]_{T_c} \Big/ [x/(1-x)]_{T_h} \tag{6.4}$$

where x is a mole fraction, T_c is the temperature of the cold end and T_h is the temperature of the hot end. The separation factor is related to the thermal diffusion ratio by the relation that

$$\ln q = -8 \int_{T_c}^{T_h} \alpha^T \, d \ln T \tag{6.5}$$

from which it follows that plotting $\frac{1}{8} \ln q$ against $\ln(T_h/T_c)$ with a constant T_h gives α^T at T_c as the slope of the graph. We concentrate on the isotopic binary mixtures of

CO for which thermal diffusion is measured in Reference 15.

We calculate $\alpha^T(T)$ and $\ln q(T)$ using the values of (ϵ/k) and $\langle\sigma\rangle$ determined above and variable $\hat{R}$ and S_s parameters. The values which give the best fit to the experimental (15) $\ln q$ points are $\hat{R} = 1.062$ and $S_s = .0566$. There is some justification in giving more weight to low temperature points since, by definition, $\ln q$ $(T = 303°K) = 0$ in all cases; however, for simplicity, we give all experimental points equal weight in our work. Other fitting procedures could be used. For instance special weight could reasonably be given to the equimass mixture since in this case there is no dominant spherical contribution due to mass differences. As a third alternative the $\hat{R}$ and S_s values could be chosen so that the inversion temperatures are in the closest possible correspondence to the temperatures reported by Boersma-Klein and deVries (15). These variations in the fitting procedure leave the best choice of parameters substantially unaffected. To a degree this indicates the uniqueness of the $\hat{R}$ and S_s values. The agreement between experiment and theory for each of the four mixtures is shown in Figures 6.3, 6.4, 6.5 and 6.6.

It has been shown by perturbation studies (55) that the thermal diffusion coefficient for isotopic mixtures can be decomposed into a sum of additive contributions arising from the differences in mass, moment of inertia

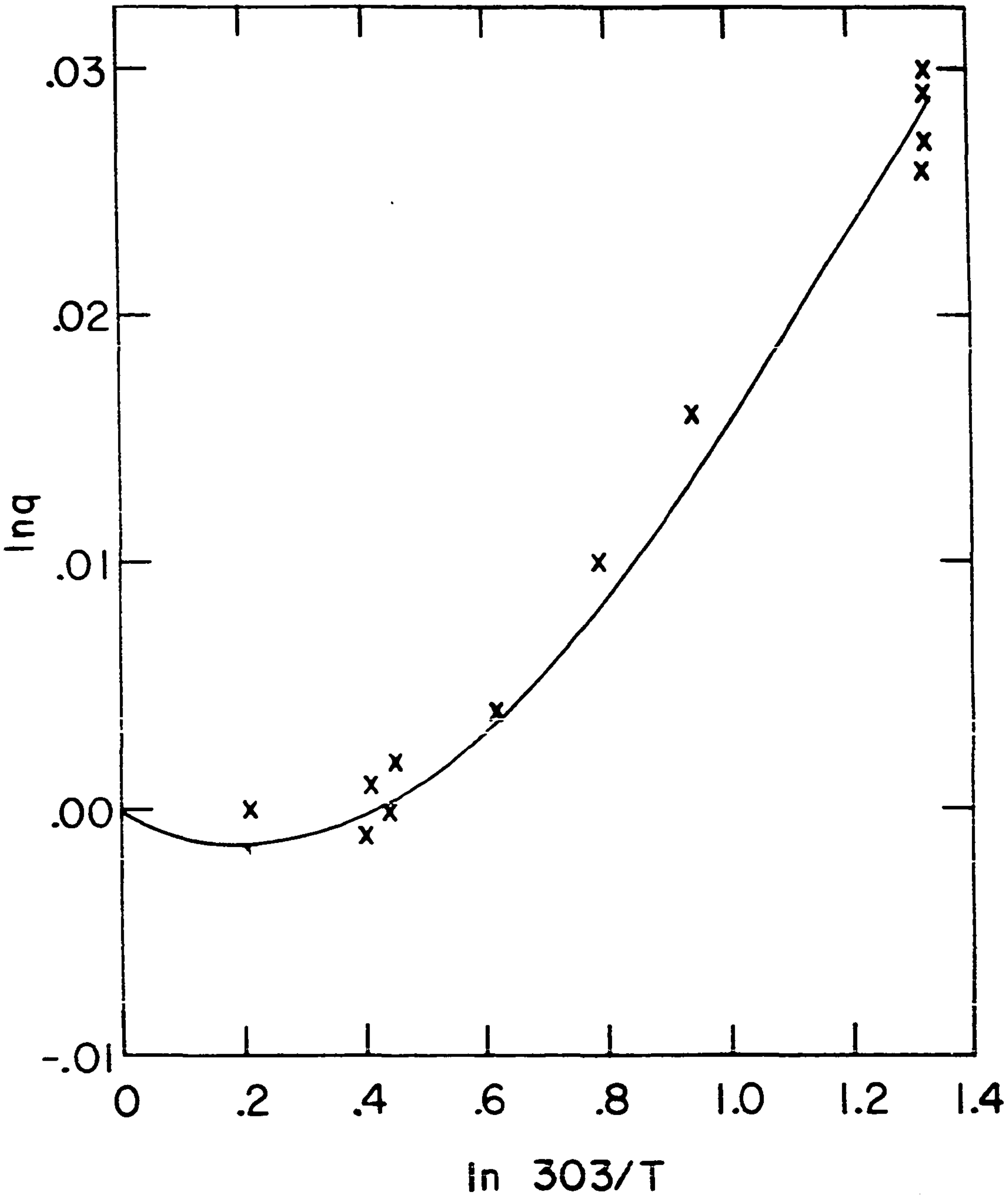


Figure 6.3. ln q vs. ln(303°K/T) for $^{14}C^{16}O$-$^{12}C^{18}O$. Symbols are as in Figure 6.1

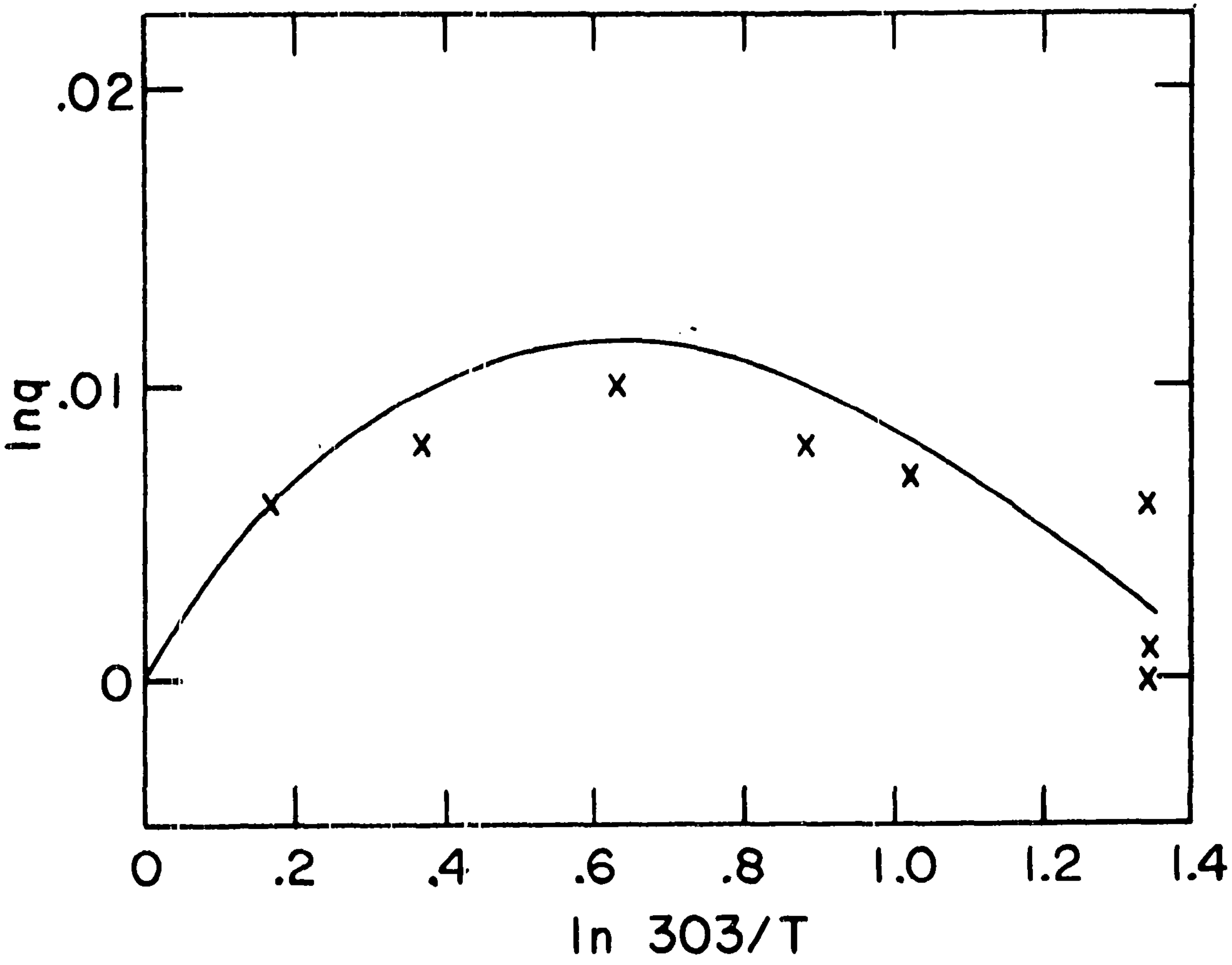


Figure 6.4. ln q vs. ln(303°K/T) for $^{13}C^{16}O$-$^{12}C^{16}O$. Symbols are as in Figure 6.1

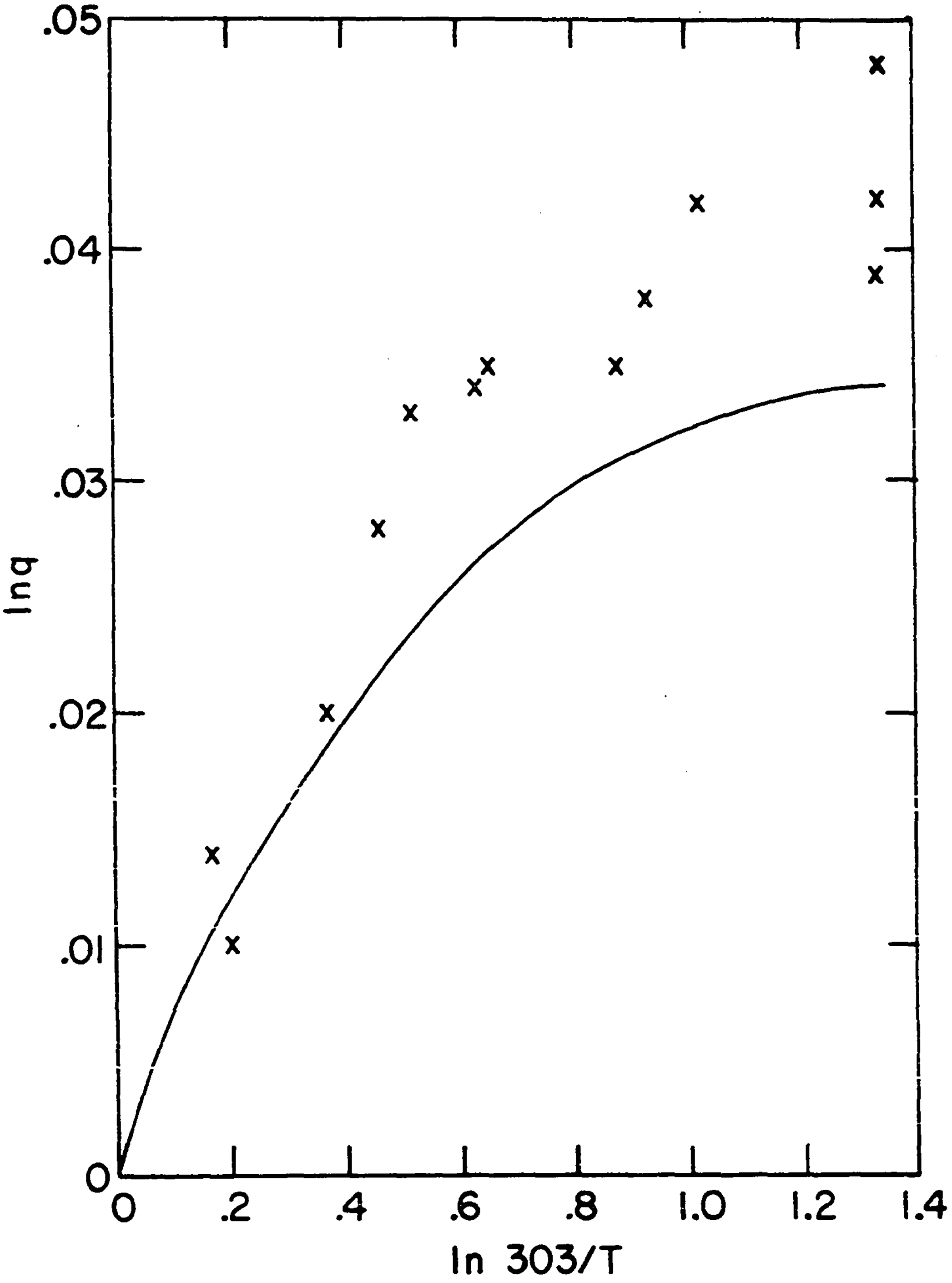


Figure 6.5. ln q vs. ln(303°K/T) for $^{12}C^{18}O$-$^{12}C^{16}O$.
Symbols are as in Figure 6.1

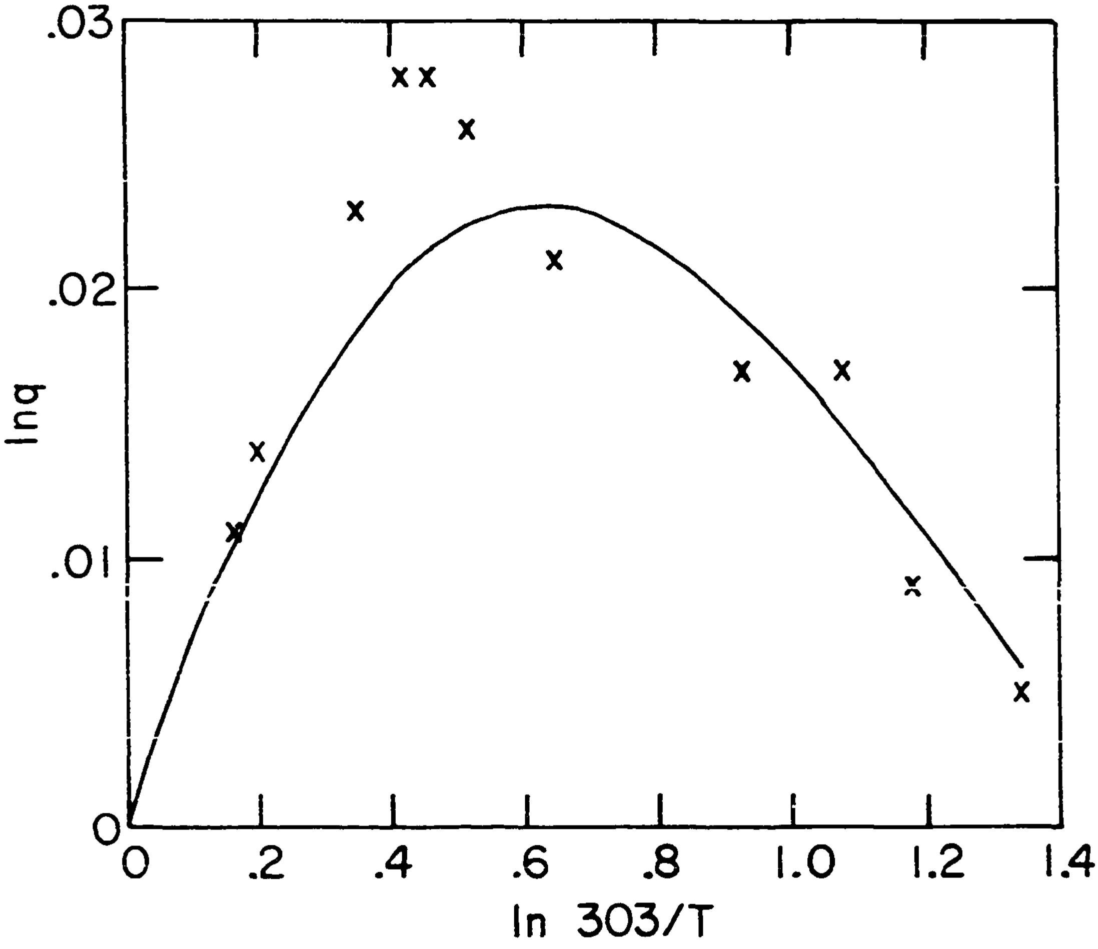


Figure 6.6. ln q vs. ln(303°K/T) for $^{14}C^{16}O$-$^{12}C^{16}O$.
Symbols are as in Figure 6.1

and load between the two species of the mixture. In Figures 6.7, 6.8, 6.9 and 6.10 these separate contributions and their sum are given for each mixture. We find in general that the load contribution increases with S_s and is very sensitive to its value. On the other hand, the moment of inertia term increases with $\hat{R}$. Since a small $\hat{R}$ and a large S_s value are employed in the calculations displayed in Figures 6.7, 6.8, 6.9 and 6.10, the load contribution dominates that of the moment of inertia. As the $\hat{R}$ value is increased the best fit of $\ln q$ requires a decreasing S_s value and hence the relative importance of the moment inertia contribution increases. For instance at $\hat{R} = 1.25$ and $S_s = -.0342$ the contribution of the moment of inertia dominates that of the load. However, the fit in this case is much poorer (by a factor of six in the $\ln q$ error). It is of interest in this regard that Boersma-Klein and deVries (15) are able to empirically fit their data (using a dimensional analysis due to Schirdewahn et al. (56)) by taking into account only the mass and moment of inertia differences while ignoring the load.

The trends in the relative importance of the moment of inertia and load differences are qualitatively similar to what is found for rigid ovaloids. Also the $\hat{R}$ and S_s values we find are in the meaningful range for rigid ovaloid calculations (31). However, because of its

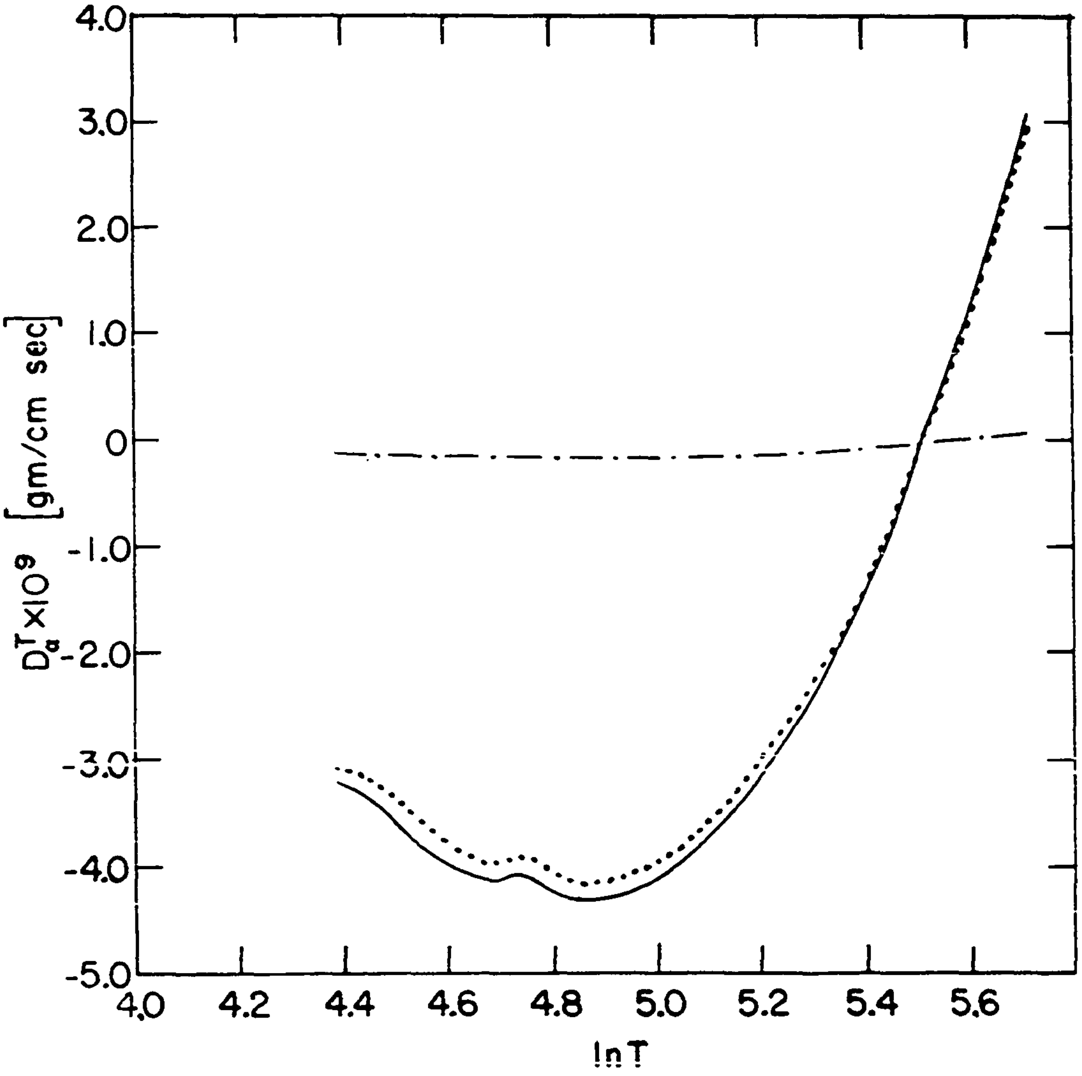


Figure 6.7. ($^{14}C^{16}O-^{12}C^{18}O$). Temperature dependence of additive contributions to D_α^T (see text). (... load, -.- moment of inertia, —— sum)

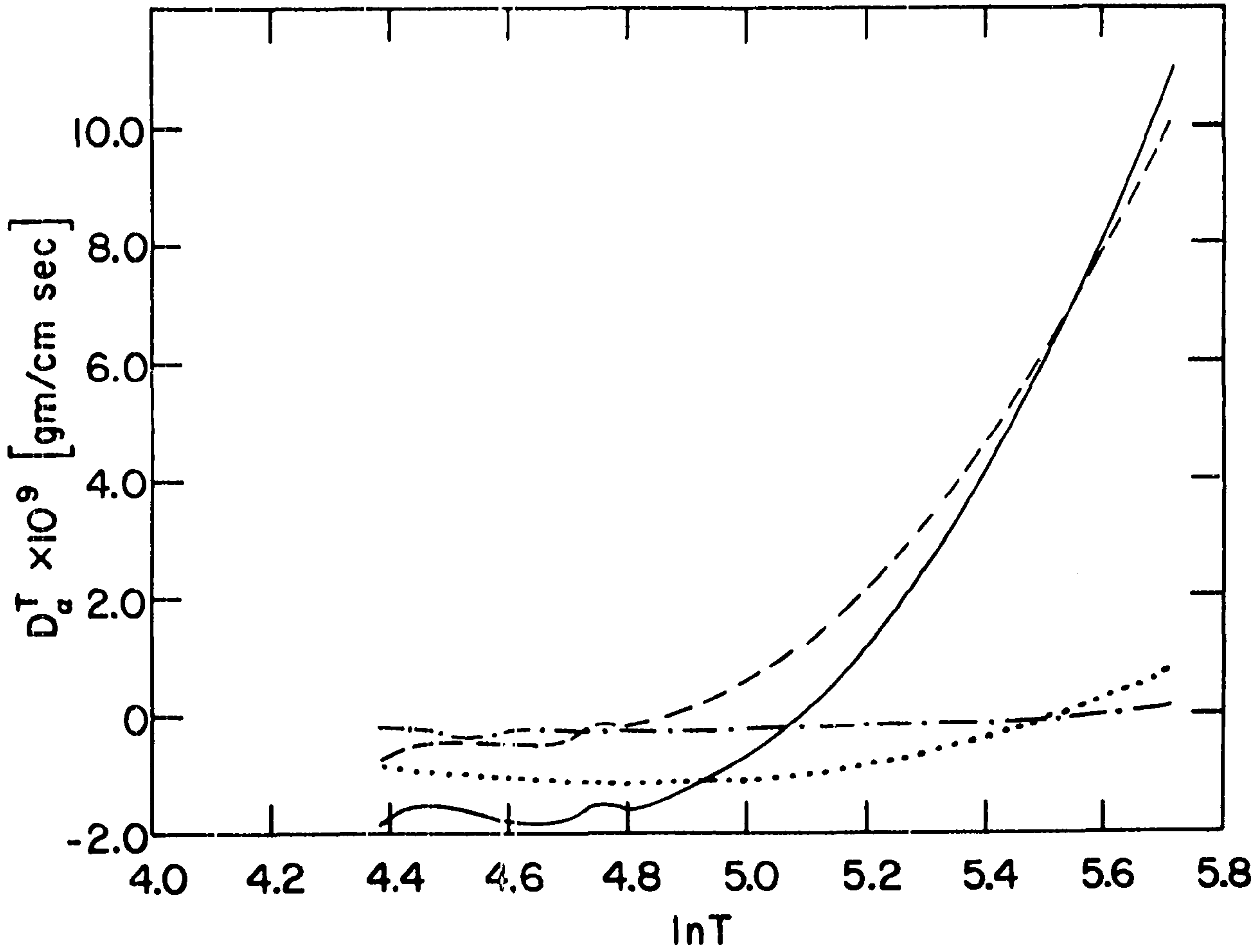


Figure 6.8. ($^{13}C^{16}O$-$^{12}C^{16}O$). Temperature dependence of additive contributions to D_α^T (see text). (--- mass, ... load, -.- moment of inertia, —— sum)

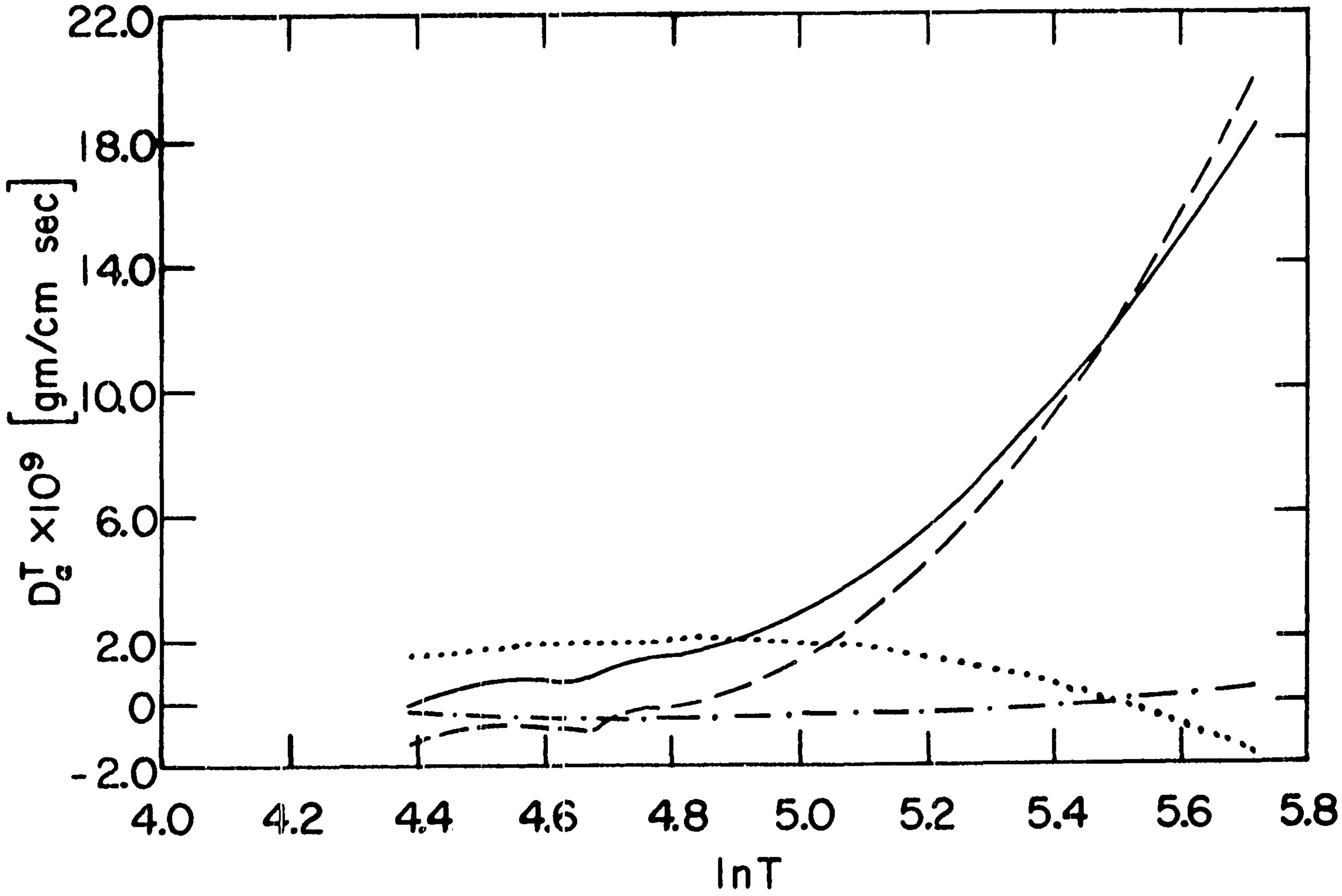


Figure 6.9. ($^{12}C^{18}O$-$^{12}C^{16}O$). Temperature dependence of additive contributions to D_α^T (see Figure 6.8)

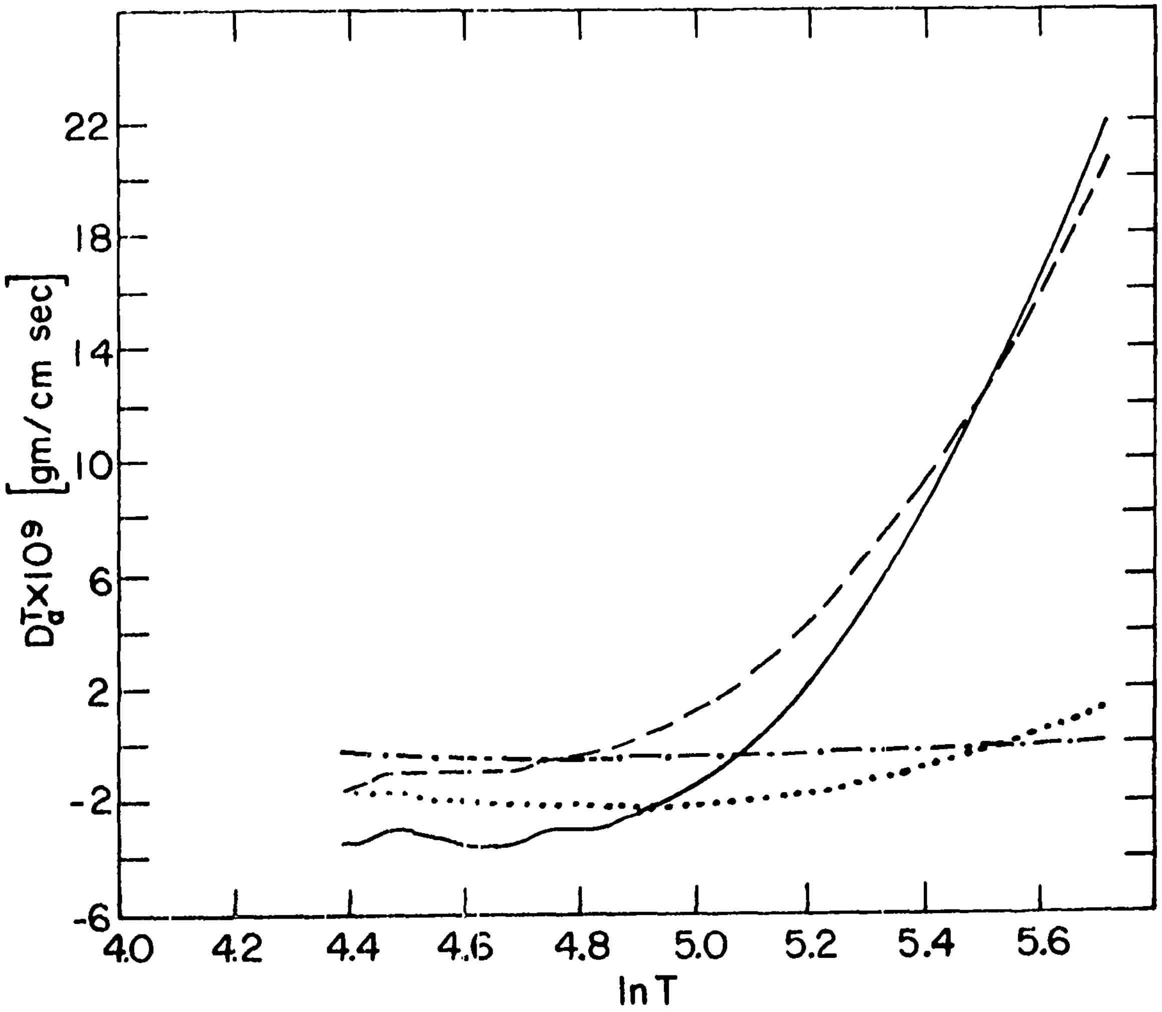


Figure 6.10. ($^{14}C^{16}O-^{12}C^{16}O$). Temperature dependence of additive contributions to D_α^T (see Figure 6.8)

previously discussed failings, the rigid ovaloid model is only useful for qualitative calculations and hence a unique set of $\hat{R}$ and S_s values cannot be determined in this case. The shift parameter, S_s , is positive, which is in agreement with the fact that oxygen is more electronegative than carbon. The value of S_s estimated from covalent radii is positive but much smaller than the one we report.

From Figures 6.3, 6.4, 6.5 and 6.6 it is seen that the best agreement with experiment is for the equimass mixture and the poorest is for $^{12}C^{18}O$-$^{12}C^{16}O$. The fit for the remaining mixtures appears to be slightly outside of the scatter of experimental data. The lack of agreement between theory and experiment for $^{12}C^{18}O$-$^{12}C^{16}O$ may be associated with the fact that this is the only mixture for which one species (i.e., $^{12}C^{18}O$) has both the largest mass and the largest load. As a consequence the behavior of the load contribution for this mixture is different from the others as can be seen in Figures 6.7, 6.8, 6.9 and 6.10.

In Table 6.1 the theoretically calculated inversion temperatures and the inversion temperatures reported by Boersma-Klein and deVries (15) are given. The latter were obtained in an empirical manner from the Schirdewahn theory While they are consistent with the data it is apparent that a rather large latitude in the values taken for the experimental inversion temperatures is permissible. In particular it is not clear from the data given in Figure 6.5 that the $^{12}C^{18}O$-$^{12}C^{16}O$ mixture undergoes temperature inversion at all. Thus the application of the new theory for performing collision integrals for a general soft potential is seen to have a wide range of application and the results are in good agreement with experiment.

Table 6.1. Thermal diffusion inversion temperatures

	T(experimental)°K	T(calculated)°K
$^{14}C^{16}O/^{12}C^{18}O$	247	247
$^{13}C^{16}O/^{12}C^{16}O$	185	165
$^{12}C^{18}O/^{12}C^{16}O$	110	82
$^{14}C^{16}O/^{12}C^{16}O$	173	163

LITERATURE CITED

1. S. G. Brush, Arch. Rational Mech. Anal. **39**, 1 (1970).
2. I. Newton, *Philosophia Naturalis Principia Mathematica* (London, 1687).
3. L. Boltzmann, Sitz. Akad. Wiss. Wien. **66**, 275 (1872); also in translation: S. G. Brush, *Kinetic Theory*, (Pergamon, Oxford, 1966).
4. S. Chapman, Phil. Trans. Roy. Soc. London **A216**, 297 (1917).
5. D. Enskog, "Kinetische Theorie der Vorgänge in Massige Verdünnten Gase", Dissertation, Uppsala (Almqvist and Wiksell, 1917).
6. H. Senftleben, Phys. Z. **31**, 961 (1930).
7. J. J. M. Beenakker, G. Scoles, H. F. P. Knaap and R. M. Jonkman, Phys. Lett. **2**, 5 (1962).
8. J. J. M. Beenakker, in *Festkörpferprobleme*, edited by O. Madelumg (Vieweg, Braunschweig, 1968) vol. 8.
9. J. J. M. Beenakker and F. R. McCourt, Ann. Rev. Phys. Chem. **21**, 47 (1970).
10. L. J. F. Hermans, J. M. Koks, A. F. Hengeveld and H. F. P. Knaap, Physica **50**, 410 (1970).
11. L. J. F. Hermans, A. Schutte, H. F. P. Knaap and J. J. M. Beenakker, Physica **46**, 491 (1970).
12. J. Korving, Physica **50**, 27 (1970).
13. H. Hulsman, E. J. van Waasdijk, A. L. J. Burgmans, H. F. P. Knaap and J. J. M. Beenakker, Physica **50**, 53 (1970).
14. T. Cowling, J. Phys. A: Gen. Phys., **3**, 774 (1970).
15. V. Boersma-Klein and A. E. deVries, Physica **32**, 717 (1966).

16. E. A. Uehling and G. E. Uhlenbeck, Phys. Rev. 43, 552 (1933); H. S. W. Massey and C. B. O. Mohr, Proc. Roy. Soc. A, 141, 434 (1933).

17. C. S. Wang-Chang and G. E. Uhlenbeck, Univ. of Mich. Rept. CM-681 (1951).

18. L. Waldmann, Z. Naturforsch. 12a, 660 (1957).

19. R. F. Snider, J. Chem. Phys. 32, 1051 (1960).

20. F. R. McCourt and R. F. Snider, J. Chem. Phys. 46, 2387 (1967).

21. F. R. McCourt and R. F. Snider, J. Chem. Phys. 47, 4117 (1967).

22. F. B. Pidduck, Proc. Roy. Soc. A, 101, 101 (1922).

23. C. F. Curtiss, J. Chem. Phys. 24, 225 (1956).

24. Yu, Kagan and A. M. Afanas'ev, Zh. Eksp. Teor. Fiz. 41, 1536 (1961) [Sov. Phys. JETP 14, 1096 (1962)].

25. J. S. Dahler and D. K. Hoffman, in Transfer and Storage of Energy by Molecules, edited by G. M. Burnett and A. M. North (Wiley-Interscience, New York, 1970) vol. 3.

26. D. K. Hoffman and J. S. Dahler, J. Stat. Phys. 1, 4 (1969).

27. W. M. Klein, D. K. Hoffman and J. S. Dahler, J. Chem. Phys. 49, 2321 (1968).

28. W. M. Klein, J. S. Dahler, E. R. Cooper and D. K. Hoffman, J. Chem. Phys. 52, 4752 (1970).

29. E. R. Cooper and D. K. Hoffman, J. Chem. Phys. 53, 1100 (1970).

30. S. I. Sandler and J. S. Dahler, J. Chem. Phys. 42, 717 (1966).

31. M. K. Matzen, D. K. Hoffman and J. S. Dahler, J. Chem. Phys. 56, 1586 (1972).

32. W. E. Köhler, Z. Naturforsch. 28a, 815 (1973).

33a. J. van de Ree and T. Scholtes, J. Chem. Phys. 57, 122 (1972).

33b. J. P. J. Heemskerk, F. G. van Kuik, H. F. P. Knaap and J. J. M. Beenakker, Physica 71, 484 (1974).

34. T. Kihara, J. Phys. Soc. Japan 6, 289 (1951).

35. D. K. Hoffman, J. Chem. Phys. 50, 4823 (1969).

36. H. Goldstein, Classical Mechanics (Addison-Wesley, Reading, 1950).

37. J. T. O'Toole and J. S. Dahler, J. Chem. Phys. 33, 1487 (1960).

38. N. N. Bogoliubov, in Studies in Statistical Mechanics, edited by J. de Boer and G. E. Uhlenbeck (Wiley-Interscience, New York, 1962) vol. 1.

39. R. Courant and D. Hilbert, Methods of Mathematical Physics (Wiley-Interscience, New York, 1953) vol. 1.

40. E. R. Cooper and D. K. Hoffman, J. Chem. Phys. 54, 223 (1971).

41. Yu, Kagan and L. Maksimov, Zh. Eksp. Teor. Fiz. 41, 842 (1961) [Sov. Phys., JETP 14, 604 (1962)]

42. S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases (Cambridge University Press, Cambridge, 1970) 2nd ed.

43. M. Hammermesh, Group Theory (Addison-Wesley, Reading, 1962).

44. E. R. Cooper and D. K. Hoffman, J. Chem. Phys. 55, 1016 (1971).

45. S. R. deGroot and P. Mazur, Non-Equilibrium Thermodynamics (North Holland, Amsterdam, 1962).

46. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids (Wiley, New York, 1964) 2nd printing.

47. D. K. Hoffman, R. C. Raffenetti and K. Ruedenberg, J. Math. Phys. 13, 528 (1972).

48. M. Klein and F. J. Smith, J. Res. Nat. Bur. Stand. (U.S.) A72, 359 (1968).

49. H. L. Johnston and E. R. Grilley, J. Chem. Phys. 14, 233 (1946).

50. R. A. Svehla, NASA Tech. Rept. R132 (1962).

51. E. R. Cooper, J. S. Dahler, J. D. Verlin, M. K. Matzen and D. K. Hoffman, J. Chem. Phys. 59, 403 (1973).

52. Y. S. Touloukian, P. E. Liley and S. C. Saxena, Thermal Conductivity-Nonmetallic Liquids and Gases. Vol. 3 of Thermophysical Properties of Matter--The TPRC Data Series, edited by Y. S. Touloukian (IFI-Plenum, New York, 1970).

53. I. Amdur and L. M. Schuler, J. Chem. Phys. 38, 188 (1963).

54. H. F. Vugts, A. J. H. Boerboom and J. Los, Physica 50, 593 (1970).

55. M. K. Matzen and D. K. Hoffman, J. Chem. Phys. 62, 500 (1975).

56. J. Schirdewahn, A. Klemm and L. Waldmann, Z. Naturforsch. 16a, 133 (1961).

ACKNOWLEDGMENTS

The author acknowledges Dr. D. K. Hoffman as the source of the overwhelming balance of the original thoughts contained in this thesis.

APPENDIX A. SUPPORTING FUNCTION GEOMETRY

The supporting function, $h^{(i)}$, of a body i with outward normal $\hat{k}^{(i)}$ is defined as

$$h^{(i)}(\hat{k}^{(i)}) = \tilde{\underline{\zeta}}^{(i)} \cdot \hat{k}^{(i)} \tag{A.1}$$

where $\tilde{\underline{\zeta}}^{(i)}$ extends from the origin in body i to a surface point specified by the unit normal $\hat{k}^{(i)}$. In order to obtain an expression for $\tilde{\underline{\zeta}}^{(i)}$ in terms of $h^{(i)}$ we define the operator $\frac{\partial}{\partial \hat{k}^{(i)}}$ by

$$\frac{\partial}{\partial \hat{k}^{(i)}} \equiv \hat{\theta}^{(i)} \frac{\partial}{\partial \theta^{(i)}} + \frac{\hat{\phi}^{(i)}}{\sin \theta^{(i)}} \frac{\partial}{\partial \phi^{(i)}} \tag{A.2}$$

where $\theta^{(i)}$ and $\phi^{(i)}$ are the spherical polar angles of $\hat{k}^{(i)}$ and $\hat{\theta}^{(i)}$ and $\hat{\phi}^{(i)}$ are the corresponding unit vectors. Then

$$\frac{\partial h^{(i)}}{\partial \hat{k}^{(i)}} = \left(\frac{\partial \tilde{\underline{\zeta}}^{(i)}}{\partial \hat{k}^{(i)}} \right) \cdot \hat{k}^{(i)} + \frac{\partial \hat{k}^{(i)}}{\partial \hat{k}^{(i)}} \cdot \tilde{\underline{\zeta}}^{(i)} \quad . \tag{A.3}$$

The term $\frac{\partial \tilde{\underline{\zeta}}^{(i)}}{\partial \hat{k}^{(i)}}$ is zero because the differential change of $\tilde{\underline{\zeta}}^{(i)}$ is in the tangent plane. It can easily be shown that

$$\frac{\partial \hat{k}^{(i)}}{\partial \hat{k}^{(i)}} = \underline{\underline{\delta}}^{(3)} - \hat{k}^{(i)} \hat{k}^{(i)} \tag{A.4}$$

and therefore we can write Equation A.1 as

$$\hat{\underline{\zeta}}^{(i)} = h^{(i)} \hat{k}^{(i)} + \frac{\partial h^{(i)}}{\partial \hat{k}^{(i)}} \tag{A.5}$$

Hence $h^{(i)}$ specifies the geometry of the body.

We now construct a set of $\bar{q}$ unit vectors $(\hat{e}_1^{(i)}, \hat{e}_2^{(i)} \cdots \hat{e}_{\bar{q}}^{(i)})$ so that they form a basis for a representation of the symmetry group to which the molecule under consideration belongs. A supporting function of the form

$$h^{(i)} = h^{(i)} (\hat{k}^{(i)} \cdot \hat{e}_1^{(i)}, \cdots, \hat{k}^{(i)} \cdot \hat{e}_{\bar{q}}^{(i)}) \tag{A.6}$$

is a basis for the totally symmetric representation of this group. By Equation A.5 the body generated by a supporting function of the form of Equation A.6 will possess the same symmetry as the molecule.

In terms of the supporting function we derive an expression for the average cross sectional area, $\langle \sigma^{(i)} \rangle$, which is the average over all orientations of the projected area of body i onto a plane perpendicular to the projection whose operation we signify by $\hat{P}_r$. The unit vector in the direction of the projection is defined as $\hat{a}^{(i)}$ and the plane perpendicular to $\hat{a}^{(i)}$ is defined as $A_\perp^{(i)}$. The normal of the body i surface points whose projections form a perimeter for the whole body's projection satisfies the condition that $\hat{k}^{(i)} \cdot \hat{a}^{(i)} = 0$. For a body whose supporting function is of the same form as Equation A.6, the supporting function of its projection's perimeter is of the same functional form except $\hat{k}^{(i)} \cdot (\hat{P}_r(\hat{e}_\gamma^{(i)}))$ replaces $\hat{k}^{(i)} \cdot \hat{e}_\gamma^{(i)}$ for all γ. We can thus show that

$$<\sigma^{(i)}> = \left(\frac{1}{8\pi}\right) \int d\hat{k}^{(i)} \int d\hat{a}^{(i)} \ \delta(\hat{k}^{(i)} \cdot \hat{a}^{(i)})$$

$$h^{(i)}(\hat{k} \cdot (\hat{P}_r(\hat{e}_\gamma^{(i)}))) \ S_p^{(i)} \qquad \text{(A.7)}$$

where $S_p^{(i)}$ is the arc length per unit angle of the perimeter of the two dimensional projection of body i. The quantity $S_p^{(i)}$ is given by

$$S_p^{(i)} = \left| \frac{\partial \tilde{\underline{\xi}}^{(i)}}{\partial \hat{k}^{(i)}} \right| \quad . \qquad \text{(A.8)}$$

When the expression for $S_p^{(i)}$ of Equation A.8 is substituted into Equation A.7, we find that

$$<\sigma^{(i)}> = \frac{1}{4} \int d\hat{k}^{(i)} \ h^{(i)} \Big\{ h^{(i)} - \sum_{\gamma=1}^{\bar{q}} (\hat{k}^{(i)} \cdot \hat{e}_\gamma^{(i)}) \ h_\gamma^{(i)}$$

$$+ \frac{1}{2} \sum_{\gamma=1}^{\bar{q}} \sum_{\ell=1}^{\bar{q}} h_{\gamma\ell}^{(i)} \left[\hat{e}_\gamma^{(i)} \hat{e}_\ell^{(i)} - (\hat{k}^{(i)} \cdot \hat{e}_\gamma^{(i)})(\hat{k}^{(i)} \cdot \hat{e}_\ell^{(i)}) \right] \Big\} \qquad \text{(A.9)}$$

where $h_\gamma^{(i)} = \partial h^{(i)} / \partial(\hat{k}^{(i)} \cdot \hat{e}_\gamma^{(i)})$ and $h_{\gamma\ell}^{(i)} = \partial h^{(i)} / \partial(\hat{k}^{(i)} \cdot \hat{e}_\gamma^{(i)}) \, \partial(\hat{k}^{(i)} \cdot e_\ell^{(i)})$. The integral of Equation A.9 can be numerically integrated.

Another expression which must be derived in terms of supporting functions is S, the ratio of the surface area on an excluded volume for two colliding rigid ovaloids to a unit solid angle of the normal to the surface of the volume. To that end we first examine the quantity $S^{(i)}$ which is the equivalent of S for body i. By taking ratios in the limit of the arc lengths which are the sides of differential parallelograms on the body i surface and on a unit sphere surface, we can write that

$$S^{(i)} = \left| \frac{1}{\sin\theta^{(i)}} \frac{\partial \tilde{\underline{\zeta}}^{(i)}}{\partial \phi^{(i)}} \times \frac{\partial \tilde{\underline{\zeta}}^{(i)}}{\partial \theta^{(i)}} \right| \qquad \text{(A.10)}$$

or, equivalently, that

$$S^{(i)} = \left\| \frac{\partial \tilde{\underline{\zeta}}^{(i)}}{\partial \hat{k}^{(i)}} \right\|^{\det}_{\perp \hat{k}^{(i)}} \qquad \text{(A.11)}$$

where $\| \underline{\underline{A}} \|_{\perp \hat{k}^{(i)}}$ is the determinant of the second rank tensor $\underline{\underline{A}}$ in the subspace perpendicular to $\hat{k}^{(i)}$. Inserting the expression for $\tilde{\underline{\zeta}}^{(i)}$ of Equation A.5 into Equation A.11, we have that

$$S^{(i)} = -\frac{1}{2} \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} \qquad \text{(A.12)}$$

where

$$G^{(i)} = h^{(i)} \underline{\underline{V}}^{(i)} + \frac{\partial^2 h^{(i)}}{\partial \hat{k}^{(i)2}} \qquad \text{(A.13)}$$

and $\underline{\underline{V}}^{(i)} = -k^{(i)} \times \underline{\underline{\delta}}^{(3)}$. In the case in which the body i is described by a supporting function of the form of Equation A.6, we find that

$$S^{(i)} = \Big[h^{(i)} - \sum_{j=1}^{\bar{q}} (\hat{k}^{(i)} \cdot \hat{e}_j^{(i)}) h_j^{(i)} \Big]^2 + \sum_{j=1}^{\bar{q}} \sum_{l=1}^{\bar{q}} h_{jl}^{(i)} (\tilde{e}_j^{(i)} \cdot \tilde{e}_l^{(i)})$$

$$\Big[h^{(i)} - \sum_{m=1}^{\bar{q}} (\hat{k}^{(i)} \cdot \hat{e}_m^{(i)}) h_m^{(i)} \Big] - \frac{1}{2} \sum_j \sum_l \sum_m \sum_n (\tilde{e}_{j\perp}^{(i)} \cdot \tilde{e}_n^{(i)})$$

$$(\tilde{e}_{l\perp}^{(i)} \cdot \tilde{e}_m^{(i)}) \; h_{jk}^{(i)} \; h_{mn}^{(i)} \qquad \text{(A.14)}$$

where $\tilde{e}_j^{(i)} = \hat{e}_j^{(i)} - (\hat{k}^{(i)} \cdot \hat{e}_j^{(i)}) \hat{k}^{(i)}$ and $\tilde{e}_{j\perp}^{(i)} = \tilde{e}_j^{(i)} \cdot V^{(i)}$. It can easily be shown that a body i is convex if and only if $S^{(i)}$ is positive everywhere.

The supporting function, h , for the excluded volume of the two colliding bodies i and j is given by

$$h = h^{(i)} + h^{(j)} . \qquad \text{(A.15)}$$

At the point of contact $\hat{k}^{(i)}$ and $\hat{k}^{(j)}$ are antiparallel and the normal to the excluded volume at the center of mass of body j , $\hat{k}$, is parallel to $\hat{k}^{(i)}$. Then we obtain from Equations A.12, A.13 and A.15 that

$$S = \frac{1}{2} (\underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(i)} + \underline{\underline{G}}^{(j)} : \underline{\underline{G}}^{(j)} - 2 \underline{\underline{G}}^{(i)} : \underline{\underline{G}}^{(j)}). \qquad \text{(A.16)}$$

An advantage of the supporting function is that it leads to an immediate expression for S of Equation A.16.

APPENDIX B. PROOF OF BILATERAL NORMALIZATION

One proof of bilateral normalization begins with the expression of Equation 2.27 for the specific transition rate for collisions which is

$$W_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\,\underline{2}'\,R) = \int d^2\underline{b}\;|\underline{p}_{21}|\;\delta(\underline{1}'-\underline{1}^*)\;\delta(\underline{2}'-\underline{2}^*) \tag{B.1}$$

where again the starred state is that unique precollision state from which the unmarked state evolves by the two particle Liouville theorem and where $|\underline{p}_{21}| = |(\underline{p}_2/m_2) - (\underline{p}_1/m_1)|$. Action by the time reversal operator on both sides of Equation B.1 yields

$$W_F(\underline{1}'\,\underline{2}'\,R \mid \underline{1}\,\underline{2}\,R) = \int d^2\underline{b}\;|\underline{p}_{2'1'}|\;\delta(\underline{1}'-\underline{1}^*_{\hat{T}F})\;\delta(\underline{2}'-\underline{2}^*_{\hat{T}F}) \tag{B.2}$$

where the subscript on the starred state means that the process which connects it to the unmarked state takes place in the presence of a time reversed field and where we have used the property of W_F of Equation 2.25. The primed and the unprimed states can be switched in Equation B.2 to give

$$W_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\,\underline{2}'\,R) = \int d^2\underline{b}'\;|\underline{p}_{21}|\;\delta(\underline{1}-\underline{1}^*_{\hat{T}F})$$

$$\delta(\underline{2}-\underline{2}^*_{\hat{T}F}) \tag{B.3}$$

where the asterisks refer to the unique postcollision state to which the primed state evolves in the presence of a time reversed field. From Equation B.1 we have that

$$W_F(\underline{1}'\,\underline{2}'\,R \mid \underline{1}\,\underline{2}\,R) = \int d^2\underline{b}' \, |g_{2'1'}| \, \delta(1-1'^{*})$$

$$\delta(\underline{2}-\underline{2}'^{*}) \qquad \text{(B.4)}$$

where the primed, starred state on the precollision hemisphere is the unique state from which the primed state evolves. Integration of Equations B.3 and B.4 over the unmarked state variables gives respectively

$$\int d\underline{1} \int d\underline{2} \; W_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\,\underline{2}'\,R) = \int d^2\underline{b}' \, |g_{2^*1^*}| \qquad \text{(B.5)}$$

and

$$\int d\underline{1} \int d\underline{2} \; W_F(\underline{1}'\,\underline{2}'\,R \mid \underline{1}\,\underline{2}\,R) = \int d^2\underline{b}' \, |g_{2'1'}| \quad . \qquad \text{(B.6)}$$

These integrals are finite because the integration over $\underline{b}$ is limited to a disc of radius R. The reason for this limitation is that the collision sphere limits the area over which a collision can be said to occur. Therefore we can write that

$$\int d\underline{1} \int d\underline{2} \; W_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\,\underline{2}'\,R) = \int d\underline{1} \int d\underline{2} \; W_F(\underline{1}'\,\underline{2}'\,R \mid \underline{1}\,\underline{2}\,R) \qquad \text{(B.7)}$$

which is the expression of bilateral normalization.

A second proof can be derived from the equation for the time rate of change of f_1 along a phase trajectory which is

$$\frac{Df_1(\underline{1})}{Dt} = \int d\underline{1}' \int d\underline{2}' \int d\underline{2} \; [W_F(\underline{1}\,\underline{2}\,R\,|\,\underline{1}'\underline{2}'R)\; f_2(\underline{1}',\underline{2}')$$

$$- W_F(\underline{1}'\underline{2}'R\,|\,\underline{1}\,\underline{2}\,R)\; f_2(\underline{1}.\underline{2})] \quad . \qquad \text{(B.8)}$$

At equilibrium the two particle distribution function can be written as a product of the single particle distribution functions of the local properties. From conservation of energy we have that

$$f_1^{[0]}(\underline{1})\; f_1^{[0]}(\underline{2}) = f_1^{[0]}(\underline{1}')\; f_1^{[0]}(\underline{2}')$$

Therefore at equilibrium we can write Equation B.8 as

$$0 = f_1^{[0]}(\underline{1}) \int d\underline{2}\; f_1^{[0]}(\underline{2}) \int d\underline{1}' \int d\underline{2}' \; [W_F(\underline{1}\,\underline{2}\,R\,|\,\underline{1}'\underline{2}'R)$$

$$- W_F(\underline{1}'\underline{2}'R\,|\,\underline{1}\,\underline{2}\,R)] \qquad \text{(B.9)}$$

where we have used the fact that $f_1^{[0]}$ does not change along its phase trajectory. There are two ways for Equation B.9 to be zero: the integral over $\underline{1}'$ and $\underline{2}'$ could be orthogonal to $f_1^{[0]}(\underline{2})$ or that same integral could itself be zero. The former case might be true at one temperature but at a different temperature $f_1^{[0]}(\underline{2})$ would change while the integral over $\underline{1}'$ and $\underline{2}'$ would not.

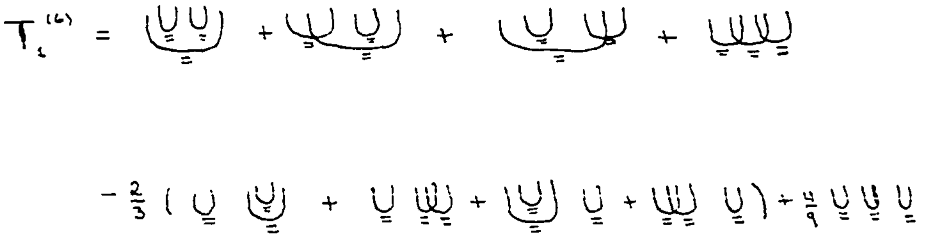
Hence orthogonality can not be the case and the integral over $\underline{1}'$ and $\underline{2}'$ must be zero i.e.

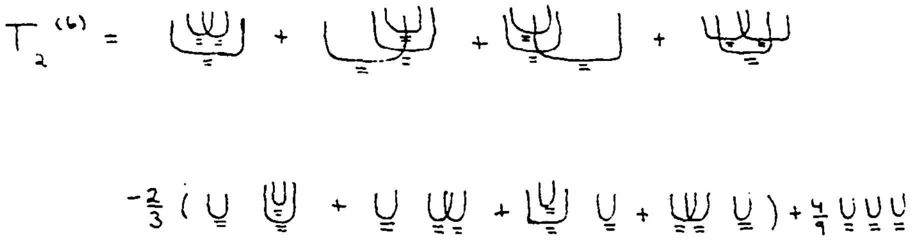
$$0 = \int d\underline{1}' \int d\underline{2}' \left[W_F(\underline{1}\,\underline{2}\,R \mid \underline{1}'\underline{2}'R) - W_F(\underline{1}'\underline{2}'R \mid \underline{1}\,\underline{2}\,R) \right] \tag{B.10}$$

which is again the statement of bilateral normalization.

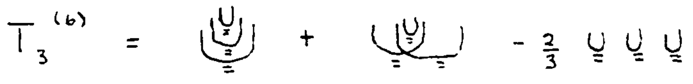
APPENDIX C. ISOTROPIC SIXTH RANK TENSORS

The isotropic sixth rank tensors which are traceless and symmetric on their first two and last two indices are





and



where $\underset{=}{U} = \underset{=}{\delta}^{(3)}$.

APPDNEIX D. CONTRACTION AND PROJECTION SCHEME FOR $(\underline{u},\underline{v})$ TENSORS

As a result of the operations of Chapter 4, a typical collision integral can be written as

$$\underline{\underline{\delta}}\odot^{u+v}\left[\underline{\underline{\Phi}}_i,\underline{\underline{\Psi}}\right]^{1,k}_{i,j}=\frac{\pi^{-1}}{\Delta_1\Delta_2}\left(\frac{2kT}{m}\right)^{1/2}\int d\hat{k}\;\underline{\underline{\delta}}\odot_3^{u+v}\underset{\approx}{\wp}_{\phi_i\psi_\ell}$$

$$\odot_{12}^{u+v}(\underline{u},\underline{v}) \qquad \text{(D.1)}$$

where we bring the projection operators and the isotropic tensor $\underline{\underline{\delta}}$ through the integral over $\hat{k}$ so that the integrand becomes a scalar by means of the operations $\odot_{12}^{u+v}$, which we call projection, and $\odot_3^{u+v}$, which we call contraction. For general potentials in the Kihara approximation, the quantity $(\underline{u},\underline{v})$ can be evaluated in terms of tensors composed of $\underline{\underline{\delta}}^{(n_1)}$, $\underline{\underline{U}}^{(2)}$ and $\hat{k}$. The integrand of Equation D.1 can then be reduced to a scalar by taking projections and contractions on $(\underline{u},\underline{v})$ in that order. This is tedious for tensors of high rank because of the large number of permutations in $(\underline{u},\underline{v})$.

For even rank tensors, considerable simplification is achieved by reversing the order of projection and contraction. The process of contracting first can be shown on two projection operators $(P_{m_\ell})_{\beta k,\alpha l}$ and $(P_{m_0})_{\alpha' i',\beta' k'}$

as follows:

$$\underset{=}{\delta}^{(3)} \odot_3^2 \underset{\approx}{P}_{m_\ell} \underset{\approx}{P}_{m_o} = \sum_{\alpha\alpha'} \sum_{ii'} \delta_{ii'} (P_{m_\ell})_{\beta k, \alpha i} (P_{m_o})_{\alpha' i', \beta' k'}$$

$$\equiv (\bar{P}_{m_\ell} | \bar{P}_{m_o})_{\beta k, \beta' k'} = (\underset{\approx}{\bar{P}}_{m_\ell} | \underset{\approx}{\bar{P}}_{m_o}) \qquad \text{(D.2)}$$

where as in Chapter 4 Greek indices extend from one to four and Latin indices extend from one to three. We call the new notation of Equation D.2 a contraction product which is a second rank tensor in the 12-D space. There are only 16 possible contraction products between the projection operators $\underset{\approx}{P}_{\Omega_1}$, $\underset{\approx}{P}_{\Omega_2}$, $\underset{\approx}{P}_{W_1}$ and $\underset{\approx}{P}_{W_2}$. The key to what we will do is that the projections can act on these contraction products in only a limited of unique ways. A method is desired to find this limited number of resulting unique forms and their frequencies of appearance.

By examining the $(\underset{\sim}{u}, \underset{\sim}{v})$ tensors of Chapter 4, we see that the result of the operation of $\odot_{12}^{u+v}$ upon a tensor composed of $\underset{=}{\delta}^{(n_o)}$, $\underset{\approx}{U}^{(2)}$ and $\hat{K}$ can be expressed as a product of two types of projection linkages of contraction products: one, which we call a chain, is of the form

$$\hat{K} \odot_{12} (\underset{\approx}{\bar{P}}_{m_{\ell,1}} | \underset{\approx}{\bar{P}}_{m_{\ell,2}}) \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \cdots \odot_{12} (\underset{\approx}{\bar{P}}_{m_{\ell,n-1}} | \underset{\approx}{\bar{P}}_{m_{\ell,n}}) \odot_{12} \hat{K}$$

and the other, which we call a loop, is of the form

$$\underset{\approx}{\underbrace{\Big|\ \odot_{12}\ (\underset{\approx}{\bar{P}}_{m_{\ell,1}} \mid \underset{\approx}{\bar{P}}_{m_{\ell,2}})\ \odot_{12}\ \underset{\approx}{\sqcup}^{[i]}\ \odot_{12} \cdots \odot_{12}\ (\underset{\approx}{\bar{P}}_{m_{\ell,n-1}} \mid \bar{P}_{m_{\ell,n}})\ \odot_{12}\ \Big|}}^{[j]}$$

where $\underset{\approx}{\sqcup}^{[i]}$ signifies either $\underset{\approx}{\sqcup}^{(2)}$ or $\underset{\approx}{\delta}^{(n_\lambda)}$. In this appendix we refer to a product of loops and chains as a combination. It can be shown that all permutations of the superscript indices of a $\underset{\approx}{J}_{\zeta}^{(a,b\ldots)}$ in all $(\hat{K})^c\ \underset{\approx}{J}_{\zeta}^{(ab\ldots)}\ (\hat{K})^d$ appear in a given $(\underset{\sim}{u},\underset{\sim}{v})$ with the same coefficient. Hence we need not distinguish the superscripts of the $\underset{\approx}{J}_{\zeta}^{(ab\ldots)}$ if we sum over all permutations of them when evaluating a combination. Explicitly the $\underset{\approx}{\delta}^{(n_\lambda)}$ and $\underset{\approx}{\sqcup}^{(2)}$ must be permuted throughout every position in every chain and loop in a combination.

In order to limit the number combinations which we must consider at one time, we concentrate on the projections upon a $(\underset{\sim}{u},\underset{\sim}{v})$ one class at a time. In this regard a class is taken to include all tensors, regardless of their $\underset{\approx}{J}_{\zeta}^{(a,b\ldots)}$ superscripts, which have the same number of $\hat{K}$'s in their first u and last v indices.

The next steps are to produce a complete set of nonduplicate chains and loops, to investigate their symmetry properties for counting purposes and to form unique combinations of chains and loops so that exactly all the contraction products in the integral appear and so that there are (for the class under consideration) the correct number of first u and last v projection operators projected onto $\hat{k}$'s. Lastly we compute the appearance number of each of these combinations. We perform these steps first for the integrals of the kind in Equation D.1 for which the index k is two (called "1-2" integrals) and then for those for which k is one (called "1-1" integrals).

For the "1-2" integrals, unique chains may be produced by first considering all the different available contraction products which cannot be written as transposes of each other. We then can immediately project these contraction products onto two $\hat{k}$'s and obtain the chains containing one contraction product. Two identical lists of these single contraction products can be projected upon the same $\underset{\approx}{U}^{(i)}$ according to Table D.1. In this table we list in the fourth column the unique projections to be formed from $\underset{\approx}{A}$ of one list and $\underset{\approx}{B}$ of the other list and in the fifth column the symmetry of each projection. To avoid duplication we project together the n'th member of the $\underset{\approx}{A}$ list with the same member and all higher numbered members of the $\underset{\approx}{B}$ list. One can see that the resulting tensors given in column four can be projected onto two $\hat{k}$'s to form a unique list of chains of two contraction products long. Whenever we form a tensor of more than one contraction product, we test to see whether the integral has the contraction products contained therein and if not we discard it. The chains containing three contraction products can be formed by breaking apart each of the tensors containing two contraction products (labeled $\underset{\approx}{C}$) and inserting one at a time the whole list of single contraction products (labeled $\underset{\approx}{D}$) according to the formula

$$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B} \equiv \underset{\approx}{F}$$

The unique $\underset{\approx}{F}$ can be formed by the procedure outlined in Table D.2. The $\underset{\approx}{F}$ tensors can be projected onto two $\hat{k}$'s to form the chains of contraction product length three. The above processes can be carried out iteratively to build up the chains to any length required. The symmetry description, that is whether the chain has a different transpose or not, is given automatically.

The loops can be generated from the list of chains by replacing the $\hat{k}$'s with another $\underset{\approx}{U}^{[\ell]}$. The only problem with this list is that the members are not unique. The procedure we use to remedy this situation begins with the determination of the symmetry of the loop. This symmetry is characterized by the group order of the C_{nv} symmetry type to which the loop written on a circle with equal spacing between its contraction products belongs. It is convenient to assign numbers one to 16 to the possible contraction products. The numerical codes of the contraction products in a loop derived from a chain are designated f_k where the subscript denotes the left to right order of the contraction product in the loop written from a chain. The f_k are expanded in a Fourier series

$$f_k = \left(\frac{1}{\sqrt{m}}\right) \sum_{j=1}^{m} a_j \, e^{(\hat{i}\, 2\pi j k)/m} \tag{D.3}$$

where m is the number of contraction products in the loop and $\hat{i} = \sqrt{-1}$. This expansion is suggested by the fact that rotational symmetry means a periodic relationship between the f_k. To find the a_j , we merely take the Fourier transform

$$a_j = \left(\frac{1}{\sqrt{m}}\right) \sum_{k=1}^{m} f_k \, e^{-(\hat{i}\, 2\pi j k)/m} \quad . \tag{D.4}$$

When there is an m/p -fold axis of rotation, it is the case that

$$\begin{aligned} f_{p+1} &= f_1 \\ f_{p+2} &= f_2 \\ &\;\;\cdots \\ f_{2p} &= f_{m/p} \\ f_{2p+1} &= f_1 \\ &\;\;\cdots \\ f_m &= f_{m/p} \end{aligned} \tag{D.5}$$

and we can write Equation D.5 as

$$a_j = \left(\frac{1}{\sqrt{m}}\right) \sum_{k=1}^{m/p} \sum_{\ell=1}^{p} f_\ell \, e^{-\hat{i}\left(\frac{2\pi \ell j}{m} + \frac{2\pi p(k-1)j}{m}\right)} \quad . \tag{D.6}$$

The summation over k in Equation D.6 can be performed first and it is equal to zero unless j is some multiple of m/p . To find the rotational symmetry, the subscript of the first nonzero a_i is found and that is the fold of the proper axis of rotation. When there is a σ_v plane of reflection, then the transpose of the chain equivalent to the loop generates another loop (transposed loop) which is only different from the first loop by a rotation. If one denotes the transposed loop by primes and by $\frac{2\pi r}{m}$ the angle of rotation by which a loop may be brought into coincidence with the transposed loop (in the case that a σ_v exists), then

$$f_1 = f'_{1+r}$$

$$f_2 = f'_{2+r}$$

$$\cdots$$

$$f_{m-r} = f'_m$$

$$f_{m-r+1} = f'_1$$

. . .

$$f_m = f'_r \tag{D.7}$$

By Equation D.5 we can write that

$$a_\gamma = \left(\frac{1}{\sqrt{m}}\right) \sum_{k=1}^{m} f'_{k+r-\hat{\eta}(k+r-m)m} \, e^{-(\hat{i}\, 2\pi \gamma k)/m} \tag{D.8}$$

where is the unit step function with discontinuity at zero. The variable of summation in Equation D.8 can be changed from k to $k' = k+r$ with the result that

$$a_\gamma = \left(\frac{1}{\sqrt{m}}\right) \sum_{k'=1}^{m} f'_{k'} \, e^{-(\hat{i}\, 2\pi \gamma (k'-r))/m}$$

$$= a'_\gamma \, e^{\hat{i}\, 2\pi \gamma r/m} \tag{D.9}$$

The significance of Equation D.9 is that if a σ_v plane exists then every nonzero a_γ is related to a'_γ by a phase angle which is the same multiple of γ . This condition is therefore a test. If there is reflectional symmetry and rotational symmetry, the group is C_{nv} with order 2n. If there is no reflectional symmetry, the group is C_n with order n.

The list of nonunique loops may now be culled using a procedure similar to the testing for reflectional and rotational symmetry. If two loops are the same they can only be out of coincidence by a rotation, by a reflection or by both. If they are off by a rotation then their a_j's only differ by a phase factor multiplied by i. If they are off by a reflection or both a rotation and a reflection then the transposed loop of one has a_j''s which differ by a phase factor multiplied by i from the a_j's of the original loop of the other. By comparison of the a_j's of one loop with the a_j's and a_j''s of the others duplicates may be eliminated and a list of unique loops found.

The process of combining lists of loops and chains in unique ways is straightforward because order is unimportant. Those combinations which do not have the proper number of the first u or the last v projection operators projected onto $\hat{k}$'s for the class under consideration or do not have exactly the contraction products appearing in the integral are merely discarded.

The appearance number of a combination is just the number of different ways this combination can be produced arising from the different permutations of indices of the tensor class upon which we are projecting. For "1-2" integrals the process of randomly placing the available contraction products in their proper positions in the combination of loops and chains can be carried out in

$$\prod_{i=1}^{\kappa} b_i! \; 2^{\frac{1}{2}b}$$

ways where b_i is the number of available contraction products of the ith kind and $\sum_{sym}$ symbolizes the summation over all b_i which refer to contraction products which are equal to their transpose. This number represents overcounting whenever there is symmetry in the combination. Combinations formed by random placement but connected by this symmetry are not the result of projections on different permutations of a tensor class. When we divide out the factors which correct for overcounting from symmetry, the appearance number of a combination for "1-2" integrals becomes

$$\left(\prod_{i=1}^{10} b_i! \quad 2^{\sum_{sym} b}\right) \Big/ \left(2^{\tilde{q}} \prod_{r} (s_r)! \prod_{t} u_t \prod_{\tilde{v}} (w_{\tilde{v}})!\right.$$

where $\tilde{q}$ is the number of chains which are equal to their transpose, s_r is the number of like chains of the rth type, u_t is the order of the group to which the tth loop belongs and $w_{\tilde{v}}$ is the number of like loops of the $\tilde{v}$th type.

There are many similarities in the formulation of the appearance numbers for a combination in the case of a "1-1" integral. However this must be treated as a special case because we no longer have projection operators which are naturally marked as to whether they are one of the first u or of the last v. Therefore we will artificially mark these projection operators at appropriate instances with an ℓ if they are one of the first u and r if they are one of the last v. Temporarily disregarding this artifice, we produce the chains and the loops in the same way as before. Then we give only those contraction products which are on the ends of chains all possible ℓ, r character noting that this might change the symmetry of a chain. The combinations are then done in the same way using this expanded list of chains.

The counting number of the way the projection operators can be randomly placed in a combination is now more complicated. The random placement now must first fill the spaces of the marked ends of the chains from the pool of available contraction products which are considered as marked and then fill the unmarked remaining spaces from the pool of all remaining contraction products considered as unmarked. We derive that the random placement can be done in

$$\frac{\prod_{i=1}^{10} (\hat{c}'_i)!}{\prod_{i=1}^{10} (\hat{c}'_i - g_i)!} \quad \prod_{j=1}^{5} (d_j - e_j)! \quad 2^{\sum_{\text{sym}}^{\text{marked}} \hat{c}'} \quad 2^{\sum_{\text{sym}}^{\text{unmarked}} (d - e)}$$

ways where $\hat{c}'_i$ is the total number of i type available contraction products considered as marked, g_i is the number of i type available marked contraction products used to full up the ends of chains, d_j is the total number of j type unmarked contraction products available and e_1 is the number of j type unmarked contraction products used to fill up the ends of the chains. The factors which adjust for overcounting from symmetry are the same as in the "1-2" integrals.

Table D.1. The unique projections $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B} = \underset{\approx}{C}$ which can be formed from two contraction products $\underset{\approx}{A}$, $\underset{\approx}{B}$ and the symmetry of these projections

Does $\underset{\approx}{A} = \underset{\approx}{B}$?	$\underset{\approx}{A} \neq \underset{\approx}{A}^T$?	$\underset{\approx}{B} \neq \underset{\approx}{B}^T$?	Unique Projections	Symmetry
Yes	Yes	Yes	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{C} \neq \underset{\approx}{C}^T$
			$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B}^T$	$\underset{\approx}{C} = \underset{\approx}{C}^T$
			$\underset{\approx}{A}^T \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B}^T$	$\underset{\approx}{C} = \underset{\approx}{C}^T$
	No	No	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{C} = \underset{\approx}{C}^T$

Table D.1 (Continued)

Does $\underset{\approx}{A} = \underset{\approx}{B}$?	$\underset{\approx}{A} \neq \underset{\approx}{A}^{T}$?	$\underset{\approx}{B} \neq \underset{\approx}{B}^{T}$?	Unique Projections	Symmetry
No	Yes	Yes	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$ $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}^{T}$ $\underset{\approx}{A}^{T} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$ $\underset{\approx}{A}^{T} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}^{T}$	$\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$ $\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$ $\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$ $\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$
		No	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$ $\underset{\approx}{A}^{T} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$ $\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$
	No	Yes	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$ $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}^{T}$	$\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$ $\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$
		No	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{C} \neq \underset{\approx}{C}^{T}$

Table D.2. The unique projections $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B} \equiv \underset{\approx}{F}$ formed from $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{B} = \underset{\approx}{C}$ for any three contraction products $\underset{\approx}{A}$, $\underset{\approx}{B}$, $\underset{\approx}{D}$ and the symmetry of these projections

Does $C = C^T$?	$D = D^T$?	Unique Projections	Symmetry
Yes	Yes	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{F} = \underset{\approx}{F}^T$
	No	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{F} \neq \underset{\approx}{F}^T$
No	Yes	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{F} \neq \underset{\approx}{F}^T$
	No	$\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{[i]} \odot_{12} \underset{\approx}{D} \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B}$ $\underset{\approx}{A} \odot_{12} \underset{\approx}{U}^{(i)} \odot_{12} D^T \odot_{12} \underset{\approx}{U}^{[j]} \odot_{12} \underset{\approx}{B}$	$\underset{\approx}{F} \neq F^T$ $\underset{\approx}{F} \neq \underset{\approx}{F}^T$