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Model calculation studies of the transport properties of a dilute gas of diatomic molecules in a static magnetic field

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TABLE OF CONTENTS

INTRODUCTION

During the past decade there has been a renewed interest in the effects of external fields on the transport properties of polyatomic gases. The revival of interest in this subject resulted from two separate and independent discoveries in the early 1960's. In 1961 Kagan and Maksimov (1) showed that magnetic field effects for paramagnetic gases could be encompassed within the Chapman-Enskog theory. Their starting point was the kinetic theory for polyatomic gases developed by Kagan and Afanas'ev (2), who were the first to consider explicitly the anisotropic dependence of the distribution function on the internal angular momentum. A year later it was shown experimentally by Beenakker et al. (3) that the magnetic field effects were quite general properties of all polyatomic gases instead of just paramagnetic gases, as earlier investigators had thought.

The original investigations of the magnetic field effects by Senftleben in 1930, and those of subsequent early workers, were concerned only with paramagnetic gases. (References for these early papers can be found in a recent review article by Beenakker (4).) Their experiments showed that in the presence of a magnetic field, $\underset{\sim}{H}$, the transport coefficients decrease slightly (0.1% to 1.0%). The effect at constant temperature is a function of H/p, where p is the pressure, and saturates at large H/p values. No effect is observed for monatomic gases.

In 1938 Gorter (5) gave a qualitative interpretation of these results. He based his interpretation on the change of the molecular mean free path by the magnetic field. This idea was elaborated more quantitatively by Zernike and Van Lier (6). Like Gorter, they imagined the rotating diatomic molecule as a disk with a magnetic moment directed along the axis of rotation, i.e., perpendicular to the disk. In the absence of a field the direction of the axis of rotation does not change during the time interval between two collisions. In the presence of a field, however, the magnetic moment, and hence the axis of rotation coupled to it, will precess around the field. This precession causes a periodic change in the collision cross section of the molecule in the time interval between collisions. Thus the preferential alignment (polarization) of the molecular angular momenta, caused by the gradients of temperature or stream velocity in the gas, will be partially destroyed by the field. Since the polarization tends to increase the mean free path, the effect of the field is to decrease the transport coefficients. The destruction is complete when the precessional frequency becomes much larger than the collisional frequency.

With this simple and fairly satisfactory model to explain the observations, there was little incentive to pursue this field of study after the 1930's. No further interest was shown, and this potential source of information about nonspherical molecular interactions was overlooked for twenty years.

The uncovering of this rich source of information in the early 1960's prompted some rather active research, especially by Beenakker and his colleagues at Leiden. In fact the effect of an electric or magnetic field on the transport properties of molecules is commonly known as the Senftleben-Beenakker effect. The Leiden group has conducted rather thorough experiments and theoretical considerations of the external field effects. Their results along with those of Kagan and colleagues are summarized in a review article by Beenakker and McCourt (7).

One of the important results of this renewed interest in the field effects was the realization that the lowering of the spatial symmetry by a magnetic field gives rise to transverse components in the transport properties. For the case of thermal conduction the transverse component corresponds to a heat flux perpendicular to both the external field and temperature gradient. In all there are three thermal conductivity coefficients (one transverse) and five shear viscosity coefficients (two transverse), instead of the single coefficients of the field-free case. Theoretical expressions for these transverse effects were obtained by Kagan and Maksimov (8), Knaap and Beenakker (9), and McCourt and Snider (10,11), and the effects have also been observed experimentally (7).

Kagan and Maksimov (1) also introduced a now widely adopted technique for solving the linearized Boltzmann equation. They expanded the distortion of the local equilibrium distribution function in irreducible Cartesian tensors in the linear and angular momenta. This expansion set was then truncated, and simple, analytical expressions were obtained for the transport coefficients by making certain approximations. The most important of these is the neglect of certain collision integrals, the justification for which is centered around the assumption that the nonsphericity is small, i.e., that the nonsphericity has only a small (but important) effect on the dominant, elastic collision cross sections.

The obvious questions arising from such an analysis are concerned with the number of expansion terms needed and with the validity of the assumption that the nonsphericity is small. Model calculations are of considerable interest in this regard, since they provide quantitative answers to these questions. The first such model calculations were done by Klein, Hoffman, and Dahler (12), on the thermal conductivity of rough spheres. Rough spheres are rigid spheres that reverse relative velocity (both linear and angular) upon impact, i.e., there is no slip upon contact. Using this same model McCourt, Knaap, and Moraal (13,14) examined in detail the effect of various approximations for the thermal conductivity and viscosity.

However, the rough-sphere model is rather unrealistic, especially for linear molecules. A much more realistic model is the spherocylinder, a cylinder with hemispherical caps, or the ellipsoid of revolution. Both of these models will be employed in this thesis to analyze the transport coefficients of linear molecules in external fields. A perturbation scheme similar to that of Kagan and Maksimov (8) will be employed to examine the assumption of small nonsphericity. The collision operator will be divided into a spherical and perturbing nonspherical part by a division which is somewhat different from that of Kagan and Maksimov.

Although the primary objective of this thesis is the study of the magnetic field problem, the electric field case will also be considered for linear $^1\Sigma$ molecules. If these molecules have only a small dipole moment, they will not have a dominant dipole-dipole collision interaction, and hence can be represented by rigid interaction models. Many of the solution techniques employed in the magnetic field case carry over directly to the electric field case, and discussion of the electric field problem fits rather naturally in the context of a treatment of the magnetic field problem.

The electric field transport coefficients for linear $^1\Sigma$ molecules are functions of E^2/p, where E is the electric field. This different field dependence results from a perturbation by the field to produce a component of the dipole along the field-free rotation axis and a component perpendicular to the axis (15,16). The electric field then causes a precession of the axis of rotation in a manner similar to the magnetic field. However, the mechanics are somewhat different in that the axis of rotation precesses rapidly about the field-free axis, which in turn precesses much more slowly about the field.

In an electric field the transverse coefficients are absent for symmetry reasons, but for nonlinear molecules, cross effects between the heat flux and viscous flow can occur. In Appendix B we consider in detail the implications of symmetry on the fluxes for the case of an electric and a magnetic field and thus obtain the Onsager-Casimir relations.

The following model calculation study of the transport properties of dilute gases begins with a discussion of the Boltzmann equation for linear polyatomic molecules. The collision model and solution techniques (both exact and by a perturbation scheme) will be discussed in detail. Finally, calculated results for both the thermal conductivity and viscosity will be presented.

BOLTZMANN'S EQUATION FOR RIGID CONVEX MOLECULES

Derivation of Boltzmann's Equation

In this chapter only rigid-body potentials are considered, and the discussion is limited to a dilute gas of linear molecules. A much more general consideration of the Boltzmann equation for polyatomic gases can be found in a recent paper by Hoffman and Dahler (17). The usual approximations of assuming molecular chaos, ignoring all but binary collisions, and ignoring chattering, will be utilized.

The equation of motion governing the N-particle distribution function, $f^{(N)}$, for a single-component gas is the Liouville equation

$$\frac{\partial f^{(N)}}{\partial t} + \sum_{i=1}^{N}\left\{\frac{\partial}{\partial \underset{\sim}{q}_i}\cdot(\dot{\underset{\sim}{q}}_i f^{(N)}) + \frac{\partial}{\partial \underset{\sim}{p}_i}\cdot(\dot{\underset{\sim}{p}}_i f^{(N)})\right\} = 0. \qquad 1.1$$

The multidimensional vectors $\underset{\sim}{q}_i$ and $\underset{\sim}{p}_i$ are conjugate coordinates and momenta of particle i and have as many components as the molecule has degrees of freedom. The vectors are to be taken as Cartesian components in the N-particle phase space in which $f^{(N)}(\underset{\sim}{q}_1,\underset{\sim}{q}_2,\ldots,\underset{\sim}{q}_N,\underset{\sim}{p}_1,\underset{\sim}{p}_2,\ldots,\underset{\sim}{p}_N,t)$ is defined, although they can be generalized coordinates and momenta of the molecule. The function $f^{(N)}$ is normalized to N!, and $f^{(N)}d\underset{\sim}{q}_1\ldots d\underset{\sim}{q}_N d\underset{\sim}{p}_1\ldots d\underset{\sim}{p}_N$ is the number of N-particle clusters (comprising an initial ensemble of systems) such that there is one particle in the range $d\underset{\sim}{q}_1$ about $\underset{\sim}{q}_1$ and $d\underset{\sim}{p}_1$ about $\underset{\sim}{p}_1$, one in the range $d\underset{\sim}{q}_2$ about $\underset{\sim}{q}_2$ and $d\underset{\sim}{p}_2$ about $\underset{\sim}{p}_2$, and so on for all N particles. The dots above $\underset{\sim}{q}_i$ and $\underset{\sim}{p}_i$ refer to time derivatives.

Integrating the Liouville equation over all the coordinates and momenta of all the particles except particle 1, we obtain

$$\frac{\partial f^{(1)}}{\partial t} + \frac{\partial}{\partial \underset{\sim}{q}_1}\cdot(\dot{\underset{\sim}{q}}_1 f^{(1)}) + \frac{1}{(N-1)!}\frac{\partial}{\partial \underset{\sim}{p}_1}\cdot\int d\tau^{N-1}\dot{\underset{\sim}{p}}_1 f^{(N)} = 0, \qquad 1.2$$

where $(N-h)!f^{(h)} = \int d\tau^{N-h} f^{(N)}$ and $d\tau^{N-h} = d\underset{\sim}{q}_{h+1}\cdots d\underset{\sim}{q}_N d\underset{\sim}{p}_{h+1}\cdots d\underset{\sim}{p}_N$. It is the single-particle distribution function $f^{(1)}$ that appears in the Boltzmann equation and is used to calculate the transport coefficients for a dilute gas.

If we now consider only pair interactions and write $\dot{\underset{\sim}{p}}_1 = \dot{\underset{\sim}{p}}_1^{(1)} + \sum_{i=2}^{N}\dot{\underset{\sim}{p}}_{1i}^{(2)}$, where $\dot{\underset{\sim}{p}}_1^{(1)}$ is the change not due to other molecules, i.e., the change occurring in free-flight motion, we obtain

$$\frac{\partial f^{(1)}}{\partial t} + \frac{\partial}{\partial \underset{\sim}{q}_1}\cdot(\dot{\underset{\sim}{q}}_1 f^{(1)}) + \frac{\partial}{\partial \underset{\sim}{p}_1}\cdot(\dot{\underset{\sim}{p}}_1^{(1)} f^{(1)}) +$$

$$\frac{\partial}{\partial \underset{\sim}{p}_1}\cdot\int d2\,\dot{\underset{\sim}{p}}_{12}^{(2)} f^{(2)} = 0, \qquad 1.3$$

where $di = d\underset{\sim}{q}_i d\underset{\sim}{p}_i$. For rigid bodies the pair interaction potential is zero outside the excluded volume (the volume excluded to the mass center of molecule 2 by molecule 1 when both molecules have a fixed orientation) and infinite within.

Therefore $f^{(2)}$ has a step function discontinuity, which can be written as $\xi f^{(2)}$, where $\xi = 1$ if molecule 2 is outside the excluded volume and $\xi = 0$ if it is inside the excluded volume. That is, for the purpose of taking derivatives, the discontinuity can be taken in ξ and $f^{(2)}$ replaced by a continuous function. We define

$$J^{(2)}(f^{(2)}) = \frac{\partial}{\partial \mathbf{p}_1} \cdot \int d2\, \dot{\mathbf{p}}_{12}^{(2)} f^{(2)} = \frac{\partial}{\partial \mathbf{p}_1} \cdot \int d2 (1-\xi) \dot{\mathbf{p}}_{12}^{(2)} f^{(2)},$$

so that equation 1.3 can be written as

$$\frac{\partial f^{(1)}}{\partial t} + \frac{\partial}{\partial \mathbf{q}_1} \cdot (\dot{\mathbf{q}}_1 f^{(1)}) + \frac{\partial}{\partial \mathbf{p}_1} \cdot (\dot{\mathbf{p}}_1^{(1)} f^{(1)}) = -J^{(2)}(f^{(2)}). \qquad 1.4$$

The quantity $J^{(2)}(f^{(2)})$ can be written as

$$J^{(2)}(f^{(2)}) = \int d2 (1-\xi) \left\{ \frac{\partial}{\partial \mathbf{p}_1} \cdot (\dot{\mathbf{p}}_{12}^{(2)} f^{(2)}) + \frac{\partial}{\partial \mathbf{p}_2} \cdot (\dot{\mathbf{p}}_{21}^{(2)} f^{(2)}) \right\},$$

since the last term integrates to zero. Further evaluation can be made by noting that

$$\frac{\partial f^{(2)}}{\partial t} + \frac{\partial}{\partial \mathbf{q}_1} \cdot (\dot{\mathbf{q}}_1 f^{(2)}) + \frac{\partial}{\partial \mathbf{q}_2} \cdot (\dot{\mathbf{q}}_2 f^{(2)}) + \frac{\partial}{\partial \mathbf{p}_1} \cdot (\dot{\mathbf{p}}_1^{(1)} f^{(2)}) +$$

$$\frac{\partial}{\partial \mathbf{p}_2} \cdot (\dot{\mathbf{p}}_2^{(1)} f^{(2)}) + \frac{\partial}{\partial \mathbf{p}_1} \cdot (\dot{\mathbf{p}}_{12}^{(2)} f^{(2)}) + \frac{\partial}{\partial \mathbf{p}_2} \cdot (\dot{\mathbf{p}}_{21}^{(2)} f^{(2)}) +$$

$$J^{(3)}(f^{(3)}) = 0. \qquad 1.5$$

This equation is obtained from the Liouville equation by integrating over all coordinates and momenta except those of particles 1 and 2. The term

$$J^{(3)}(f^{(3)}) = \frac{\partial}{\partial \underset{\sim}{p}_1}\cdot\int d3\dot{\underset{\sim}{p}}_{13}^{(2)} f^{(3)} + \frac{\partial}{\partial \underset{\sim}{p}_2}\cdot\int d3\dot{\underset{\sim}{p}}_{23}^{(2)} f^{(3)}.$$

We define the derivative, $\frac{Df}{Dt}$, which ignores forces between molecules 1 and 2, by

$$\frac{Df}{Dt} = \frac{\partial f}{\partial t} + \frac{\partial}{\partial \underset{\sim}{q}_1}\cdot(\dot{\underset{\sim}{q}}_1 f) + \frac{\partial}{\partial \underset{\sim}{q}_2}\cdot(\dot{\underset{\sim}{q}}_2 f) + \frac{\partial}{\partial \underset{\sim}{p}_1}\cdot(\dot{\underset{\sim}{p}}_1^{(1)} f) + \frac{\partial}{\partial \underset{\sim}{p}_2}\cdot(\dot{\underset{\sim}{p}}_2^{(1)} f). \tag{1.6}$$

Then we can write $J^{(2)}(f^{(2)})$ as

$$J^{(2)}(f^{(2)}) = -\int d2(1-\xi)\left\{\frac{D}{Dt}(\xi f^{(2)}) + \xi J^{(3)}(f^{(3)})\right\}. \tag{1.7}$$

The last term integrates to zero, since $\xi(1-\xi)J^{(3)}(f^{(3)})$ is zero both inside and outside the excluded volume, and the first term reduces to

$$J^{(2)}(f^{(2)}) = -\int d2(1-\xi) f^{(2)}\frac{D\xi}{Dt}. \tag{1.8}$$

The volume element d2 is now replaced by $d\underset{\sim}{p}_2 d\underset{\sim}{\alpha}_2 d\underset{\sim}{r}_e$, where $\underset{\sim}{r}_e = \underset{\sim}{r}_2 - \underset{\sim}{r}_1$, $\underset{\sim}{r}_i$ locates the mass center of molecule i, and α_2 gives the orientation of molecule 2. We write $d\underset{\sim}{r}_e = d\Sigma d\ell$, where $d\Sigma$ is the surface element on the excluded volume and $\underset{\sim}{\ell} = \ell\hat{k}$ is a vector perpendicular to the surface of the excluded volume. Here $\hat{k}$ is a unit vector. If $\ell > 0$, then $\xi = 1$, and if $\ell < 0$, then $\xi = 0$. We now write $\frac{D\xi}{Dt} = \frac{\partial \xi}{\partial \ell}\frac{D\ell}{Dt} = \delta(\ell)\frac{D\ell}{Dt}$, where $\delta(\ell)$ is the Dirac-delta function. Thus the integration over ℓ is effectively over extremely small values, for which

$\underset{\sim}{r}_e=\rho_1-\rho_2+\underset{\sim}{\ell}$. Here ρ_i is a vector from the mass center of body i to the edge of the body where contact is made. Now

$$\frac{D\ell}{Dt} = \hat{k}\cdot\frac{D\underset{\sim}{\ell}}{Dt} = \hat{k}\cdot(\dot{\underset{\sim}{r}}_e - \frac{D\rho_1}{Dt} + \frac{D\rho_2}{Dt}).$$

Since for a general convex body $\rho_i=\rho_i(\hat{k}\cdot\hat{e}_{ai},\hat{k}\cdot\hat{e}_{bi})$, where $\hat{e}_{ai}$ and $\hat{e}_{bi}$ are two unit vectors in body i, we can write $\frac{D\rho_i}{Dt}$ as

$$\frac{D\rho_i}{Dt} = \underset{\sim}{\omega}_i\times(\hat{e}_{ai}\cdot\frac{\partial\rho_i}{\partial\hat{e}_{ai}} + \hat{e}_{bi}\cdot\frac{\partial\rho_i}{\partial\hat{e}_{bi}}).$$

Using a supporting function (discussed in Appendix A) to define ρ_i, we can show that $\frac{D\ell}{Dt} = \hat{k}\cdot(\dot{\underset{\sim}{r}}_e-\underset{\sim}{\omega}_1\times\rho_1+\underset{\sim}{\omega}_2\times\rho_2)$. After integration over ℓ, equation 1.8 becomes

$$J^{(2)}(f^{(2)}) = -\int d\underset{\sim}{p}_2 d\underset{\sim}{\alpha}_2 \int d\Sigma\,\hat{k}\cdot\underset{\sim}{g}\,f^{(2)}, \qquad 1.9$$

where $\underset{\sim}{g}=\dot{\underset{\sim}{r}}_e-\underset{\sim}{\omega}_1\times\rho_1+\underset{\sim}{\omega}_2\times\rho_2$ and $\underset{\sim}{\omega}_i$ is the angular velocity.

We now divide this integral into two parts, the post-collision for which $\hat{k}\cdot\underset{\sim}{g}>0$ and the precollision for which $\hat{k}\cdot\underset{\sim}{g}<0$. Since the collisions are instantaneous, we have $f^{(2)}_{post}=f'^{(2)}_{pre}$, where the prime denotes a function of pre-collisional variables. If we now invoke molecular chaos, which allows us to factor $f^{(2)}$ into $f_1^{(1)}f_2^{(1)}$ for precollisional states, equation 1.9 becomes

$$J^{(2)}(f^{(2)}) = -\int d\underset{\sim}{V}_2 \int d\hat{k}\,\delta\,\hat{k}\cdot\underset{\sim}{g}\left\{\underset{\hat{k}\cdot\underset{\sim}{g}>0}{f_1'^{(1)}f_2'^{(1)}} + \underset{\hat{k}\cdot\underset{\sim}{g}<0}{f_1^{(1)}f_2^{(1)}}\right\}, \qquad 1.10$$

where $d\underset{\sim}{V}_2=d\underset{\sim}{p}_2 d\underset{\sim}{\alpha}_2$ and $d\Sigma=d\hat{k}\,\delta(\hat{k},\underset{\sim}{\alpha}_1,\underset{\sim}{\alpha}_2)$. The explicit positional dependence of $f^{(2)}$ has not been indicated, since for a dilute gas (but not for a dense gas) we can ignore the difference over distances of the order of a molecular length. Hence $f_1^{(1)}$ and $f_2^{(1)}$ are each evaluated at $\underset{\sim}{r}_1$ but at $\underset{\sim}{p}_1$ and $\underset{\sim}{p}_2$, respectively. (For convenience we henceforth delete the subscript 1 for the first particle and employ the subscript 1 for the second particle.)

Although the Boltzmann equation has been derived for convex bodies, there are no changes for rigid spherocylinders. When the two cylinders are parallel and in contact, there is no unique $\hat{k}$. However, there is little difficulty in evaluating the differential element of excluded-volume surface. This has been done by Klein et al. (18).

If the discussion is now limited to molecules with C_∞ symmetry, we can choose as independent variables $\underset{\sim}{r}$, $\underset{\sim}{v}$ (the velocity of the center of mass), $\hat{e}$ (a unit vector along the symmetry axis), and $\underset{\sim}{\omega}$ (where $\underset{\sim}{\omega}\cdot\hat{e}=0$). The latter are not conjugate variables but can be treated as such. Instead of $\hat{e}$ and $\underset{\sim}{\omega}$, we can select the angular momentum in the space frame, $\underset{\sim}{M}$, and φ, the phase of $\hat{e}$ in the plane perpendicular to $\underset{\sim}{M}$. If we choose the latter, the Boltzmann equation becomes

$$\left(\frac{\partial}{\partial t} + \underset{\sim}{v}\cdot\frac{\partial}{\partial \underset{\sim}{r}} + \dot{\underset{\sim}{M}}\cdot\frac{\partial}{\partial \underset{\sim}{M}} + \dot{\varphi}\frac{\partial}{\partial\varphi}\right)f^{(1)} = J^{(2)}(f^{(2)}), \qquad 1.11$$

where the only external force is from a magnetic field. The time scale of the Boltzmann equation is the time between collisions, so it is inconsistent to retain any dependence on φ in $f^{(1)}$, since φ varies rapidly between collisions. Hence we average over φ to obtain

$$\left(\frac{\partial}{\partial t} + \mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}} + F\right)f^{(1)} = \partial_c(f^{(1)},f_1^{(1)}), \tag{1.12}$$

where $\partial_c(f^{(1)},f_1^{(1)})$ is $J^{(2)}(f^{(2)})$ averaged over φ and $F=\dot{\mathbf{M}}\cdot\frac{\partial}{\partial \mathbf{M}}$. For a magnetic field, $\mathbf{H}$, $\dot{\mathbf{M}}=\gamma\mathbf{M}\times\mathbf{H}$, where γ is the gyromagnetic ratio (8). For an electric field, $\mathbf{E}$, $\dot{\mathbf{M}}=(3/2)d_E^2 I(\mathbf{M}\cdot\mathbf{E})/M^4$, where d_E is the dipole moment lying perpendicular to $\mathbf{M}$ and I is the moment of inertia (15). The electric field equation given here is not applicable to NO, which has a nonvanishing moment along $\mathbf{M}$ due to electronic orbital angular momentum. Formally such molecules can be considered to be symmetrical tops with a fixed, but nonzero component along the symmetry axis.

Linearization of Boltzmann's Equation

To generate a solution of Boltzmann's equation we employ the Chapman-Enskog method. That is, we introduce an ordering parameter ϵ and write $f^{(1)} = f^{(0)} + \epsilon f^{[1]} + \epsilon^2 f^{[2]} + \cdots$. This parameter enters the Boltzmann equation as

$$\epsilon\left[\frac{\partial_0}{\partial t} + \epsilon\frac{\partial_1}{\partial t} + \epsilon^2\frac{\partial_2}{\partial t} + \cdots + \mathbf{v}\cdot\frac{\partial}{\partial \mathbf{r}}\right]f^{(1)} = -F(f^{(1)}) + \partial_c(f^{(1)},f_1^{(1)}). \tag{1.13}$$

The ordering procedure is discussed in detail by Chapman and

Cowling (19) and Hoffman and Dahler (17). The first two equations of this sequence are as follows:

$$0 = -F(f^{(0)}) + \partial_c(f^{(0)},f_1^{(0)}) \qquad 1.14$$

and

$$\left(\frac{\partial_0}{\partial t} + \underset{\sim}{v}\cdot\frac{\partial}{\partial \underset{\sim}{r}}\right)f^{(0)} = -f^{(0)}F(\chi) - J(\chi), \qquad 1.15$$

where $f^{[1]}=\chi f^{(0)}$ and $J(\chi) = -\partial_c(\chi f^{(0)},f_1^{(0)}) -\partial_c(f^{(0)},\chi_1 f_1^{(0)})$. Solution of these equations is sufficient for a linear phenomenological theory.

The solution of equation 1.14 is the local equilibrium distribution function

$$f^{(0)} = n(m/2\pi kT)^{3/2}(4\pi IkT)^{-1}\exp(-W^2-Q^2), \qquad 1.16$$

where $\underset{\sim}{W}=(m/2kT)^{1/2}(\underset{\sim}{v}-\underset{\sim}{u})$, $\underset{\sim}{Q}=(2IkT)^{-1/2}\underset{\sim}{M}$, k is Boltzmann's constant, m is the molecular mass, and n, $\underset{\sim}{u}$, and T are the local density, stream velocity, and temperature, respectively. Since

$$\begin{Bmatrix} n \\ \underset{\sim}{u} \\ (5/2)kT \end{Bmatrix} = \int d\underset{\sim}{c} f^{(0)} \begin{Bmatrix} \psi^1 \\ \underset{\sim}{\psi}^2 \\ \psi^3 \end{Bmatrix} = \int d\underset{\sim}{c} f^{(0)}(1+\chi) \begin{Bmatrix} \psi^1 \\ \underset{\sim}{\psi}^2 \\ \psi^3 \end{Bmatrix}, \qquad 1.17$$

where $d\underset{\sim}{c}=d\underset{\sim}{v}d\underset{\sim}{M}/M$, $\psi^1=1$, $\underset{\sim}{\psi}^2=\underset{\sim}{v}$, and $\psi^3=(m/2)(\underset{\sim}{v}-\underset{\sim}{u})^2 + M^2/2I$, it follows that $\int d\underset{\sim}{c}\psi^i\chi f^{(0)} = 0$. For solutions of equation 1.15 to exist, the inhomogeneous portion (left-hand side) of the equation must be orthogonal to all solutions of the homogeneous adjoint equation $-f^{(0)}F^{\dagger}(\chi) + J^{\dagger}(\chi) = 0$, where $J^{\dagger}$ and $F^{\dagger}$ are defined in Appendix B. These solutions are the summational invariants ψ^{i} (20). The orthogonality conditions

$$\int d\underset{\sim}{c}\,\psi^{i}\left(\frac{\partial}{\partial t} + \underset{\sim}{v}\cdot\frac{\partial}{\partial \underset{\sim}{r}}\right)f^{(0)} = 0$$

give the macroscopic hydrodynamic equations, from which we can obtain the time derivative $(\frac{\partial}{\partial t})$ part of $f^{(0)}$ as space derivatives of $\underset{\sim}{u}$ and T. We can then express the Boltzmann equation as

$$f^{(0)}\Big\{[2\overset{\circ}{\underset{\sim}{W}\underset{\sim}{W}} + (4W^2/15 - 2Q^2/5)\underset{\approx}{\delta}^{(1)}]:\frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{r}} + [(W^2-5/2) + (Q^2-1)](2kT/m)^{1/2}\underset{\sim}{W}\cdot\frac{\partial}{\partial \underset{\sim}{r}}(\ln T)\Big\} = -f^{(0)}F(\chi) + J(\chi), \quad 1.18$$

where $\overset{\circ}{\underset{\sim}{W}\underset{\sim}{W}} = \underset{\sim}{W}\underset{\sim}{W} - W^2/3\,\underset{\approx}{\delta}^{(1)}$ and $(\underset{\approx}{\delta}^{(1)})_{ij} = \delta_{ij}$, the Kronecker delta.

The solution of the linear equation 1.18, which is consistent with the subsidiary conditions, equation 1.17, is of the form

$$\chi = -n^{-1}[(2kT/m)^{1/2}\underset{\sim}{A}\cdot\frac{\partial}{\partial \underset{\sim}{r}}(\ln T) + \underset{\approx}{B} : \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{r}}]. \quad 1.19$$

This allows us to separate the Boltzmann into the two parts

$$f^{(0)}[(W^2-5/2) + (Q^2-1)]\underset{\sim}{W} = n^{-1}f^{(0)}F(\underset{\sim}{A}) + n^{-1}J(\underset{\sim}{A}) \quad 1.20$$

and

$$f^{(0)}[2\overset{\circ}{\underset{\sim}{W}\underset{\sim}{W}} + (4W^2/15 - 2Q^2/5)\underset{\approx}{\delta}^{(1)}] = n^{-1}f^{(0)}F(\underset{\approx}{B}) + n^{-1}J(\underset{\approx}{B}). \quad 1.21$$

To solve for χ, we must find $\underset{\sim}{A}$ and $\underset{\approx}{B}$, from which we obtain the thermal conductivity and viscosity tensors, respectively.

Solution of Boltzmann's Equation

The most widely used method for solving equations 1.20 and 1.21 is that of Kagan and Maksimov (8). These authors expanded the unknown $\underset{\sim}{A}$ or $\underset{\approx}{B}$ in irreducible Cartesian tensors in $\underset{\sim}{W}$ and $\underset{\sim}{Q}$. The tensors anisotropic in $\underset{\sim}{Q}$ are of utmost importance, since they are necessary for a prediction of the field effect. To solve for the tensor expansion coefficients, one employs the usual method of moments, which results in an infinite set of equations for the expansion coefficients.

Even for a small, truncated expansion set, an exact solution of these equations is extremely difficult. Therefore, approximate methods have been used to obtain solutions. The most common method of approximation is to assume that the nonsphericity is small, hence allowing for the neglect of certain terms. Usually the collision operator, J, is divided in some way into a "spherical" and "nonspherical" part. Such a division, especially with regard to model calculations, has recently been given by Cooper and Hoffman (21) and will be outlined below.

We can represent the collision operator in any complete set of functions which depend on the direction of $\underset{\sim}{W}$ and $\underset{\sim}{Q}$. Specifically, we can use the irreducible Cartesian tensors $[\underset{\sim}{W}]^{(p)}$ of rank p and $[\underset{\sim}{Q}]^{(q)}$ of rank q in their natural form multiplied by scalar functions of W^2 and Q^2. An irreducible tensor in natural form is characterized by being totally symmetric and contractionless on all sets of indices (22). The operation of J on such a product function cannot alter its tensor symmetry. Therefore, the matrix elements $\underset{\approx}{J}_{ij}\left({}^{p}_{p'},{}^{q}_{q'}\right)=\langle\underset{\approx}{\Psi}_i(p,q),J(\underset{\approx}{\Psi}_j(p',q'))\rangle$ have the tensor symmetry of the functions $\underset{\approx}{\Psi}^t_i(p,q)\underset{\approx}{\Psi}_j(p',q')$ or of $[\underset{\sim}{Q}]^{(q)}[\underset{\sim}{W}]^{(p)}[\underset{\sim}{W}]^{(p')}[\underset{\sim}{Q}]^{(q')}$, where $\langle\underset{\approx}{x}_1,\underset{\approx}{x}_2\rangle = n^{-1}\int d\underset{\sim}{c}\underset{\approx}{x}^t_1\underset{\approx}{x}_2$. Here i and j are labels for the scalar functions, p and q denote the rank of the irreducible tensors, and the tensor $\underset{\approx}{T}^t_{ijkl}=\underset{\approx}{T}_{lkji}$. Now $\underset{\approx}{J}_{ij}\left({}^{p}_{p'},{}^{q}_{q'}\right)$ is an isotropic tensor, which can be written as a linear combination of a given set of linearly independent isotropic Cartesian tensors (of the appropriate rank), each of which is a basis for the totally symmetric representation of the 3-dimensional rotation group. Thus the direct product $[\underset{\sim}{Q}]^{(q)}[\underset{\sim}{W}]^{(p)}[\underset{\sim}{W}]^{(p')}[\underset{\sim}{Q}]^{(q')}$ in the integrand must be a basis for a representation containing the totally symmetric representation at least once in order that $\underset{\approx}{J}_{ij}\left({}^{p}_{p'},{}^{q}_{q'}\right)$ be nonzero.

If we approximate J by some spherical limiting form, then $\underset{\sim}{Q}$ is collisionally invariant. Therefore $[\underset{\sim}{Q}]^{(q)}[\underset{\sim}{Q}]^{(q')}$ and $[\underset{\sim}{W}]^{(p)}[\underset{\sim}{W}]^{(p')}$ must each be a basis for a representation containing the totally symmetric representation if a nonvanishing matrix element of J_s (J in the spherical limit) is to exist. From group theoretical considerations it can be shown that each of the products will contain a basis once and only once, if and only if, p=p' and q=q'. Each nonzero matrix element of J_s then is the isotropic Cartesian tensor $\underset{\approx}{\delta}^{(p,q)}$ times a scalar, where $\underset{\approx}{\delta}^{(p,q)}$ is of rank 2(p+q) with the middle 2p indices those of $\underset{\approx}{\delta}^{(p)}$ and the outer 2q indices those of $\underset{\approx}{\delta}^{(q)}$. Here $\underset{\approx}{\delta}^{(n)}$ is the isotropic tensor which is the basis for the totally symmetric representation contained in the product representation of $[\underset{\sim}{x}]^{(n)}[\underset{\sim}{x}]^{(n)}$, where $\underset{\sim}{x}$ is $\underset{\sim}{W}$ or $\underset{\sim}{Q}$. The tensor $\underset{\approx}{\delta}^{(n)}$ is identical with $\underset{\approx}{E}^{(n)}$ of Coope and Snider (23) and is normalized so that $[\underset{\sim}{y}]^{(n)} = \underset{\approx}{\delta}^{(n)} \odot^{n} [\underset{\sim}{y}]^{(n)}$, where $\underset{\sim}{y}$ is any 3-dimensional vector and $\odot^{n}$ denotes a contraction of n indices.

We now represent the collision operator as $J = J^{(0)} + \epsilon J^{(1)}$. Since $\underset{\approx}{J}_{ij}\binom{p,q}{p,q}$ can be written as a linear combination of isotropic tensors, one of which is $\underset{\approx}{\delta}^{(p,q)}$, arising from the product of the basis of the totally symmetric representation in $[\underset{\sim}{W}]^{(p)}[\underset{\sim}{W}]^{(p)}$ and $[\underset{\sim}{Q}]^{(q)}[\underset{\sim}{Q}]^{(q)}$, and the others from direct products of other bases in $[\underset{\sim}{W}]^{(p)}[\underset{\sim}{W}]^{(p)}$ and $[\underset{\sim}{Q}]^{(q)}[\underset{\sim}{Q}]^{(q)}$, we define the matrix elements of $J^{(0)}$ as those elements of J which have the tensor character $\underset{\approx}{\delta}^{(p,q)}$. That is, $\underset{\approx}{J}_{ij}^{(0)}\binom{p,q}{p,q}$ is a scalar times $\underset{\approx}{\delta}^{(p,q)}$. The tensor character of $J^{(0)}$ is the same as J_s but the scalar coefficients are in general slightly different. In particular, the matrix elements of J_s between functions, one of which is only a function of $\underset{\sim}{Q}$, are always zero, whereas this is in general not the case for $J^{(0)}$. The operator $J^{(1)}$ contains the other elements of J, which are assumed small compared with those of $J^{(0)}$, since they result from the nonspherical nature of the interaction. The parameter ϵ serves to identify these elements of J.

We can now write the Boltzmann equation in the generic form

$$\underset{\sim}{C} = \mathcal{J}^{(0)}(\underset{\sim}{\xi}) + \epsilon\mathcal{J}^{(1)}(\underset{\sim}{\xi}), \qquad 1.22$$

where $\underset{\sim}{C}$ stands for the left-hand side of equation 1.20 or 1.21 and $\underset{\sim}{\xi}$ for $\underset{\sim}{A}$ or $\underset{\approx}{B}$, $\mathcal{J}^{(0)} = n^{-1}f^{(0)}F - n^{-1}J^{(0)}$, and $\mathcal{J}^{(1)} = -n^{-1}J^{(1)}$. Using the perturbation idea of Kagan and Maksimov (8), we obtain for $\underset{\sim}{\xi}$

$$\underset{\sim}{\xi} = I^{(0)}\underset{\sim}{C} - \epsilon I^{(0)}\mathcal{J}^{(1)}I^{(0)}\underset{\sim}{C} + \epsilon^2 I^{(0)}\mathcal{J}^{(1)}I^{(0)}\mathcal{J}^{(1)}I^{(0)}\underset{\sim}{C} -$$

$$\epsilon^3(I^{(0)}\mathcal{J}^{(1)})^3\underset{\sim}{C} + \ldots, \qquad 1.23$$

where $I^{(0)} = \mathcal{J}^{-1(0)}$. Thus the problem now is to evaluate $I^{(0)}$. For the magnetic field case we can evaluate $I^{(0)}$ for diamagnetic species without much difficulty, but for the paramagnetic species the problem is somewhat more difficult. In both cases $\mathcal{J}^{(0)}$ is diagonal with respect to the tensor product $[\underset{\sim}{W}]^{(p)}[\underset{\sim}{Q}]^{(q)}$, i.e., $\mathcal{J}^{(0)}$ does not mix tensors of different symmetry. In the diamagnetic case $\mathcal{J}^{(0)}$ is diagonal with respect to eigenfunctions of $J^{(0)}$, which greatly simplifies the calculation of the inverse in terms of the eigenfunctions. This is not the case for paramagnetic species, but it is not of much consequence in practice when we use a small expansion set. The operator F is diagonal for any set of orthogonal basis functions for the diamagnetic case, so in practice one might find it easier to calculate the inverse of $\mathcal{J}^{(0)}$ instead of finding the eigenfunctions of $J^{(0)}$. However, to find a general expression for the inverse, it is necessary to use the eigenfunctions of $J^{(0)}$.

The electric field case for ${}^1\Sigma$ molecules presents a rather formidable problem in general, since $\mathcal{J}^{(0)}$ is not diagonal in the tensors $[\underset{\sim}{W}]^{(p)}[\underset{\sim}{Q}]^{(q)}$. The nonzero elements of F are between tensors with identical values of p and values of q that differ by one. Hence $\mathcal{J}^{(0)}$ is an infinite matrix of coupled angular momentum tensors. However, for a small expansion set the evaluation of the inverse is fairly simple. The specific evaluation of $I^{(0)}$ will be given in the viscosity and thermal conductivity chapters for such truncated sets. Only for diamagnetic species in a magnetic field will a general form of the inverse be given.

$I^{(0)}$ for Diamagnetic Species in a Magnetic Field

We denote the eigenfunctions of $J^{(0)}$ by $\underset{\approx}{\Phi}{}_k^{(0)}(p,q)$, where k denotes a scalar function of W^2 and Q^2 and p and q label the irreducible Cartesian tensors in $\underset{\sim}{W}$ and $\underset{\sim}{Q}$. Thus $\mathcal{J}^{(0)}$ is represented by a diagonal matrix with elements $\underset{\approx}{J}{}_{kk}^{(0)}\left(\begin{smallmatrix}p,q\\p,q\end{smallmatrix}\right) + \underset{\approx}{F}{}_{kk}\left(\begin{smallmatrix}p,q\\p,q\end{smallmatrix}\right)$, where $\underset{\approx}{F}{}_{kk}\left(\begin{smallmatrix}p,q\\p,q\end{smallmatrix}\right) = \langle\!\langle \underset{\approx}{\Phi}{}_k^{(0)}(p,q), f^{(0)}F(\underset{\approx}{\Phi}{}_k^{(0)}(p,q))\rangle\!\rangle$ and $\underset{\approx}{J}{}_{kk}^{(0)}\left(\begin{smallmatrix}p,q\\p,q\end{smallmatrix}\right) = \varphi_k^{(0)}(p,q)\,\underset{\approx}{\delta}{}^{(p,q)}$. Here $\varphi_k^{(0)}(p,q)$ denotes the eigenvalue of $J^{(0)}$ operating on $\underset{\approx}{\Phi}{}_k^{(0)}(p,q)$. The tensor

$\underset{\approx}{F}_{kk}\binom{p,q}{p,q}$ can be written as $H\langle\gamma\underset{\approx}{\Phi}_k^{(0)}(p,q),f^{(0)}\underset{\approx}{\Phi}_k^{(0)}(p,q)\rangle\chi_q\hat{h}$, where $\hat{h}$ is a unit vector parallel to $\underset{\sim}{H}$ and χ_q indicates the sum of terms obtained by crossing $\hat{h}$ into the first q right-hand indices of $\underset{\approx}{F}_{kk}\binom{p,q}{p,q}$. We can write $\underset{\approx}{F}_{kk}\binom{p,q}{p,q}$ as $\underset{\approx}{F}_{kk}\binom{p,q}{p,q} = b_k(p,q)\underset{\approx}{\delta}^{(p,q)}\chi_q\hat{h}$, where

$$b_k(p,q) = H\langle\underset{\approx}{\Phi}_k^{(0)}(p,q),\gamma f^{(0)}\underset{\approx}{\Phi}_k^{(0)}(p,q)\rangle \odot^{2(p+q)}\underset{\approx}{\delta}^{(p,q)}/$$
$$(2p+1)(2q+1).$$

Thus we must compute the inverse $I^{(0)}$, with matrix elements $\underset{\approx}{I}_k(p,q)$, such that

$$\underset{\approx}{I}_k(p,q)\odot^{p+q}(\varphi_k^{(0)}(p,q)\underset{\approx}{\delta}^{(p,q)} + b_k(p,q)\underset{\approx}{\delta}^{(p,q)}\chi_q\hat{h}) = \underset{\approx}{\delta}^{(p,q)}.$$

In order to further examine $\underset{\approx}{I}_k(p,q)$ (a tensor which is traceless and symmetric on its first and last p and q indices and invariant to rotations about the field direction), we need to consider a linearly independent basis set of tensors of rank 2q which are traceless and symmetric on their first and last q indices and are each a basis for the totally symmetric representation of the group of rotations about an axis along the field. Such a set is

$$\underset{\approx}{B}_m^{(a)}(q) = N_{qm}\,\mathring{\Sigma}(\hat{h})^{q-m}(\underset{\approx}{U}^{(2)})^m(\hat{h})^{q-m} \quad m=0,1,2,\dots,q \qquad 1.24$$

and

$$\underset{\approx}{B}_m^{(b)}(q) = N_{qm}\,\mathring{\Sigma}(\hat{h})^{q-m}\underset{\approx}{V}\cdot(\underset{\approx}{U}^{(2)})^m(\hat{h})^{q-m} \quad m=1,2,\dots,q \qquad 1.25$$

where

$$N_{qm} = 2^{q-m}(q+m)!(q-m)!/(m!(2q)!),$$

$(\hat{h})^m$ is a polyad in $\hat{h}$ of rank m,

$$\underset{\approx}{U}^{(2)} = \underset{\approx}{\delta}^{(1)} - \hat{h}\hat{h},$$

$$\underset{\approx}{V} = -\hat{h}\times\underset{\approx}{\delta}^{(1)},$$

$$(\underset{\approx}{U}^{(2)})^m_{a_1\ldots a_{2m}} = \delta_{a_1a_{2m}}\delta_{a_2a_{2m-1}}\ldots\delta_{a_ma_{m+1}}, \qquad a_i=1,2,$$

and $\mathring{\Sigma}$ is the sum over all different permutations of the first and last q indices. The symbol ° indicates that the necessary terms are added to make the tensor traceless on all its first and last q indices. The above tensors are orthogonal in the following sense:

$$\underset{\approx}{B}_m^{(a)}(q)\odot^q\underset{\approx}{B}_n^{(a)}(q) = \underset{\approx}{B}_m^{(a)}(q)\delta_{mn}, \qquad 1.26$$

$$\underset{\approx}{B}_m^{(b)}(q)\odot^q\underset{\approx}{B}_n^{(b)}(q) = -\underset{\approx}{B}_m^{(a)}(q)\delta_{mn}, \qquad 1.27$$

$$\underset{\approx}{B}_m^{(a)}(q)\odot^q\underset{\approx}{B}_n^{(b)}(q) = \underset{\approx}{B}_m^{(b)}(q)\odot^q\underset{\approx}{B}_n^{(a)}(q) = \underset{\approx}{B}_m^{(b)}(q)\delta_{mn}. \qquad 1.28$$

The tensors $\underset{\approx}{B}_m^{(a)}(q)$ are also the identity elements, in Cartesian form, of the irreducible real representations of the group (C_∞) of rotations about the field direction (the basis for the representation being the tensors $[\underset{\sim}{X}]^{(q)}$, where $\underset{\sim}{X}=\underset{\sim}{W}$ or $\underset{\sim}{Q}$). The $\underset{\approx}{B}_m^{(b)}(q)$ are also elements of the representation corresponding to rotation by $\pi/2m$. Since each irreducible representation for m=0 to q is contained once and only in the representation (with $[\underset{\sim}{x}]^{(q)}$ as the basis), it follows that

$$\underset{\approx}{\delta}^{(q)} = \sum_{m=0}^{q}\underset{\approx}{B}_m^{(a)}(q). \tag{1.29}$$

Since $\underset{\approx}{I}_k(p,q)$ is a basis for the totally symmetric representation of C_∞, then

$$\underset{\approx}{I}_k(p,q) = a_0\underset{\approx}{\tilde{B}}_0^{(a)}(q) + \sum_{m=1}^{q}(a_m\underset{\approx}{\tilde{B}}_m^{(a)}(q) + b_m\underset{\approx}{\tilde{B}}_m^{(b)}(q)), \tag{1.30}$$

where a_i and b_i are to be determined. The tilde above the tensors means that $\underset{\approx}{\delta}^{(p)}$ has been inserted in the middle of the tensors to give a new tensor of rank 2(p+q). The same orthogonality conditions also hold for these tensors.

We can write $\underset{\approx}{F}_{kk}(p,q)$ as

$$\underset{\approx}{F}_{kk}(p,q) = -b_k(p,q)\sum_{m=1}^{q}m\underset{\approx}{\tilde{B}}_m^{(b)}(q), \tag{1.31}$$

since

$$\underset{\approx}{\delta}^{(p,q)}\chi_q\hat{h} = \sum_{m=0}^{q}\underset{\approx}{\tilde{B}}_m^{(a)}(q)\chi_q\hat{h} = -\sum_{m=1}^{q}m\underset{\approx}{\tilde{B}}_m^{(b)}(q).$$

Thus we have the relation

$$\begin{aligned}\underset{\approx}{I}_k(p,q)\odot^{p+q}(\varphi_k^{(0)}(p,q)\underset{\approx}{\delta}^{(p,q)} - b_k(p,q)\sum_{m=1}^{q}m\underset{\approx}{\tilde{B}}_m^{(b)}(q)) = \\ a_0\varphi_k^{(0)}(p,q)\underset{\approx}{\tilde{B}}_0^{(a)}(q) + \sum_{m=1}^{q}[(a_m\varphi_k^{(0)}(p,q) + \\ mb_mb_k(p,q))\underset{\approx}{\tilde{B}}_m^{(a)}(q) + (b_m\varphi_k^{(0)}(p,q) - \\ ma_mb_k(p,q))\underset{\approx}{\tilde{B}}_m^{(b)}(q)] = \sum_{m=0}^{q}\underset{\approx}{\tilde{B}}_m^{(a)}(q).\end{aligned} \tag{1.32}$$

Since the $\underset{\approx}{\tilde{B}}{}_m^{(a)}(q)$ and $\underset{\approx}{\tilde{B}}{}_m^{(b)}$ are linearly independent, we have that

$$a_0 = 1/\varphi_k^{(0)}(p,q),$$

$$\varphi_k^{(0)}(p,q)a_m = (1 + m^2 d_k^2(p,q))^{-1},$$

$$b_m = ma_m d_k(p,q),$$

$$d_k(p,q) = b_k(p,q)/\varphi_k^{(0)}(p,q),$$

and finally

$$\underset{\approx}{I}{}_k(p,q) = (\varphi_k^{(0)}(p,q))^{-1}(\underset{\approx}{\tilde{B}}{}_0^{(a)}(q) + \sum_{m=1}^{q}[(\underset{\approx}{\tilde{B}}{}_m^{(a)}(q) + md_k(p,q)\underset{\approx}{\tilde{B}}{}_m^{(b)}(q))/(1 + m^2 d_k^2(p,q))]). \qquad 1.33$$

The saturation limit ($H \rightarrow \infty$) is just $\underset{\approx}{\tilde{B}}{}_0^{(a)}(q)/\varphi_k^{(0)}(p,q)$. Therefore for a solution of the kinetic equations for $H=\infty$, only the $[\underset{\sim}{Q}]^{(q)} \odot {}^{q}\underset{\approx}{B}{}_0^{(a)}(q)$ part of $[\underset{\sim}{Q}]^{(q)}$ is needed in the trial functions. This is not surprising since $\underset{\approx}{B}{}_0^{(a)}(q)$ is the identity element for the totally symmetric representation of the C_∞ group and hence just projects out the part of $[\underset{\sim}{Q}]^{(q)}$ which is a basis for the totally symmetric representation of C_∞. This is equivalent to averaging $[\underset{\sim}{Q}]^{(q)}$ about the field, since only a basis of the totally symmetric representation survives such averaging. For example, $[\underset{\sim}{Q}]^{(2)}$ averaged about the field yields $[(\hat{h}\cdot\underset{\sim}{Q})^2 - Q^2/3](\hat{h}\hat{h} - \underset{\approx}{U}{}^{(2)}/2)$, which is identical with $[\underset{\sim}{Q}]^{(2)} \odot {}^{2}\underset{\approx}{B}{}_0^{(a)}(2)$. This says that all the tensor polarization of $[\underset{\sim}{Q}]^{(q)}$ is destroyed except for the $[\underset{\sim}{Q}]^{(q)} \odot {}^{q}\underset{\approx}{B}{}_{0}^{(a)}(q)$ part. This is also true for the paramagnetic case, since there is no coupling of different angular momenta tensors either. However, for the electric field problem, where such coupling occurs, not only does the $[\underset{\sim}{Q}]^{(q)} \odot {}^{q}\underset{\approx}{B}{}_{0}^{(a)}(q)$ part of $[\underset{\sim}{Q}]^{(q)}$ escape destruction by the field, but small contributions from other parts are also not destroyed.

THERMAL CONDUCTIVITY

Kinetic Theory

The heat flux vector for a dilute gas with no viscothermal coupling is given by

$$\underset{\sim}{q} = \int d\underset{\sim}{c}(\underset{\sim}{v}-\underset{\sim}{u})(m(\underset{\sim}{v}-\underset{\sim}{u})^2/2 + M^2/2I)f^{(1)} \qquad 2.1$$

or

$$\underset{\sim}{q} = -(2k^2T/m)\langle f^{(0)}(W^2 + Q^2)\underset{\sim}{W},\underset{\sim}{A}\rangle\cdot\frac{\partial T}{\partial \underset{\sim}{r}}. \qquad 2.2$$

Since in a linear phenomenology $\underset{\sim}{q}$ is defined by $\underset{\sim}{q} = -\underset{\approx}{\lambda}\cdot\frac{\partial T}{\partial \underset{\sim}{r}}$, we recognize the thermal conductivity tensor $\underset{\approx}{\lambda}$ as

$$\underset{\approx}{\lambda} = (2k^2T/m)\langle f^{(0)}(W^2 + Q^2)\underset{\sim}{W},\underset{\sim}{A}\rangle. \qquad 2.3$$

We expand $\underset{\sim}{A}$ in irreducible tensors in $\underset{\sim}{W}$ and $\underset{\sim}{Q}$ as follows:

$$\underset{\sim}{A} = \sum_{p,q,s,t} S^{(s)}_{p+1/2}(W^2)S^{(t)}_{q}(Q^2)[\underset{\sim}{W}]^{(p)}[\underset{\sim}{Q}]^{(q)} \odot^{p+q} \underset{\approx}{A}^{pqst}, \qquad 2.4$$

where the $S^{(n)}_{m}(x^2)$ are Sonine polynomials, which are given by

$$S^{(n)}_{m}(x^2) = \sum_{p=0}^{n} (n+m+1)(-x^2)^p/p!(n-p)!\Gamma(p+m+1)$$

and obey the orthogonality condition

$$\int_0^\infty dx\exp(-x^2)S^{(n)}_{m}(x^2)S^{(n')}_{m}(x^2)x^{2m+1} = \delta_{nn'}\Gamma(n+m+1)/2(n!).$$

The tensors $\underset{\approx}{A}^{pqst}$ are field-dependent expansion coefficients that transform according to the totally symmetric group of rotations about the field direction. The subsidiary conditions (equation 1.17) require that $\underset{\approx}{A}^{1000}=0$ and that p must be an odd integer. Thus we can write $\underset{\approx}{\lambda}$ as

$$\underset{\approx}{\lambda} = (2k^2T/m)\langle \underset{\sim}{D},\underset{\sim}{A}\rangle = -(k^2T/m)(5\underset{\approx}{A}^{1010} + 2\underset{\approx}{A}^{1001}), \qquad 2.5$$

where $\underset{\sim}{D} = -f^{(0)}[(5/2-W^2) + (1-Q^2)]\underset{\sim}{W} = -f^{(0)}(S_{3/2}^{(1)}(W^2) + S_0^{(1)}(Q^2))\underset{\sim}{W}$. This direct dependence of $\underset{\approx}{\lambda}$ on $\underset{\approx}{A}^{1010}$ and $\underset{\approx}{A}^{1001}$ is a result of our choice of polynomial subscripts. A choice of p-1/2 instead of p+1/2 would result in a direct dependence of $\underset{\approx}{\lambda}$ on $\underset{\approx}{A}^{1020}$ and $\underset{\approx}{A}^{1001}$ with the subsidiary conditions giving $\underset{\approx}{A}^{1000}=\underset{\approx}{A}^{1010}$. This latter choice would require the evaluation of collision integrals which are more numerous and more difficult.

We now truncate the expansion for $\underset{\sim}{A}$. From equation 2.5 we already know two terms that are definitely of importance. To study the effects of angular momentum anisotropy we must include some tensors with $q\neq 0$. For the magnetic field case we include one term which is odd in the angular momentum ($q=1$) and one which is even ($q=2$). In a sense this is just a trial and error process. However, it will be found that the term with $q=2$ gives the dominant contribution. This means that for the electric field case we must include a term with $q=3$, since the dominant term couples directly with $q=1,3$. Thus, for the electric field case we approximate $\underset{\sim}{A}$ by

$$\underset{\sim}{A} = \underset{\sim}{\phi}_1\cdot\underset{\approx}{A}^1 + \underset{\sim}{\phi}_2\cdot\underset{\approx}{A}^2 + \underset{\approx}{\phi}_3\odot^3\underset{\approx}{A}^3 + \underset{\approx}{\phi}_4\odot^2\underset{\approx}{A}^4 + \underset{\approx}{\phi}_5\odot^4\underset{\approx}{A}^5, \qquad 2.6$$

where

$$\underset{\sim}{\phi}_1 = (5/2-W^2)\underset{\sim}{W}, \qquad \underset{\approx}{A}^1 = \underset{\approx}{A}^{1010},$$

$$\underset{\sim}{\phi}_2 = (1-Q^2)\underset{\sim}{W}, \qquad \underset{\approx}{A}^2 = \underset{\approx}{A}^{1001},$$

$$\underset{\approx}{\phi}_3 = \underset{\sim}{W}[\underset{\sim}{Q}]^{(2)}, \qquad \underset{\approx}{A}^3 = \underset{\approx}{A}^{1200},$$

$$\underset{\approx}{\phi}_4 = \underset{\sim}{W}\underset{\approx}{Q}, \qquad \underset{\approx}{A}^4 = \underset{\approx}{A}^{1100},$$

$$\underset{\approx}{\phi}_5 = \underset{\sim}{W}[\underset{\approx}{Q}]^{(3)}, \qquad \underset{\approx}{A}^5 = \underset{\approx}{A}^{1300},$$

and in the magnetic field case we ignore $\underset{\approx}{\phi}_5$.

If we multiply equation 1.20 by each of the $\underset{\approx}{\phi}_i^t$ and integrate over all the variables of particle 1 (except r), we obtain the following set of tensor equations for the expansion coefficients:

$$\underset{\approx}{d}_k = [k,1]\cdot\underset{\approx}{A}^1 + [k,2]\cdot\underset{\approx}{A}^2 + [k,3]\odot^3\underset{\approx}{A}^3 + [k,4]\odot^2\underset{\approx}{A}^4 + [k,5]\odot^4\underset{\approx}{A}^5, \qquad 2.7$$

where k=1 to 5, $\underset{\approx}{d}_1 = 5/4\underset{\approx}{\delta}^{(1)}$, $\underset{\approx}{d}_2 = 1/2\underset{\approx}{\delta}^{(1)}$, $d_3 = d_4 = d_5 = 0$. Here $[k,m] = \underset{\approx}{h}_{km} + (k,m)$, where $\underset{\approx}{h}_{km} = n^{-1}\langle\underset{\approx}{\phi}_k, J(\underset{\approx}{\phi}_m)\rangle$ and $(k,m) = n^{-1}\langle\underset{\approx}{\phi}_k, F(\underset{\approx}{\phi}_m)\rangle$. The collision integrals $\underset{\approx}{h}_{km}$ are tabulated in Appendix A. For diamagnetic species $\gamma = \mu_N g_r/\hbar$, where μ_N is the nuclear magneton and g_r is the rotational g factor. Hence we obtain for the diamagnetic species in a magnetic field

$$(4,4) = -(\beta_D/6)\underset{\approx}{\tilde{B}}_1^{(b)}(1),$$

$$(3,3) = -(2\beta_D/15)\sum_{m=1}^{2} m\underset{\approx}{\tilde{B}}_m^{(b)}(2),$$

and

$$(5,5) = -\beta_D \sum_{m=1}^{3} m\underset{\approx}{\tilde{B}}_m^{(b)}(3),$$

where $\beta_D = (mkT/\pi)^{1/2}(\mu_N g_r/d^2\hbar)(H/p)$ and d is the internuclear distance. For the $^2\Pi_{3/2}$ state of NO, $\gamma = -3\mu_B\hbar/M^2$, and μ_B is the Bohr magneton. Here

$$(4,4) = (\beta_P/2)\underset{\approx}{\tilde{B}}_1^{(b)}(1),$$

$$(3,3) = (\beta_P/10)\sum_{m=1}^{2} m\underset{\approx}{\tilde{B}}_m^{(b)}(2),$$

and

$$(5,5) = \beta_P \sum_{m=1}^{3} m\underset{\approx}{\tilde{B}}_m^{(b)}(3),$$

where $\beta_P = (m/\pi kT)^{1/2}(\mu_B h/d^2 I)(H/p)$. The units of the (k,m) integrals are $(1/d^2)(m/\pi kT)^{1/2}$. For the electric field case the only nonzero field integrals are

$$(3,4) = (\beta_E/20)\underset{\approx}{\tilde{B}}_1^{(b)}(2)\cdot\hat{h}$$

and

$$(3,5) = (3\beta_E/140)\hat{h}\cdot\sum_{m=1}^{2} m\underset{\approx}{\tilde{B}}_m^{(b)}(3)$$

where $(k,m) = -(m,k)^t$ and $\beta_E = (d_E^2/d^2kT)(m/2\pi I)^{1/2}(E^2/p)$.

It is convenient to divide the tensors $\underset{\approx}{A}^i$ into a field-off part $\underset{\approx}{X}^i$ and a field-on part $\underset{\approx}{Y}^i$. In the field-off limit, the tensors must be spatially isotropic so that $\underset{\approx}{X}^i = x^i\underset{\approx}{\delta}^{(1)}$ for i=1,2, $\underset{\approx}{X}^3 = x^3\underset{\approx}{\delta}^{(2)}$, $\underset{\approx}{X}^4 = x^4\underset{\approx}{\epsilon}$, where ϵ_{ijk} is the Levi-Civita density, and $\underset{\approx}{X}^5 = 0$. The field-on tensors are expanded in a complete set of isotropic tensors (of the appropriate rank and symmetry) invariant to rotations about the field direction. Hence we have $\underset{\approx}{Y}^i = \sum_{j=1}^{3} y^i_j \underset{\approx}{J}^j$ for i=1,2, $\underset{\approx}{Y}^3 = \sum_{j=1}^{9} y^3_j \underset{\approx}{I}^j$, $\underset{\approx}{Y}^4 = \sum_{j=1}^{7} y^4_j \underset{\approx}{K}^j$, and $\underset{\approx}{Y}^5 = \sum_{j=1}^{9} y^5_j \underset{\approx}{Y}^{(5)}_j$, where $\underset{\approx}{J}^j$, $\underset{\approx}{I}^j$, and $\underset{\approx}{K}^j$ have been defined by Klein, Hoffman, and Dahler (12). The nine fifth rank tensors, $\underset{\approx}{Y}^{(5)}_i$, can be obtained by double dotting each of the third rank tensors $\hat{h}\hat{h}\hat{h}$, $\hat{h}\underset{\approx}{U}^{(2)}$, and $\underset{\approx}{(\hat{h})}^{(2)}$ into $\underset{\approx}{B}^{(b)}_m(3)$ (m=1,2) and $\underset{\approx}{B}^{(a)}_m(3)$ (m=0,1,2). Since the tensors $\underset{\approx}{Y}^{(5)}_i$ are traceless and symmetric on their first three indices, the tensors $\underset{\approx}{B}^{(b)}_m(3)$ and $\underset{\approx}{B}^{(a)}_m(3)$ provide a convenient method for constructing them.

Using the linear independence of the tensors we can arrive at a set of scalar equations for the x^i_j and y^i_j. These equations have been solved numerically for certain model parameters. The results will be presented in the next section where we also compare this exact solution with the perturbation solution.

The zeroth and higher order perturbation solutions are given by

$$ {}^{(0)}\underset{\approx}{\lambda} = (2k^2T/m)\langle \underset{\sim}{D}, I^{(0)}\underset{\sim}{D}\rangle, \tag{2.8} $$

$$ {}^{(1)}\underset{\approx}{\lambda} = 0, \tag{2.9} $$

$$ {}^{(2)}\underset{\approx}{\lambda} = (2k^2T/m)\langle \underset{\sim}{D}, I^{(0)}\mathcal{J}^{(1)}I^{(0)}\mathcal{J}^{(1)}I^{(0)}\underset{\sim}{D}\rangle , \qquad 2.10 $$

and

$$ {}^{(n)}\underset{\approx}{\lambda} = (2k^2T/m)\langle \underset{\sim}{D}, (I^{(0)}\mathcal{J}^{(1)})^n I^{(0)}\underset{\sim}{D}\rangle . \qquad 2.11 $$

we recognize that $\underset{\sim}{D} = -f^{(0)}(\underset{\sim}{\phi}_1 + \underset{\sim}{\phi}_2)$ is orthogonal to $\underset{\approx}{\phi}_i$ for i=3,4,5. Thus for our truncated basis set, we do not write $I^{(0)}$ in terms of the eigenfunctions of $J^{(0)}$ with the basis functions $\underset{\sim}{\phi}_1$ and $\underset{\sim}{\phi}_2$, but just calculate the inverse directly. (The inverse is much easier to construct than the eigenfunctions.) Here $\underset{\approx}{I}_{11}^{(0)} = \underset{\approx}{h}_{22}/G$, $\underset{\approx}{I}_{22}^{(0)} = \underset{\approx}{h}_{11}/G$, and $\underset{\approx}{I}_{12}^{(0)} = \underset{\approx}{I}_{21}^{(0)} = -\underset{\approx}{h}_{12}/G$, where $G = h_{11}h_{22} - h_{12}^2$. For the mag-field case the other elements are $\underset{\approx}{I}_{ii}^{(0)} = \underset{\approx}{I}_i(1,q)$ where $\phi_i^{(0)}(1,q) = h_{ii}^1$ for i=3,4,5. Thus we obtain to fourth order (fourth order since for our models $\underset{\approx}{\phi}_4$ does not contribute until then)

$$ {}^{(0)}\underset{\approx}{\lambda} = {}^{(0)}\lambda_0\underset{\approx}{\delta}^{(1)} = (k^2T/2m)(5x_1 + 2x_2)\underset{\approx}{\delta}^{(1)} , \qquad 2.12 $$

$$ {}^{(2)}\underset{\approx}{\lambda} = {}^{(2)}\lambda_0\underset{\approx}{\delta}^{(1)} + \Delta^{(2)}\lambda_1\underset{\approx}{B}_0^{(a)}(1) + \Delta^{(2)}\lambda_2\underset{\approx}{B}_1^{(a)}(1) + $$
$$ \Delta^{(2)}\lambda_3\underset{\approx}{B}_1^{(b)}(1), \qquad 2.13 $$

$$ {}^{(n)}\underset{\approx}{\lambda} = {}^{(n)}\lambda_0\underset{\approx}{\delta}^{(1)} + \Delta^{(n)}\lambda_1\underset{\approx}{B}_0^{(a)}(1) + \Delta^{(n)}\lambda_2\underset{\approx}{B}_1^{(a)}(1) + $$
$$ \Delta^{(n)}\lambda_3\underset{\approx}{B}_1^{(b)}(1), \qquad 2.14 $$

and ${}^{(n)}\lambda_0\underset{\approx}{\delta}^{(1)} = {}^{(n)}\underset{\approx}{\lambda}_{H=0}$. Here

$$ x_1 = (5h_{22}/4 - h_{12}/2)/G, $$

$$x_2 = (h_{11}/2 - 5h_{12}/4)/G,$$

$$^{(2)}\lambda_0 = (2k^2T/m)(5M_3^2/3h_{33}^1 - 2M_4^2/h_{44}^1),$$

$$\Delta^{(2)}\lambda_i = (2k^2T/m)(w_iM_3^2/h_{33}^1 + a_iM_4^2/h_{44}^1),$$

$$M_k = (h_{1k}x_1 + h_{2k}x_2)/G,$$

$$w_1 = -w^2/(1+w^2), \qquad a_1 = 2a^2/(1+a^2),$$

$$w_2 = -3w^2(3+4w^2)/2(1+w^2)(1+4w^2), \qquad a_2 = a_1/2,$$

$$w_3 = w(5+8w^2)/2(1+w^2)(1+4w^2), \qquad a_3 = -a/(1+a^2),$$

$$w = b_1(1,2)/h_{33}^1, \qquad a = b_1(1,1)/h_{44}^1,$$

$$^{(3)}\lambda_0 = -(2k^2T/m)P_3[(55/18)]$$

$$\Delta^{(3)}\lambda_i = (2k^2T/m)w_i'P_3,$$

$$P_3 = M_3^2h_{33}^1/2h_{33}^2,$$

$$w_1' = -13/6 + 2/3(1+w^2) + 3/2(1+w^2)^2 + w^2/2(1+w^2)^2,$$

$$w_2' = -3 + 1/6(1+w^2) + 1/3(1+4w^2) + 1/2(1+w^2)^2 +$$
$$1/(1+w^2)(1+4w^2) - w^2/2(1+w^2) - 2w^2/(1+w^2)(1+4w^2) +$$
$$1/(1+4w^2) - 4w^2/(1+4w^2)^2,$$

$$w_3' = w/6(1+w^2) + 2w/3(1+4w^2) + w/(1+w^2)^2 +$$
$$3w/(1+w^2)(1+4w^2) + 4w/(1+4w^2)^2,$$

$$^{(4)}\lambda_0 = -(2k^2T/m)P_4[(25/2)]$$

$$\Delta^{(4)}\lambda_i = (2k^2T/m)w_i''P_4,$$

$$P_4 = M_3^2h_{34}^2/4h_{44}^1h_{33}^2,$$

$$w_1'' = 25/2 + g_1^2 + 2(g_1^2/4 - g_5^2)/(1+a^2) + 2g_1g_5a/(1+a^2),$$

$$w_2'' = 25/2 + g_3^2 - g_6^2 + (g_2^2 - g_4^2)/(1+a^2) -2g_2g_4a/(1+a^2),$$

$$w_3'' = 2g_3g_6 + 2g_2g_4/(1+a^2) + a(g_2^2 - g_4^2)/(1+a^2),$$

$$g_1 = w/(1+w^2), \qquad g_2 = w/(1+w^2) + 2w/(1+4w^2),$$

$$g_3 = -w/2(1+w^2) - 4w/(1+4w^2),$$

$$g_4 = -1/2 - 1/(1+w^2) - 1/(1+4w^2),$$

$$g_5 = 1 + 3/2(1+w^2) \qquad g_6 = 1/2(1+w^2) + 2/(1+4w^2).$$

For the electric field the elements $\underset{\approx}{I}_{ij}^{(0)}$ (for i,j=1,2) remain the same, and the only other terms contributing in second order are

$$\underset{\approx}{I}_{33}^{(0)} = (h_{33}^1)^{-1}[\underset{\approx}{S}^{(1,2)} - \underset{\approx}{\tilde{B}}_1^{(a)}(2)(x_{11}^2 + x_{21}^2)/(1 + x_{11}^2 + x_{21}^2) - \underset{\approx}{\tilde{B}}_2^{(a)}(2)x_{22}^2/(1 + x_{22}^2)]$$

and

$$\underset{\approx}{I}_{44}^{(0)} = (h_{44}^1)^{-1}[\underset{\approx}{S}^{(1,1)} - \underset{\approx}{\tilde{B}}_1^{(a)}(1)x_{11}^2/(1 + x_{11}^2 + x_{21}^2)],$$

where $x_{11} = (b_E/20)(2h_{33}^1h_{44}^1)^{-1/2}$, $b_E = (\beta_E/d^2)(m/\pi kT)^{1/2}$,

$x_{21} = (3b_E/140)[8/15h^1_{33}h^1_{55}]^{1/2}$, and $x_{22} = (5/2)^{1/2}x_{21}$. Thus we obtain for the second-order solution

$$\Delta^{(2)}\lambda_1 = -(2k^2T/m)[(M_3^2/h^1_{33})(x_{11}^2 + x_{21}^2)/(1 + x_{11}^2 + x_{21}^2) - (M_4^2/h^1_{44})(2x_{21}^2)/(1 + x_{11}^2 + x_{21}^2)] \qquad 2.15$$

and

$$\Delta^{(2)}\lambda_2 = -(2k^2T/m)[(M_3^2/h^1_{33})[(x_{11}^2 + x_{21}^2)/2(1 + x_{11}^2 + x_{21}^2) + x_{22}^2/(1 + x_{22}^2)] - (M_4^2/h^1_{44})x_{21}^2/(1 + x_{11}^2 + x_{21}^2)]. \qquad 2.16$$

We have omitted the field-off solutions, since they are identical with the magnetic field results. No higher order solutions have been given either, since we present the exact solution in the next section, and since we expect the convergence to be similar to the magnetic field case.

If we take the saturation limit ($E\rightarrow\infty$),

$$\underset{\approx}{I}^{(0)}_{44} \longrightarrow (h^1_{44})^{-1}[\tilde{\underset{\approx}{B}}^{(a)}_0(1) + \tilde{\underset{\approx}{B}}^{(a)}_1(1)/(1+s)],$$

where $s = 245h^1_{55}/48h^1_{44}$. This is slightly different from the magnetic field limit of $(h^1_{44})^{-1}\tilde{\underset{\approx}{B}}^{(a)}_0(1)$. Thus we see that there is less destruction of the tensor polarization of $\underset{\approx}{WQ}$. Since for our models $M_4=0$, we expect this different saturation limit to contribute in higher order. This will be seen in the next section where we compare exact solutions of both the magnetic and electric field cases. The element $\underset{\approx}{I}_{33}^{(0)}$ does not give a different saturation value from the magnetic field case because we truncated the expansion set after the term with $q=3$. The inclusion of terms with $q>3$ would result in a different saturation value.

Numerical Results

The objectives of the numerical calculations here and for the viscosity are as follows: (a) to find model parameters to best fit the available experimental data, (b) to understand why good or poor agreement is obtained, (c) to attempt some correlation between the simple "disk" picture of the rapidly rotating molecule and the mathematics, (d) to examine the importance of various expansion terms, and to examine the convergence of the perturbation solution. It has been shown by Cooper and Hoffman (24) that the transport properties are nearly independent of the exact type of rigid ovaloid used if the molecules have roughly the same dimensions, so we will use both the spherocylinder and ellipsoid interchangeably in our examples. The basic parameters of the ellipsoid are R, the ratio of major to minor axis, and $\langle\sigma\rangle$, the average cross-sectional area. (For greater detail see Appendix A.) For the spherocylinder the parameters are S, the radius of the cylinder and hemispherical caps, and L, the length of the cylinder.

Experimental data is available for N_2, CO, and NO, so we limit our discussion to these molecules. The quantities which have been measured experimentally are λ_0, $\Delta\lambda/\lambda_0$, λ_{tr}/λ_0, and $\Delta\lambda_\perp/\lambda_0$, where $\Delta\lambda = (\Delta\lambda_1 + \Delta\lambda_2)/2$, $\lambda_{tr} = \Delta\lambda_3$, and $\Delta\lambda_\perp = \Delta\lambda_2$. Bond lengths and rotational g factors for these species are given in Table I. The procedure for determining S and L for N_2 is illustrated in Fig. 1, where we have plotted ratios of theoretical to experimental values of λ_0, $\beta_{1/2}$ (β_D at half-saturation), and $(\Delta\lambda/\lambda_0)_{sat}$ (the saturation value of $\Delta\lambda/\lambda_0$). From these plots it is clear how we choose optimal values for S and L. This task is facilitated by the fact that λ_0 and $\beta_{1/2}$ are sensitive only to S, i.e., the molecular size,whereas $(\Delta\lambda/\lambda_0)_{sat}$ is sensitive to the nonsphericity, i.e., L. Thus we observe that λ_0 and $\beta_{1/2}$ are mean free path quantities which depend mainly on the effective cross section, while $(\Delta\lambda/\lambda_0)_{sat}$ is related to the change in the effective cross section induced by the magnetic field. Our approach then is to use experimental values of λ_0 and $\beta_{1/2}$ to determine S and $(\Delta\lambda/\lambda_0)_{sat}$ to determine L. A similar approach can be employed to obtain the ellipsoid parameters.

The experimental measurements of λ_{tr}/λ_0 have been conducted at much lower temperatures than have those of $\Delta\lambda/\lambda_0$. At low temperatures molecular collisions are less energetic and penetrating that at higher temperatures, so it is to expected that the collision cross section, and hence S, will increase with decreasing temperatures. Thus the values for S determined from high temperature experiments will be unreliable at low temperature. We can follow a somewhat similar procedure to that outlined above to determine the optimal parameters.

In Table II we list the experimental values of λ_0, $\beta_{1/2}$, and $(\Delta\lambda/\lambda_0)_{sat}$ with the theoretical values obtained from the optimal choice of S and L (assuming that the experimental values of λ_0 and $\beta_{1/2}$ are equally trustworthy). We also obtain theoretical estimates of $(\Delta\lambda_{\perp}/\lambda_0)_{sat}$, $\beta^{\perp}_{1/2}$, $(\Delta\lambda_{\parallel}/\lambda_0)_{sat}$, and $\beta^{\parallel}_{1/2}$, and compare with experiment when possible. Here $\Delta\lambda_{\parallel} = \Delta\lambda_1$. Figs. 2-7 show the predicted variations in these coefficients with β_D or β_P. We have also shown the comparison of the shapes of the curves when possible. The experimental and theoretical curves are quite similar except in the immediate neighborhood of $\beta_{1/2}$.

Figs. 2 and 3 also show the effect of $\underset{\approx}{\phi}_4$, which is odd in the angular momentum. If this term is omitted from the trial function for $\underset{\sim}{A}$, the saturation effect is enhanced by about 1.5%. This term and probably other terms odd in $\underset{\sim}{Q}$ have little numerical importance for the thermal conductivity. In Table III we compare predicted and experimental values of $(\lambda_{tr}/\lambda_0)_{max}$. We note that the optimal values of S are considerably larger than for the higher temperature case, as was discussed previously. The field dependence of λ_{tr}/λ_0 is shown in Figs. 8-10. Here again the effect of $\underset{\approx}{\phi}_4$ is minimal.

The description of NO is somewhat complicated in that at room temperature NO cannot be accurately described by Hund's case (a) or case (b). According to Korving (25) the experimental data suggest that NO behaves like a pure paramagnetic state with a magnetic moment somewhat smaller than the $^2\pi_{3/2}$ state. We have based our calculations for Figs. 6 and 10 on Van Vleck's (26) calculated value for the effective magnetic moment. The results are quite good, but this is not to say that the description of NO here is adequate.

We can give some quantitative meaning to the simple "disk" concept of the rotating molecule by employing the Pidduck approximation, where we approximate G by $h_{11}h_{22}$ instead of $G = h_{11}h_{22} - h_{12}^2$. We thus obtain for λ_0

$$\lambda_0 = \lambda_{trans} + \lambda_{rot},$$

where in units of $k^2T/2m$ $\lambda_{trans} = 25/4h_{11} - 5h_{12}/2h_{11}h_{22}$ and $\lambda_{rot} = 1/h_{22} - 5h_{12}/2h_{11}h_{22}$. The coefficients $1/h_{11}$ and $1/h_{22}$ are related to the relaxation times associated with a decay of the terms $\underset{\sim}{\phi}_1$ and $\underset{\sim}{\phi}_2$, respectively. As seen in Fig. 11, these relaxation times decrease with increasing R, as might be expected since as a molecule becomes more nonspherical at constant $\langle\sigma\rangle$ it should suffer more collisions. If the detailed nature of the collision processes is of little importance and only the frequency of collisions is of consequence in the relaxation process, then we would expect that relaxation times calculated using an average cross section which holds the frequency of collisions fixed should be constant. Such an average cross section should be approximately that of a disk formed by the rapidly rotating molecule. The curves marked $\langle\sigma_d\rangle$ are computed holding this disk cross section constant, and they demonstrate that this expectation is approximately realized. The term $h_{12}/h_{11}h_{22}$ represents a coupling between translational and rotational degrees of freedom. It is zero for spheres and increases steadily with R. A plot of $\beta_{1/2}$ versus R $(R>1)$ for the constant disk cross section gives an even more horizontal line. This is expected if we interpret β (representing $\beta_D$or β_P for a magnetic field and β_E for an electric field) as a measure of the ratio of the Larmor precession frequency to the collision frequency (kept constant by keeping the disk cross section constant).

In the calculation of λ_0 and $\beta_{1/2}$ the important collision integrals are $\underset{\approx}{h}_{11}$ and $\underset{\approx}{h}_{33}$, respectively, both of which have a dominant spherical contribution. Thus the value of R can be more or less arbitrarily chosen to determine the saturation value. Since the saturation value is the only quantity strongly dependent on the nonsphericity, we might expect that the good agreement between experiment and theory is somewhat fortuitous. As we later find, the dominant viscosity integral does not have a large spherical contribution, and hence the viscosity provides a more critical test of the model.

Next we test the convergence of the perturbation expansion discussed earlier. We use an ellipsoid model with an average cross-sectional area of $3.24\pi\text{Å}^2$. (This approximates the cross section of diatomic molecules in the first row of the periodic chart.) We limit the variation of the nonsphericity R to 1.1 and 1.2, since these span the range of nonsphericity for most diatomic gases.

In Figs. 12 and 13 we compare the perturbation solutions with the exact solutions for only $\Delta\lambda_1$ and $\Delta\lambda_3$, since $\Delta\lambda_2$ is qualitatively similar to $\Delta\lambda_1$. The comparison of the exact solution (omitting $\underset{\approx}{\phi}_4$) with the second and third-order contributions gives evidence that the perturbation scheme converges rapidly. The fourth-order contribution from $\underset{\approx}{\phi}_4$ reduces the third-order result to about the same extent as does the inclusion of $\underset{\approx}{\phi}_4$ in the exact solution. Thus the small effect of the term odd in the angular momentum is well accounted for in its lowest nonzero order (fourth order for our model). The convergence is to within about 1% of the exact solution for third-order contributions with R=1.1 and about 5% with R=1.2. Thus omitting higher than third-order contributions is not of much consequence for realistic values of R.

Finally in Fig. 14 we compare the electric and magnetic field results for CO. The saturation values of the electric field case are only about 0.1% larger than the magnetic field results and appear the same for the graphical scale used. We have also plotted the second-order perturbation solution. For the magnetic field $\Delta\lambda_1$ is always less than $\Delta\lambda_2$, whereas for the electric field $\Delta\lambda_2$ is less than $\Delta\lambda_1$ at first, and then at $\beta_E=250$, $\Delta\lambda_1$ becomes less than $\Delta\lambda_2$. The shapes of the curves are substantially different, although the saturation values are almost identical. The convergence of the perturbation solution seems to be about the same as for the magnetic field, so we need go only to third order to obtain adequate convergence. The half-saturation value for the electric field case occurs at very high fields. Sparking occurs experimentally before such fields can be obtained, so there is no experimental data available to compare with the calculations. Since our magnetic field predictions are fairly good, the electric field predictions should also represent rather closely the results of an experiment.

Table I. Values of the bond lengths, d, and the rotational g factors, g_r.

Gas	N_2	CO	NO
d(Å)[a]	1.098	1.128	1.150
g_r^b	-0.28	-0.27	...

[a] Source: (27).

[b] Source: (25).

Table II. Comparison of experimental (in parentheses if available) and theoretical (spherocylinder) values for λ_0 in cal/cm sec deg, $(\Delta\lambda/\lambda_0)$ and $\beta_{1/2}$ (β_D for N_2 and CO, β_P for NO).

Gas	N_2	CO	NO
L(Å)	0.52	0.533	0.51
S(Å)	1.884	2.04	1.74
$\lambda_0 \text{x} 10^5$	5.28 (6.0)[a]	4.53 (5.45)[a]	5.93 (5.74)[a]
$-(\Delta\lambda/\lambda_0)_{sat} \text{x} 10^3$	8.04 (7.9)[a]	8.26 (8.20)[a]	6.76 (6.75)[a]
$\beta_{1/2}$	-30.33 (-34.51)[a]	-33.88 (-41.04)[a]	36.37 (35.20)[a]
$-(\Delta\lambda_{\parallel}/\lambda_0)_{sat} \text{x} 10^3$	6.40	6.58	5.39
$\beta^{\parallel}_{1/2}$	-39.15	-42.50	47.18
$-(\Delta\lambda_{\perp}/\lambda_0)_{sat} \text{x} 10^3$	9.67 (10.5)[b]	9.93 (10.5)[b]	8.13
$\beta^{\perp}_{1/2}$	-25.18	-28.09	30.16

[a] Source: (25).

[b] Source: (28).

Table III. Comparison of experimental (in parentheses) and theoretical (spherocylinder) values for λ_0 in cal/cm sec deg, $(\lambda_{tr}/\lambda_0)_{max}$ and β_{max}.

Gas	N_2	CO	NO
L(Å)	0.55	0.50	0.40
S(Å)	2.65	2.7	2.7
$\lambda_0 x10^5$	1.41 (1.7)[a]	1.36 (1.58)[b]	1.37 (1.67)[b]
$-(\lambda_{tr}/\lambda_0)_{max} x10^3$	5.28 (5.14)[c]	3.87 (3.66)[c]	1.72 (1.62)[c]
β_{max}	-48.25 (-58.39)[c]	-46.25 (-53.65)[c]	104.5 (124.8)[c]

[a] Source: (29).

[b] Source: (30).

[c] Source: (31).

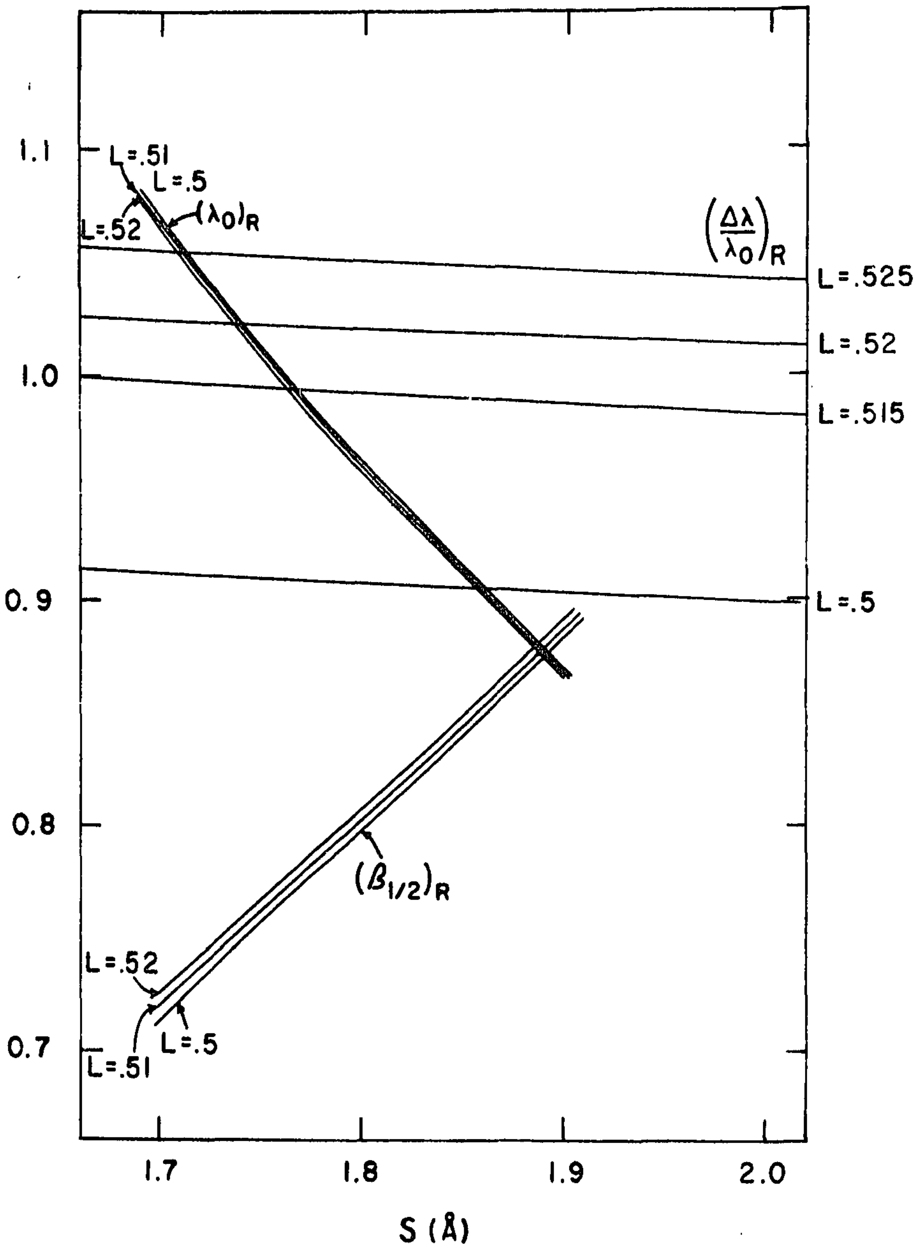


Fig. 1. L is in angstroms and $(X)_R = X_{calc}/X_{exptl}$.

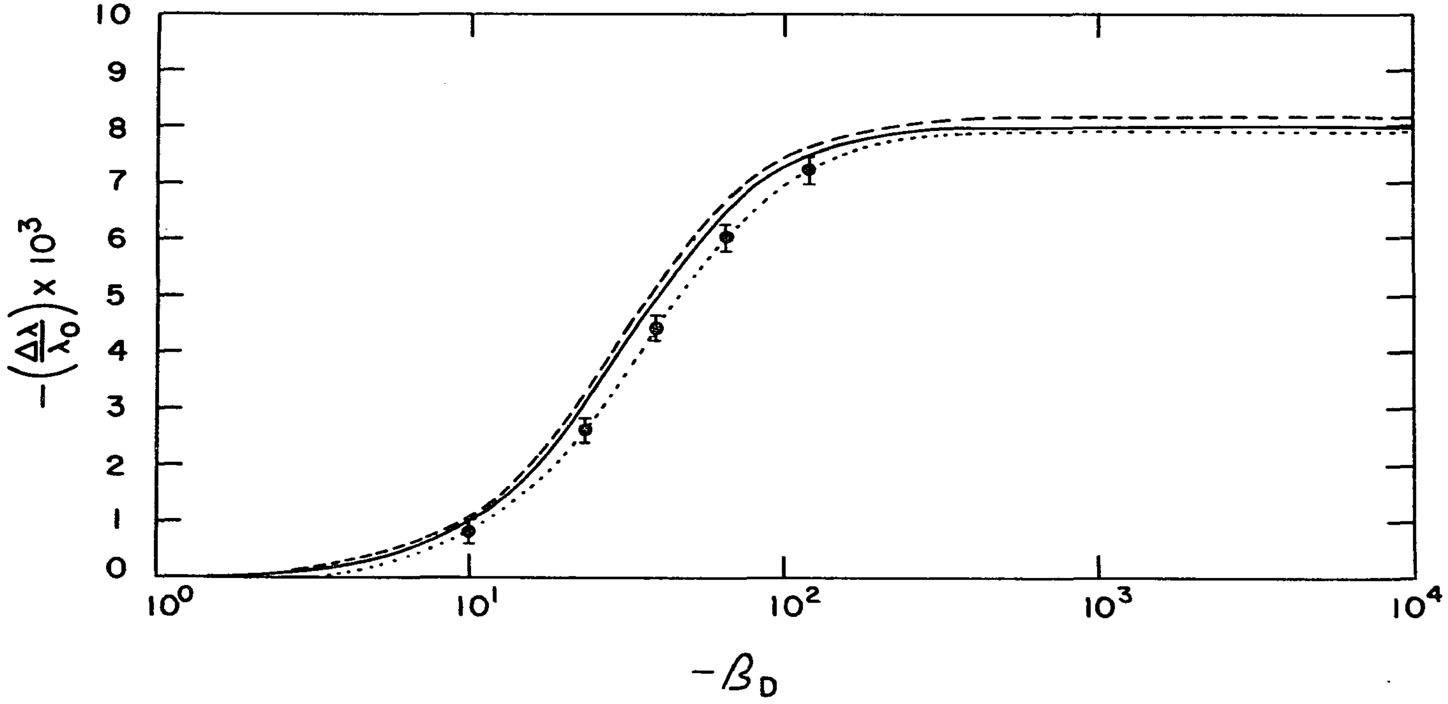


Fig. 2. (N_2) The dashed line is ($\Delta\lambda/\lambda_0$) calculated without the $\underset{\approx}{\mathrm{WQ}}$ term and the solid line is ($\Delta\lambda/\lambda_0$) calculated with the $\underset{\approx}{\mathrm{WQ}}$ term. The dotted line is the experimental ($\Delta\lambda/\lambda_0$) with the error bars indicating the spread of experimental points.

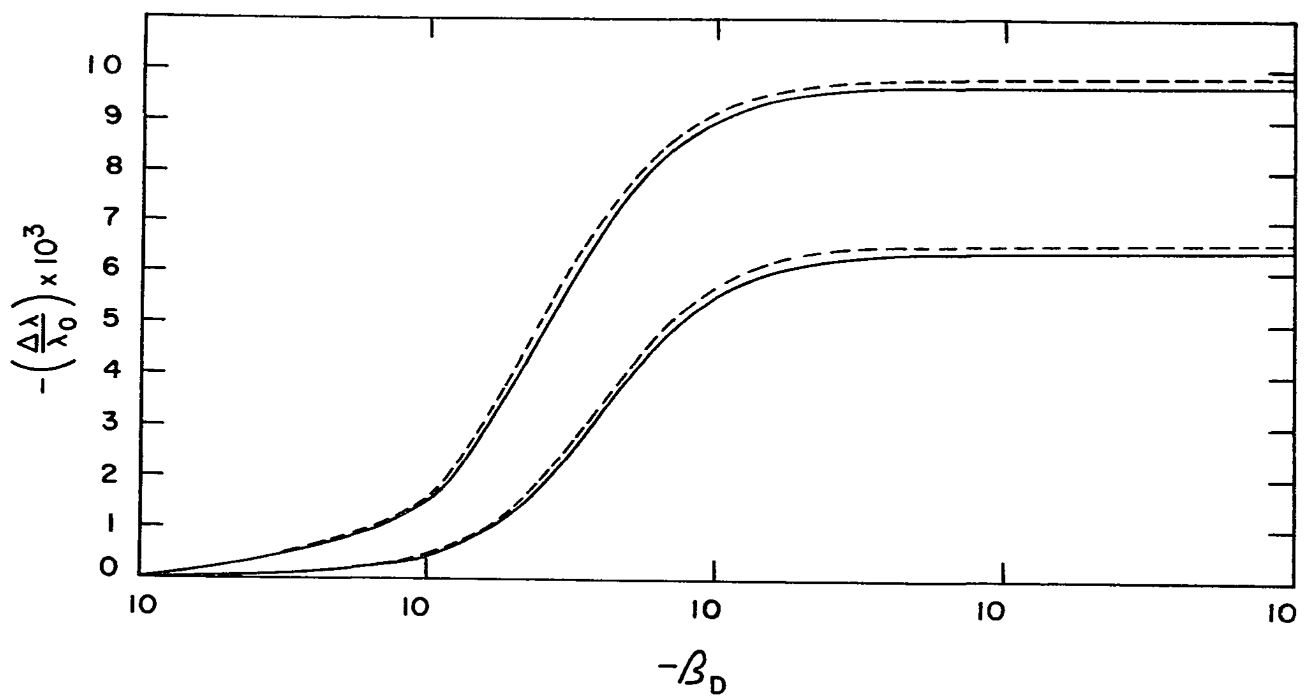


Fig. 3. (N_2) The upper curves are ($\Delta\lambda_\perp/\lambda_0$) and the lower curves are ($\Delta\lambda_\parallel/\lambda_0$). The dashed lines refer to the calculation without the $\underset{\approx}{WQ}$ term and the solid lines to the calculation with this term.

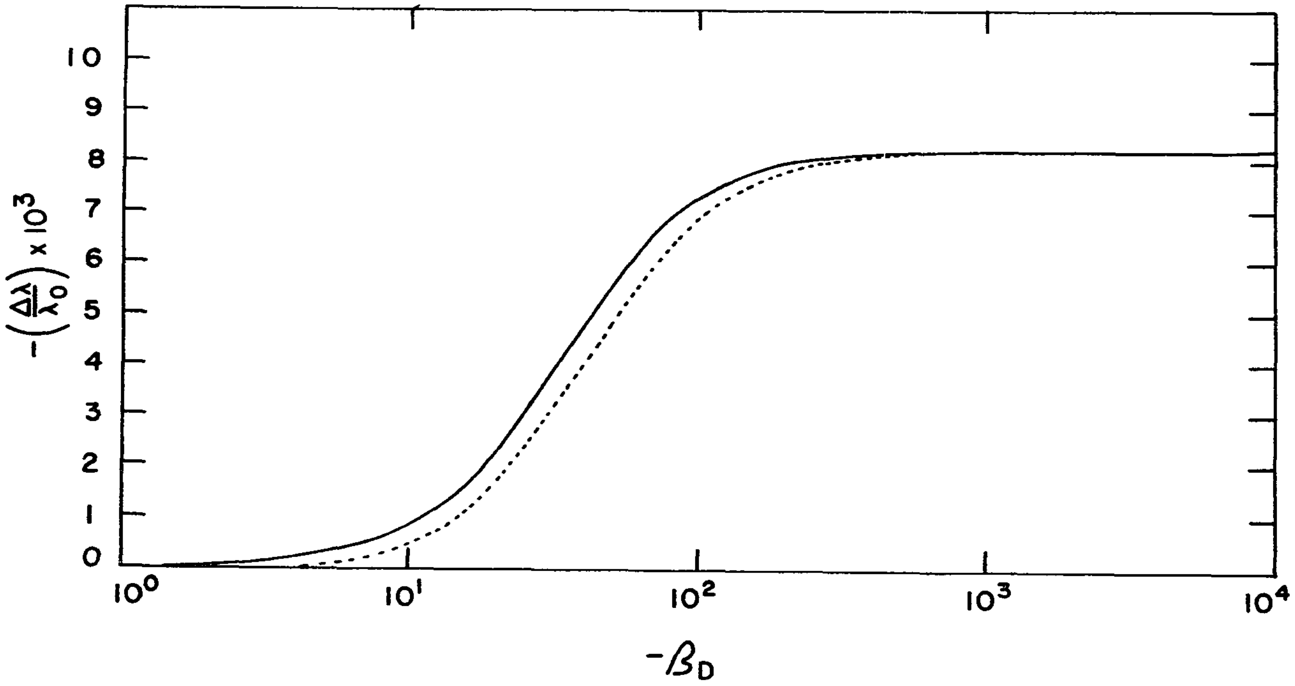


Fig. 4. (CO) The solid line is the calculated $(\Delta\lambda/\lambda_0)$ and the dotted line is the experimental $(\Delta\lambda/\lambda_0)$.

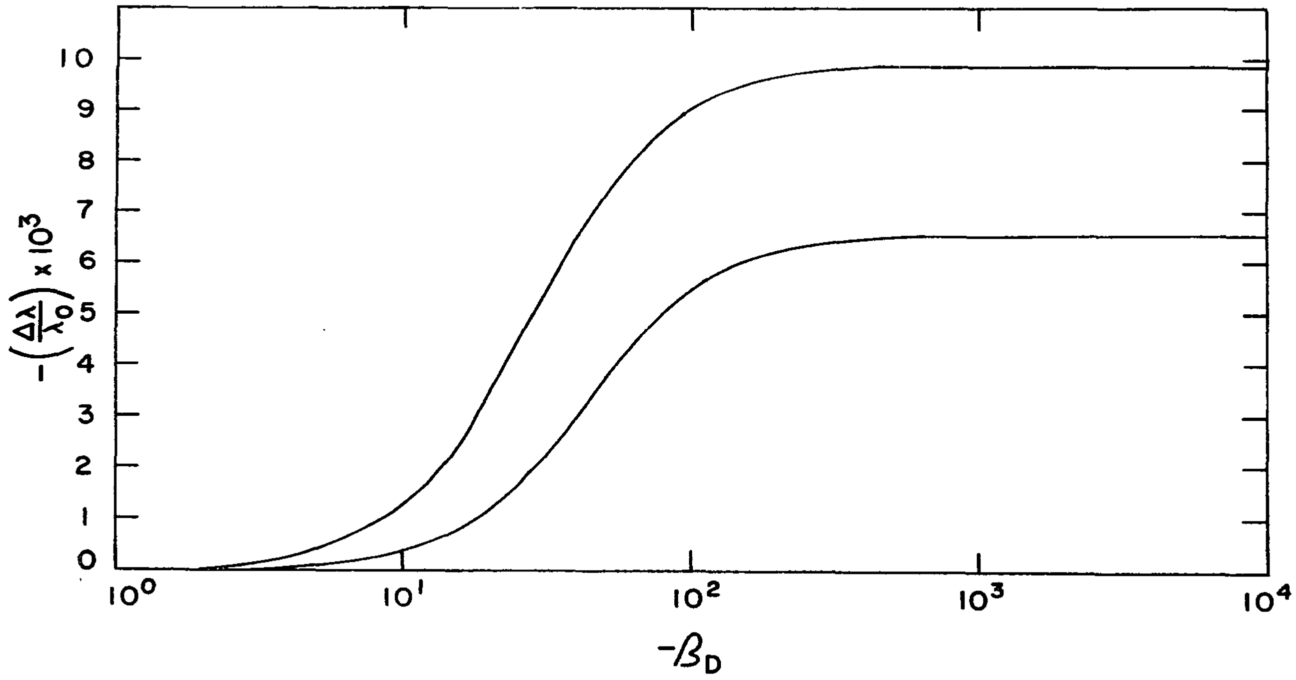


Fig. 5. (CO) The upper curve is the theoretically predicted $(\Delta\lambda_\perp/\lambda_0)$ and the lower curve is $(\Delta\lambda_\parallel/\lambda_0)$.

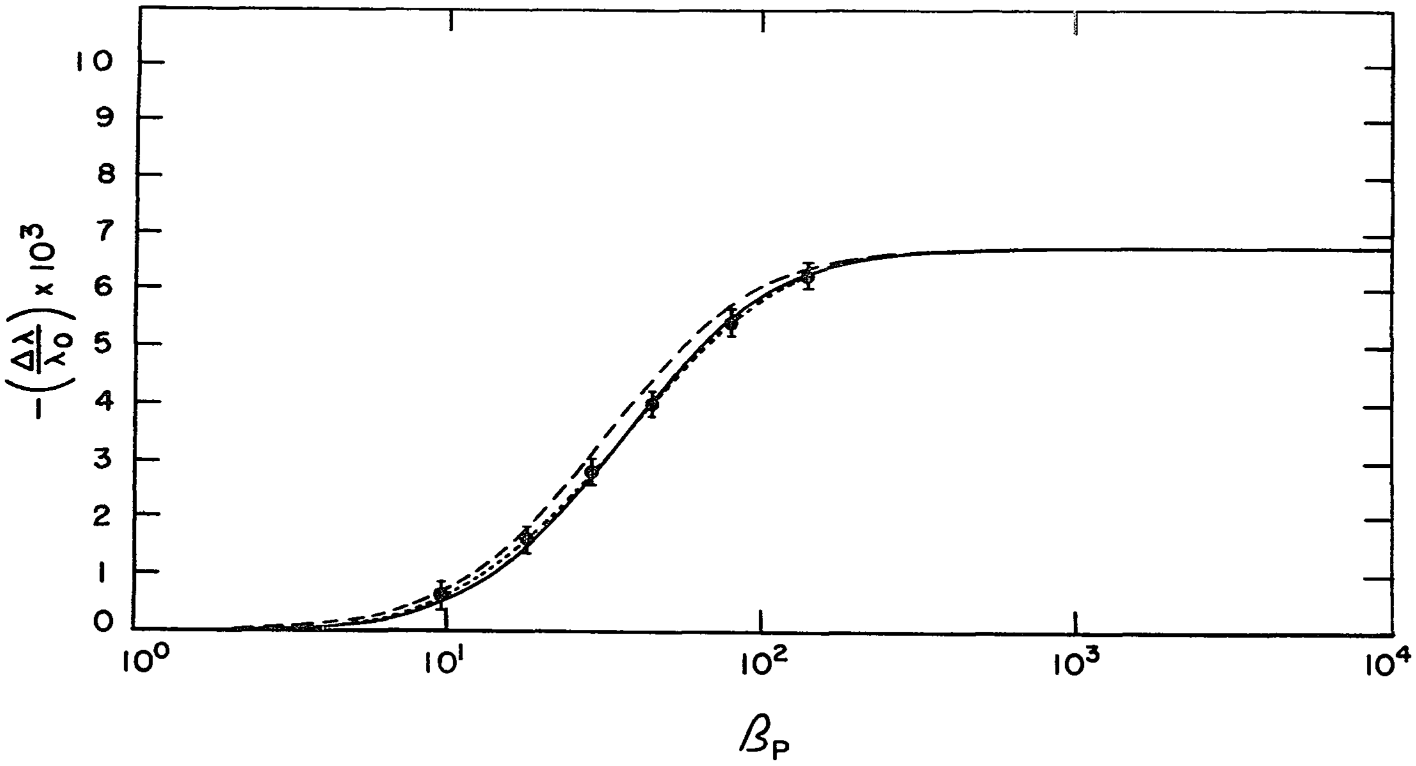


Fig. 6. (NO) The dashed line is the calculated $(\Delta\lambda/\lambda_0)$ for the pure paramagnetic gas, the solid line is the calculated $(\Delta\lambda/\lambda_0)$ for the gas with a reduced magnetic moment, and the dotted line is the experimental $(\Delta\lambda/\lambda_0)$.

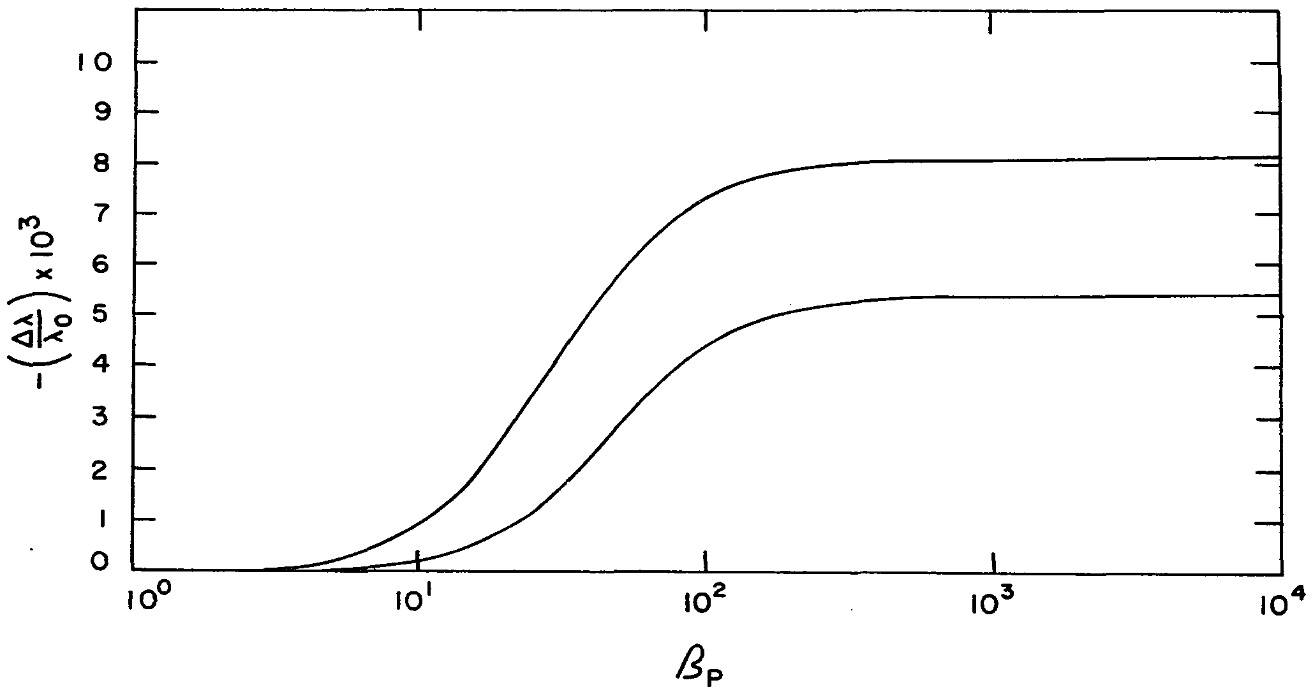


Fig. 7. (NO) The upper curve is the theoretically predicted $(\Delta\lambda_\perp/\lambda_0)$ and the lower curve is $(\Delta\lambda_\parallel/\lambda_0)$.

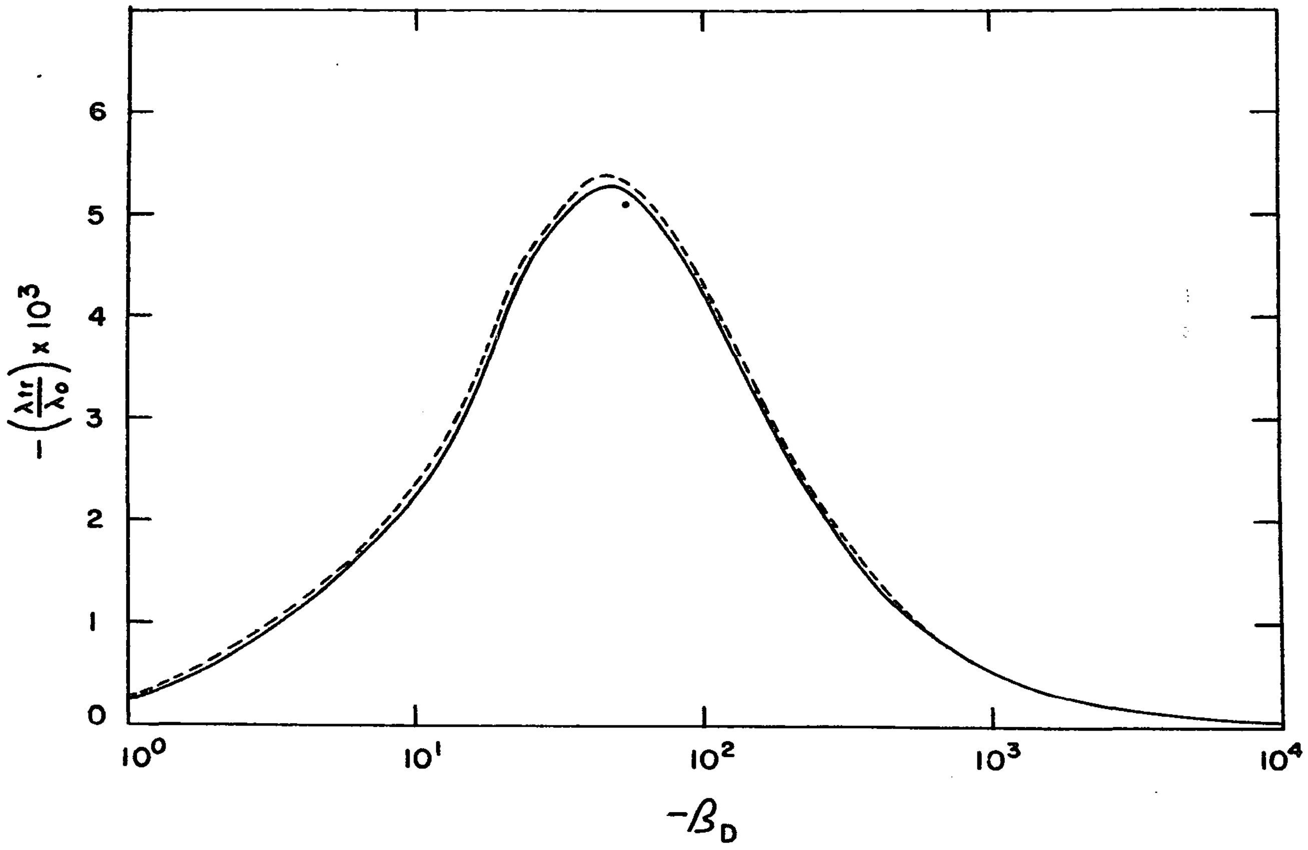


Fig. 8. (N_2) The dashed curve is (λ_{tr}/λ_0) calculated without $\underset{\approx}{WQ}$ and the solid curve is (λ_{tr}/λ_0) calculated with $\underset{\approx}{WQ}$. The dot denotes the experimental maximum.

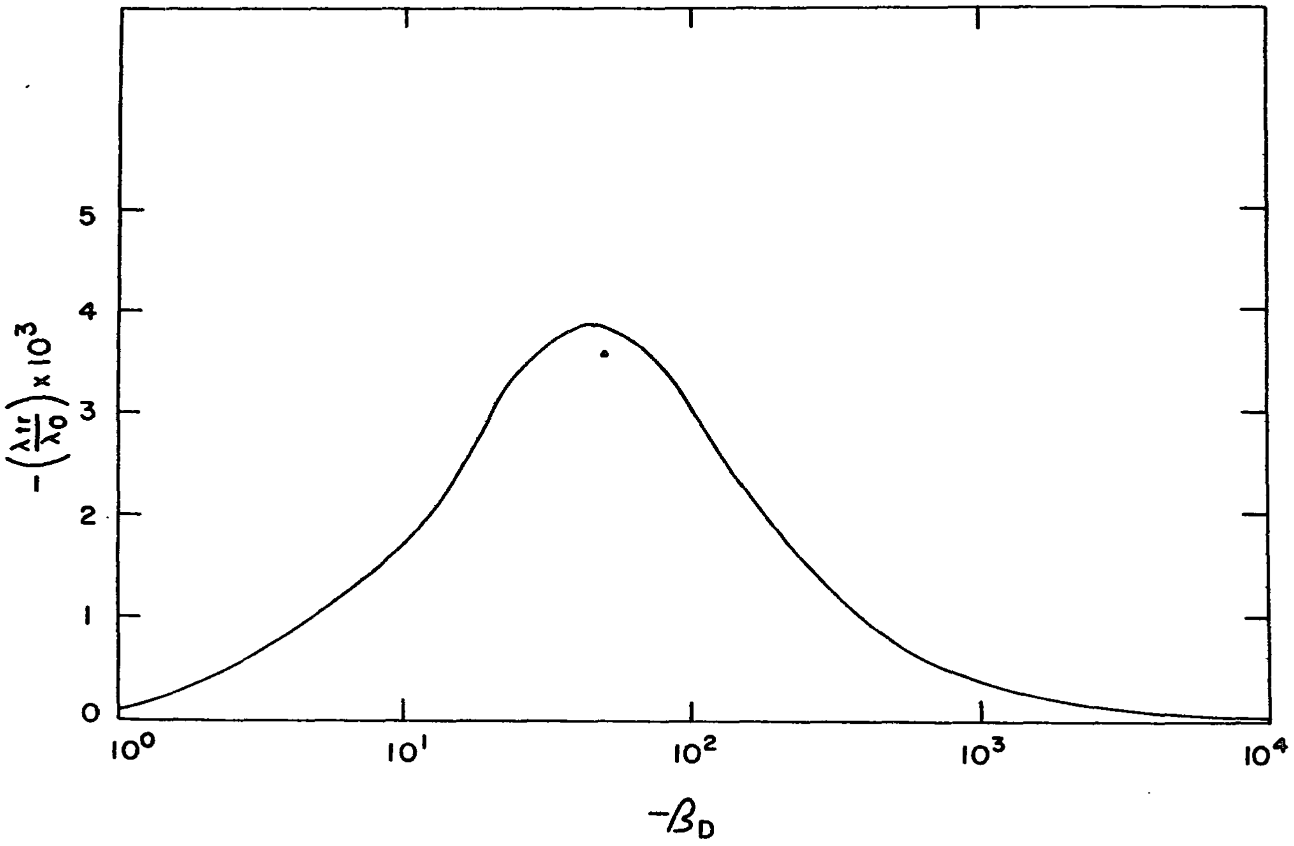


Fig. 9. (CO) The solid curve is the calculated (λ_{tr}/λ_0) and the dot denotes the experimental maximum.

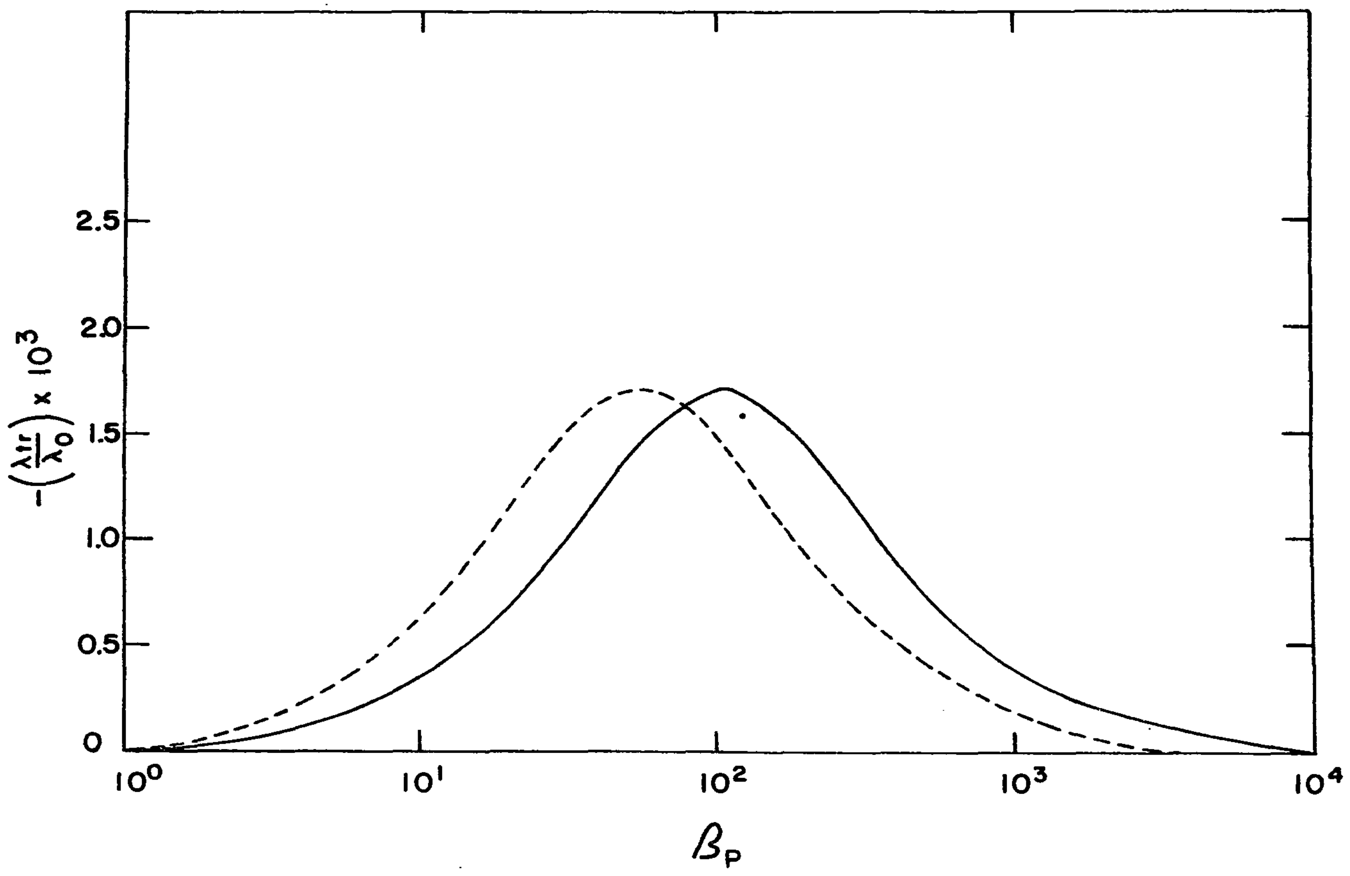


Fig. 10. (NO) The dashed curve is (λ_{tr}/λ_0) calculated for the pure paramagnetic gas and the solid curve is (λ_{tr}/λ_0) calculated for the gas with a reduced magnetic moment. The dot denotes the experimental maximum.

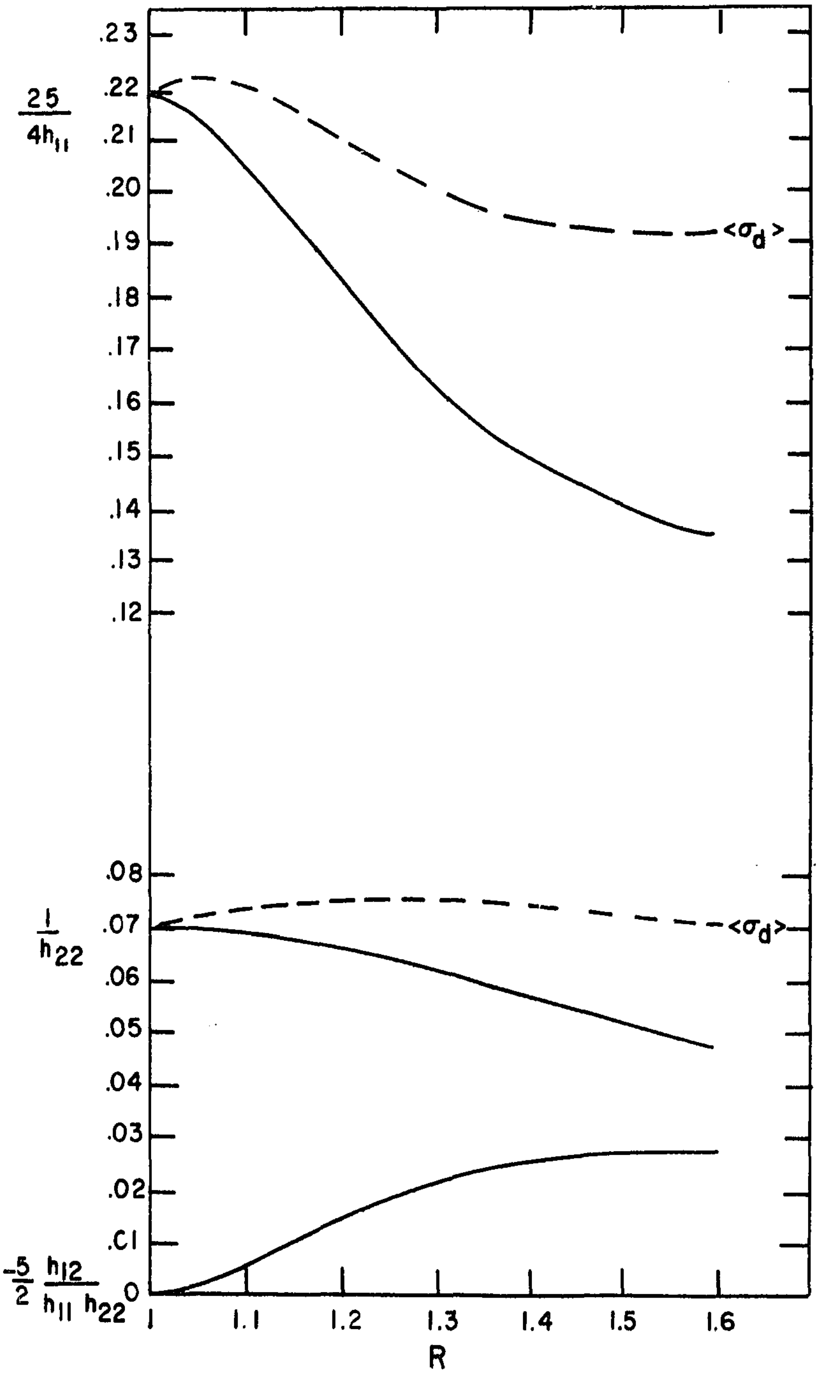


Fig. 11. The solid curves give λ_0 for constant ellipsoid cross section and the dashed curves for constant disk cross section (see text).

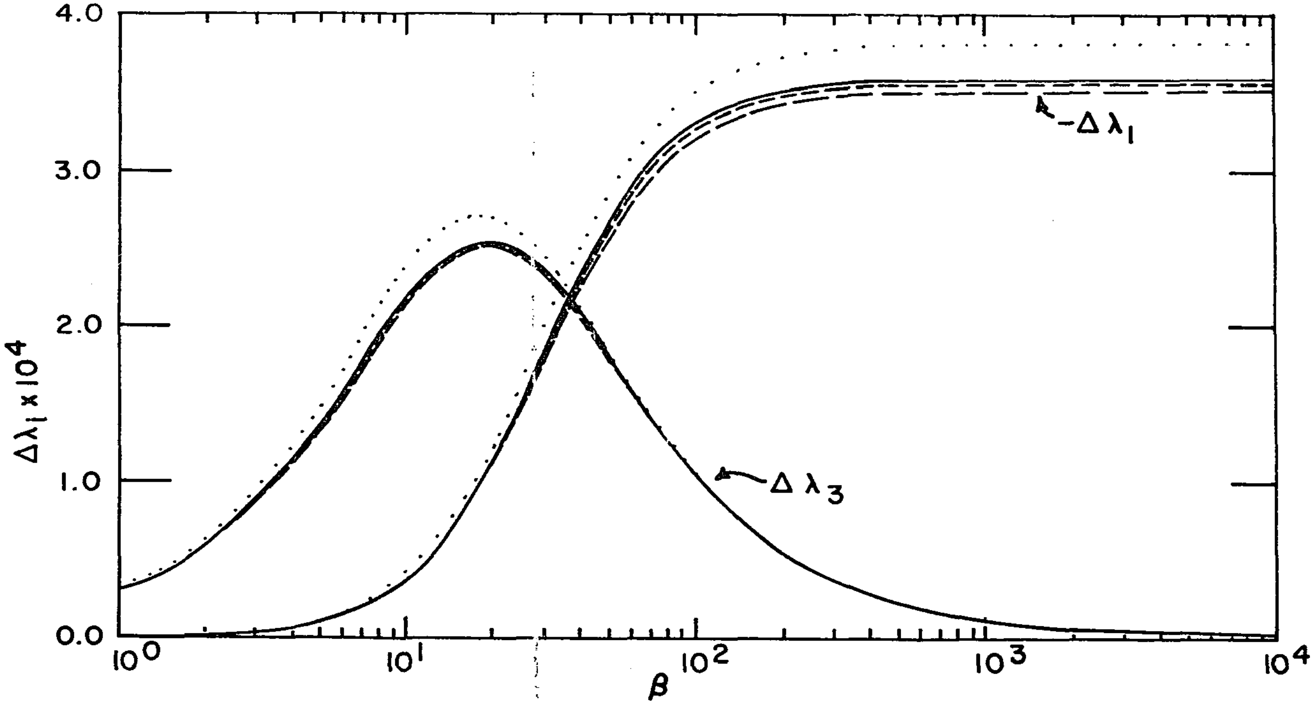


Fig. 12. The ratio R=1.1 and $\Delta\lambda$ is in units of $(k^3T/\pi m)^{1/2}/2d^2$. The dotted curves are the second-order calculations and the upper dashed curves are the third-order calculations. The lower dashed curves are fourth-order contributions from $\underset{\sim}{W}\underset{\sim}{Q}$, the solid curve is the exact three-term calculation, and the exact four-term calculation coincides with the upper dashed curve.

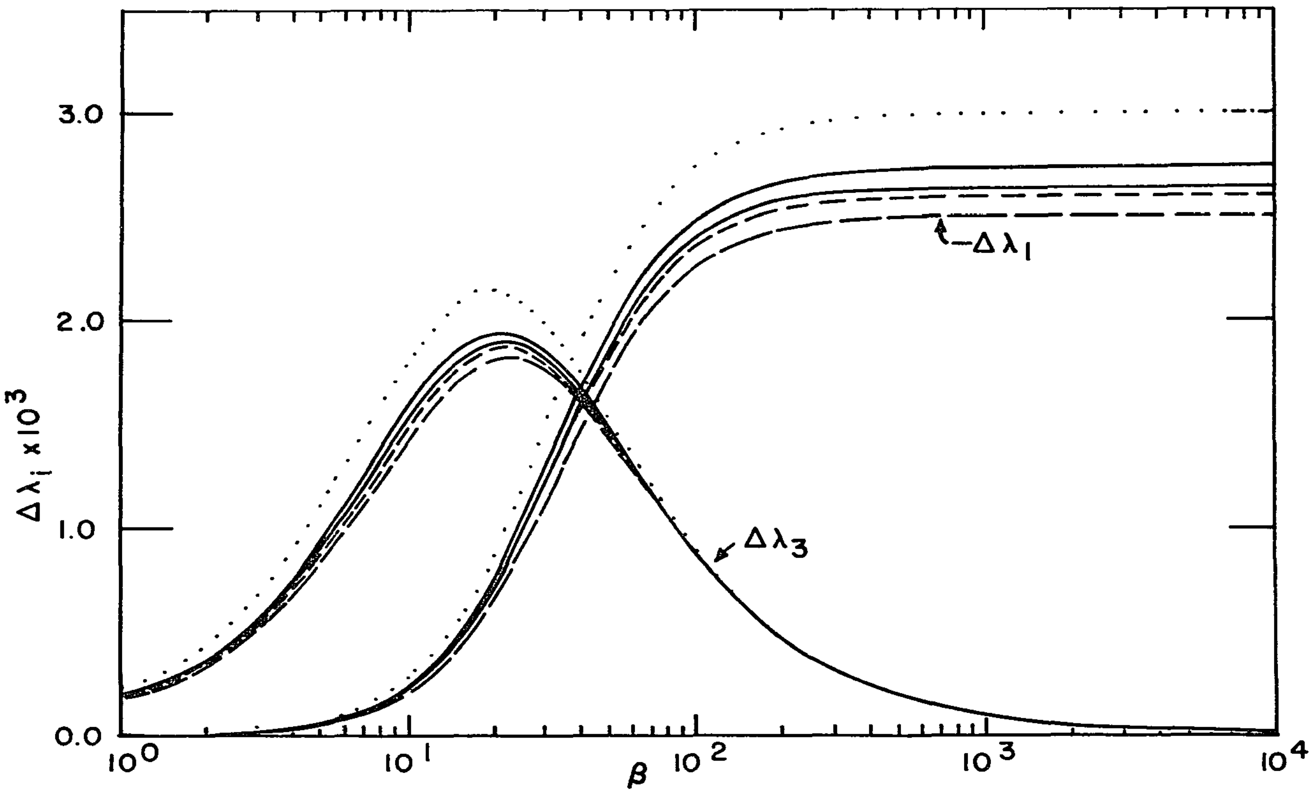


Fig. 13. Here R=1.2. and the exact four-term calculation is the lower solid curve. Otherwise the curve identification is the same as for Fig. 12.

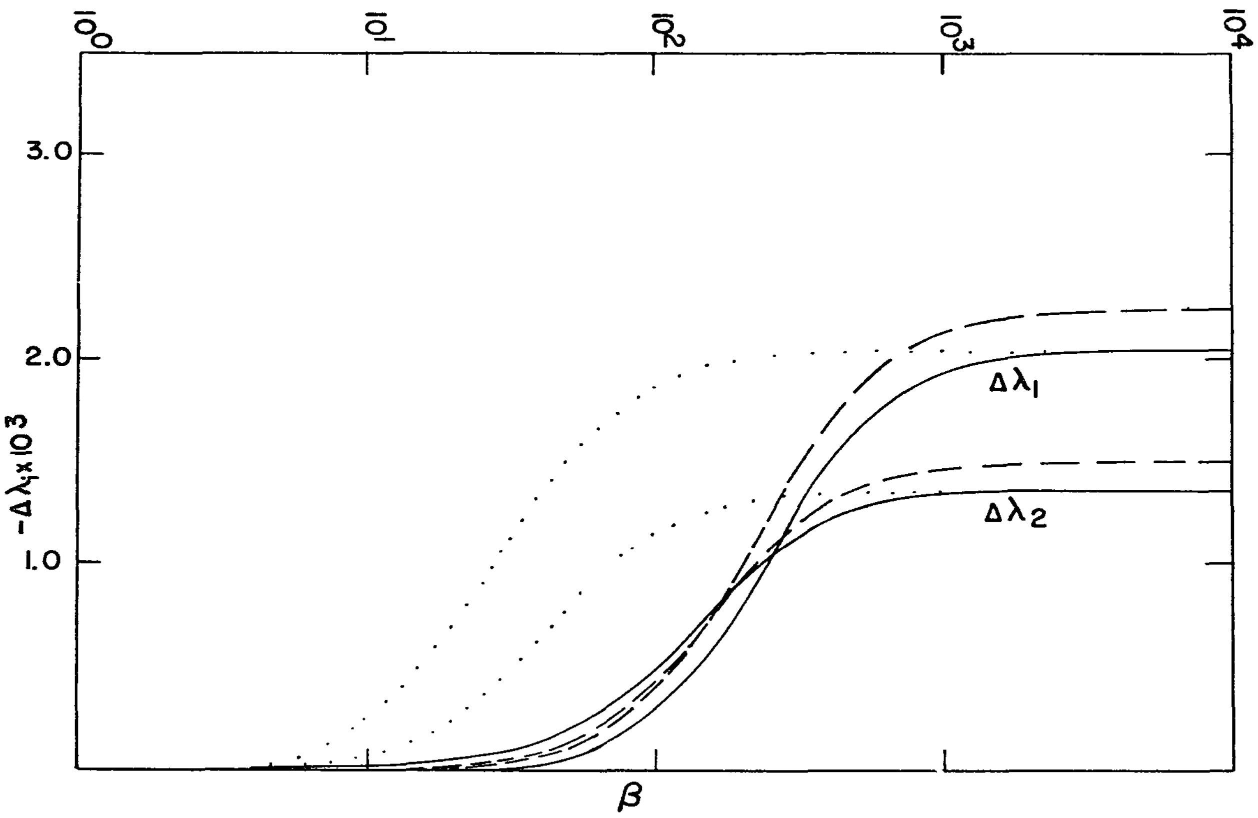


Fig. 14. The dotted lines are the magnetic field coefficients and the other curves are electric field coefficients. The dashed curves are the second-order calculations.

VISCOSITY

Kinetic Theory

The pressure tensor $\underset{\approx}{P}$ for a dilute gas with no viscothermal coupling is given by

$$\underset{\approx}{P} = \int d\underset{\sim}{c}\, m(\underset{\sim}{v}-\underset{\sim}{u})(\underset{\sim}{v}-\underset{\sim}{u})f^{(1)} = nkT\underset{\approx}{\delta}^{(1)} - 2kT\langle f^{(0)}\underset{\sim}{W}\underset{\sim}{W},\underset{\approx}{B}\rangle\odot^{2}\frac{\partial\underset{\sim}{u}}{\partial\underset{\sim}{r}}. \qquad 3.1$$

Recognizing p=nkT as the hydrostatic pressure, we can rewrite equation 3.1 as

$$\underset{\approx}{P} = p\underset{\approx}{\delta}^{(1)} - kT(\underset{\approx}{\delta}^{(1)}\langle D_1,\underset{\approx}{B}\rangle + \langle\underset{\approx}{D}_2,\underset{\approx}{B}\rangle)\odot^{2}\frac{\partial\underset{\sim}{u}}{\partial\underset{\sim}{r}}, \qquad 3.2$$

where $D_1 = f^{(0)}(4W^2/15 - 2Q^2/5)$ and $\underset{\approx}{D}_2 = 2f^{(0)}\overset{\circ}{\underset{\sim}{W}\underset{\sim}{W}}$. Since there is no term on the left-hand side of the Boltzmann equation proportional to the antisymmetric part of $\frac{\partial\underset{\sim}{u}}{\partial\underset{\sim}{r}}$, we can write the pressure tensor as

$$\underset{\approx}{P} = p\underset{\approx}{\delta}^{(1)} - kT\langle\underset{\approx}{D}_2,\underset{\approx}{B}\rangle\odot^{2}\underset{\approx}{S} - (kT/3)\langle D_1,\underset{\approx}{B}\rangle\odot^{2}\underset{\approx}{\delta}^{(1)}\frac{\partial}{\partial\underset{\sim}{r}}\cdot\underset{\sim}{u}\underset{\approx}{\delta}^{(1)} -$$

$$kT\langle D_1,\underset{\approx}{B}\rangle\odot^{2}\underset{\approx}{S}\underset{\approx}{\delta}^{(1)} - (kT/3)\langle\underset{\approx}{D}_2,\underset{\approx}{B}\rangle\odot^{2}\underset{\approx}{\delta}^{(1)}\frac{\partial}{\partial\underset{\sim}{r}}\cdot\underset{\sim}{u}, \qquad 3.3$$

where $\underset{\approx}{S} = (1/2)[\frac{\partial\underset{\sim}{u}}{\partial\underset{\sim}{r}} + (\frac{\partial\underset{\sim}{u}}{\partial\underset{\sim}{r}})^{t}] - (1/3)\frac{\partial}{\partial\underset{\sim}{r}}\cdot\underset{\sim}{u}\underset{\approx}{\delta}^{(1)}$. If we cast $\underset{\approx}{P}$ in the standard linear phenomenological form,

$$\underset{\approx}{P} = p\underset{\approx}{\delta}^{(1)} - 2\eta\odot^{2}\underset{\approx}{S} - \kappa\frac{\partial}{\partial\underset{\sim}{r}}\cdot\underset{\sim}{u}\underset{\approx}{\delta}^{(1)} + \underset{\approx}{L}_{\pi\pi}^{(02)}\odot^{2}\underset{\approx}{S}\underset{\approx}{\delta}^{(1)} +$$

$$\underset{\approx}{L}_{\pi\pi}^{(20)}\frac{\partial}{\partial\underset{\sim}{r}}\cdot\underset{\sim}{u}, \qquad 3.4$$

we can identify the shear and bulk viscosities, η and κ, as

$$\eta = (kT/2)\langle \underset{\approx}{D}_2, \underset{\approx}{B}\rangle \qquad 3.5$$

and

$$\kappa = (kT/3)\langle D_1, \underset{\approx}{B}\rangle \odot^2 \underset{\approx}{\delta}^{(1)}. \qquad 3.6$$

A coupling of shear and bulk viscosity effects exists through the coefficients $\underset{\approx}{L}^{(02)}_{\pi\pi}$ and $\underset{\approx}{L}^{(20)}_{\pi\pi}$, which are given by

$$\underset{\approx}{L}^{(02)}_{\pi\pi} = -kT\langle D_1, \underset{\approx}{B}\rangle \qquad 3.7$$

and

$$\underset{\approx}{L}^{(20)}_{\pi\pi} = -(kT/3)\langle \underset{\approx}{D}_2, \underset{\approx}{B}\rangle \odot^2 \underset{\approx}{\delta}^{(1)}. \qquad 3.8$$

The coupling coefficients obey the Onsager relations $\underset{\approx}{L}^{(02)}_{\pi\pi}(\underset{\sim}{H}) = \underset{\approx}{L}^{t(20)}_{\pi\pi}(-\underset{\sim}{H})$. (See Appendix B.)

As in the case of the thermal conductivity, we expand $\underset{\approx}{B}$ in irreducible Cartesian tensors as follows:

$$\underset{\approx}{B} = \sum_{p,q,s,t} S^{(s)}_{p+1/2}(W^2) S^{(t)}_q(Q^2)[\underset{\sim}{W}]^{(p)}[\underset{\sim}{Q}]^{(q)} \odot^{p+q} \underset{\approx}{B}^{pqst}, \qquad 3.9$$

where now the $\underset{\approx}{B}^{pqst}$ are the expansion coefficients. The subsidiary conditions require that

$$\underset{\approx}{B}^{0000} = \underset{\approx}{B}^{0010} + (2/3)\underset{\approx}{B}^{0001}, \qquad 3.10$$

and that p must be even. We now obtain expressions for the transport coefficients in terms of the expansion coefficients as follows:

$$\eta = (kT/2)(\underset{\approx}{B}^{2000} - (1/3)\underset{\approx}{B}^{2000} \odot^2 \underset{\approx}{\delta}^{(1)} \underset{\approx}{\delta}^{(1)}), \qquad 3.11$$

$$\kappa = -(kT/3)\underset{\approx}{B}^{0010}\odot^{2}\underset{\approx}{\delta}^{(1)}, \qquad 3.12$$

$$\underset{\approx}{L}_{\pi\pi}^{(20)} = -(kT/3)\underset{\approx}{B}^{2000}\odot^{2}\underset{\approx}{\delta}^{(1)}, \qquad 3.13$$

and

$$\underset{\approx}{L}_{\pi\pi}^{(02)} = kT(\underset{\approx}{B}^{0010} - (1/3)\underset{\approx}{B}^{0010}\odot^{2}\underset{\approx}{\delta}^{(1)}\underset{\approx}{\delta}^{(1)}). \qquad 3.14$$

The problem of truncation here is somewhat different from the thermal conductivity case because of the coupling between the shear and bulk viscosities. However, we might expect that q=2 terms again give the dominant field effect. Indeed we find that the p=0,q=2 term is dominant for the shear viscosity field effect, and that the p=2,q=2 term is dominant for the bulk viscosity and coupling coefficients. The simplest expansion set which includes one term odd in the angular momentum and yields nonzero values for all the viscosity coefficients is then

$$\underset{\approx}{B} = \psi_1\underset{\approx}{B}^{0010} + \underset{\approx}{\psi}_2\odot^{2}\underset{\approx}{B}^{2000} + \underset{\approx}{\psi}_3\odot^{2}\underset{\approx}{B}^{0200} + \underset{\approx}{\psi}_4\odot^{4}\underset{\approx}{B}^{2200} + \underset{\approx}{\psi}_5\odot^{3}\underset{\approx}{B}^{2100}, \qquad 3.15$$

where

$$\psi_1 = (3/2 - W^2) - (3/2)(1 - Q^2),$$

$$\underset{\approx}{\psi}_2 = [\underset{\sim}{W}]^{(2)}, \qquad \underset{\approx}{\psi}_3 = [\underset{\sim}{Q}]^{(2)},$$

$$\underset{\approx}{\psi}_4 = [\underset{\sim}{W}]^{(2)}[\underset{\sim}{Q}]^{(2)}, \qquad \underset{\approx}{\psi}_5 = [\underset{\sim}{W}]^{(2)}\underset{\sim}{Q}.$$

The solution of Boltzmann's equation for this expansion set can be reduced to the solution of a set of sixty scalar equations. Since this is a rather large number of equations to solve exactly, we limit our considerations to the perturbation scheme. However, we do solve exactly the twelve equations for η, using only the most important terms, $\underset{\approx}{\psi}_2$ and $\underset{\approx}{\psi}_3$, in the expansion. These results will be presented graphically in the next section.

Since there is only one term for each set of p,q values, the matrix elements of $I^{(0)}$ can easily be calculated from equation 1.33. We have (for the appropriate p and q) $\varphi_1^{(0)}(p,q)=b_{ii}$ for i=1,2,3, and $\varphi_1^{(0)}(p,q)=b_{ii}^1$ for i=4,5. The b_{ii} are defined in Appendix A along with the collision integrals, $\underset{\approx}{b}_{ij} = (n)^{-1}\langle\underset{\approx}{\psi}_i, J(\underset{\approx}{\psi}_j)\rangle$. We now give the perturbation results to second order. The higher order results are extremely cumbersome and will be presented graphically in the next section. As before, the term odd in the angular momentum does not contribute until fourth order for our models. We have

$$^{(n)}\eta = (kT/2)\langle\underset{\approx}{D}_2, (I^{(0)}\mathcal{J}^{(1)})^n\underset{\approx}{D}_2\rangle, \tag{3.16}$$

$$^{(n)}\kappa = kT\langle D_1, (I^{(0)}\mathcal{J}^{(1)})^n D_1\rangle, \tag{3.17}$$

$$^{(n)}\underset{\approx}{L}_{\pi\pi}^{(20)} = -kT\langle\underset{\approx}{D}_2, (I^{(0)}\mathcal{J}^{(1)})^n D_1\rangle, \tag{3.18}$$

and

$$ {}^{(n)}\underset{\approx}{L}_{\pi\pi}^{(02)} = -kT\langle D_1, (I^{(0)}\mathcal{J}^{(1)})^n\underset{\approx}{D}_2\rangle . \qquad 3.19 $$

Thus for zeroth and second order (all first-order results being zero), we have

$$ {}^{(0)}\underset{\approx}{L}_{\pi\pi}^{(20)} = {}^{(0)}\underset{\approx}{L}_{\pi\pi}^{(02)} = 0, \qquad 3.20 $$

$$ {}^{(0)}\kappa = {}^{(0)}\kappa_0 = kT/b_{11}, \qquad 3.21 $$

$$ {}^{(0)}\underset{\approx}{\eta} = {}^{(0)}\eta_0\underset{\approx}{\delta}^{(2)} = (kT/2b_{22})\underset{\approx}{\delta}^{(2)}, \qquad 3.22 $$

$$ {}^{(2)}\underset{\approx}{L}_{\pi\pi}^{(20)} = {}^{(2)}\underset{\approx}{L}_{\pi\pi}^{(02)} = -(kTz/2)(\hat{h}\hat{h} - (1/3)\underset{\approx}{\delta}^{(1)}), \qquad 3.23 $$

$$ {}^{(2)}\kappa = {}^{(2)}\kappa_0 + \Delta^{(2)}\kappa, \qquad 3.24 $$

and

$$ {}^{(2)}\underset{\approx}{\eta} = {}^{(2)}\eta_0\underset{\approx}{\delta}^{(2)} + \Delta^{(2)}\underset{\approx}{\eta}. \qquad 3.25 $$

Here the subscript zero indicates the field-off limit,

$$ {}^{(2)}\kappa_0 = 5kTb_{14}^2/b_{11}^2 b_{44}^1, $$

$$ \Delta^{(2)}\kappa = -({}^{(2)}\kappa_0/5)(2z_{14}^2 + 8z_{24}^2), $$

$$ {}^{(2)}\eta_0 = (kT/2)(N + 7N'/12 - 3N''/2), $$

$$ \Delta^{(2)}\underset{\approx}{\eta} = \Delta\eta_1\underset{\approx}{B}_0^{(a)}(2) + \Delta\eta_2\underset{\approx}{B}_1^{(a)}(2) + \Delta\eta_3\underset{\approx}{B}_2^{(a)}(2) + $$
$$ \Delta\eta_4\underset{\approx}{B}_1^{(b)}(2) + \Delta\eta_5\underset{\approx}{B}_2^{(b)}(2), $$

$$ z = (b_{14}b_{24}/b_{11}b_{22}b_{44}^1)(-z_{14}^2 + 8z_{24}^2), $$

$$N = b_{23}^{2}/b_{22}^{2}b_{33}, \quad N' = b_{24}^{2}/b_{22}^{2}b_{44}^{1}, \quad N'' = b_{25}^{2}/b_{22}^{2}b_{55}^{1},$$

$$\Delta\eta_i = (kT/2)(N_i + N_i' + N_i''),$$

$$N_1 = 0,$$

$$N_1' = -(1/12)N'(z_{14}^{2} + 16z_{24}^{2}),$$

$$N_1'' = (3/2)N''z_{15}^{2},$$

$$N_2 = -Nz_{13}^{2},$$

$$N_2' = -(1/24)N'(7z_{14}^{2} + 24z_{24}^{2}),$$

$$N_2'' = (5/4)N''z_{15}^{2},$$

$$N_3 = -4Nz_{23}^{2},$$

$$N_3' = -(1/12)N'(3z_{14}^{2} + 8z_{24}^{2}),$$

$$N_3'' = (1/2)N''z_{15}^{2},$$

$$N_4 = Nz_{13}^{2}/z_3,$$

$$N_4' = (1/24)N'(5z_{14}^{2} - 12z_{24}^{2}),$$

$$N_4'' = -(1/4)N''z_{15}^{2}/z_5,$$

$$N_5 = 2Nz_{23}^{2}/z_3,$$

$$N_5' = (1/24)N'(6z_{14}^{2} + 8z_{24}^{2}),$$

$$N_5'' = -(1/2)N''z_{15}^{2}/z_5,$$

$$z_{1i}^2 = z_i^2/(1 + z_i^2) \text{ for } i=3,4,5,$$

$$z_{2i}^2 = z_i^2/(1 + 4z_i^2) \text{ for } i=3,4,5,$$

$$z_3 = b_1(0,2)/b_{33},$$

$$z_4 = b_1(2,2)/b_{44}^1,$$

and

$$z_5 = b_1(2,1)/b_{55}^1.$$

We now consider the shear viscosity separately and enlarge the basis set with additional terms in the dominant tensors $[\underset{\sim}{W}]^{(2)}$ and $[\underset{\sim}{Q}]^{(2)}$, since, as it will be shown in the next section, the expansion set given by equation 3.15 does not give good agreement with experiment. The truncated set used to determine the effect of additional Sonine polynomials is

$$\underset{\approx}{B} = \underset{\approx}{\psi}_{21} \odot {}^2\underset{\approx}{B}^{2000} + \underset{\approx}{\psi}_{22} \odot {}^2\underset{\approx}{B}^{2010} + \underset{\approx}{\psi}_{23} \odot {}^2\underset{\approx}{B}^{2001} + \underset{\approx}{\psi}_{31} \odot {}^2\underset{\approx}{B}^{0200} + \underset{\approx}{\psi}_{32} \odot {}^2\underset{\approx}{B}^{0210} + \underset{\approx}{\psi}_{33} \odot {}^2\underset{\approx}{B}^{0201}, \qquad 3.26$$

where $\underset{\approx}{\psi}_{21}=\underset{\approx}{\psi}_2$, $\underset{\approx}{\psi}_{31}=\underset{\approx}{\psi}_3$, $\underset{\approx}{\psi}_{22}=(7/2-W^2)\underset{\approx}{\psi}_{21}$, $\underset{\approx}{\psi}_{23}=(1-Q^2)\underset{\approx}{\psi}_{21}$, $\underset{\approx}{\psi}_{32}=(3/2-W^2)\underset{\approx}{\psi}_{31}$, and $\underset{\approx}{\psi}_{33}=(3-Q^2)\underset{\approx}{\psi}_{31}$. The effect of the polynomials is shown graphically in the next section, and the pertinent integrals $\underset{\approx}{b}_{ij,km} = (n)^{-1}\langle\underset{\approx}{\psi}_{ij}, J(\underset{\approx}{\psi}_{km})\rangle$ are tabulated in Appendix A.

For the electric field shear viscosity problem we use the expansion terms $[\underset{\sim}{W}]^{(2)}$, $[\underset{\sim}{Q}]^{(2)}$, $\underset{\sim}{Q}$, and $[\underset{\sim}{Q}]^{(3)}$. The latter two do not contribute in the magnetic field case. We obtain, to second order in the nonsphericity, the same result as before for the shear viscosity if we set $N'=N''=0$, $\Delta\eta_4=\Delta\eta_5=0$, and replace $\Delta\eta_2$ and $\Delta\eta_3$ by

$$\Delta\eta_2 = -(kT/2)N(y_{11}^2 + y_{21}^2)/(1 + y_{11}^2 + y_{21}^2) \qquad 3.27$$

and

$$\Delta\eta_3 = -(kT/2)Ny_{22}^2/(1 + y_{22}^2), \qquad 3.28$$

where $y_{11} = (b_E/10)(2b_{66}b_{33})^{-1/2}$, $y_{21}^2 = (3b_E/70)^2(8/15b_{33}b_{77})$, and $y_{22}^2 = (5/2)y_{21}^2$. The index 6 refers here to $\underset{\sim}{\psi}_6=\underset{\approx}{Q}$ and the index 7 refers to $\underset{\approx}{\psi}_7=[\underset{\sim}{Q}]^{(3)}$. We observe that the saturation limit here is the same as for the magnetic field case. This is a consequence of the limited expansion set and the fact that $\underset{\approx}{Q}$ does not couple with $\underset{\approx}{D}_2$. In the next section we present the numerical results of the second-order solution and those of an exact solution.

Numerical Results

Experimental data is available only for the shear viscosity coefficients, for which we limit our considerations to the prototype N_2. For the five shear viscosity coefficients of N_2 (in a magnetic field), we show in Fig. 15 a comparison of the theoretical (using only $\underset{\approx}{\psi}_2$ and $\underset{\approx}{\psi}_3$) results with the experimental results of Hulsman (32) and Hulsman et al. (33). The ellipsoid parameters are R=1.075 and $\langle\sigma\rangle=3.4225\pi\text{Å}^2$, and the viscosity coefficients are given in the scheme of de Groot and Mazur (34), whose viscosity coefficients are related to ours by

$$\eta_1' = \eta_1, \qquad \eta_2' = (\eta_1 + \eta_3)/2, \qquad \eta_3' = \eta_2,$$

$$\eta_4' = \eta_5, \text{ and } \qquad \eta_5' = -\eta_4,$$

where the prime denotes coefficients in the scheme of de Groot and Mazur. The magnitudes and shapes of the curves are quite similar, but the theoretical maxima and half-saturation values occur at a value of β_D which is an order of magnitude too low. The discrepancy could conceivably be eliminated by enlarging the expansion set. This problem is considered in conjunction with the perturbation solution.

In Figs. 16 and 17 we show the shear viscosity coefficients as functions of β for $\langle\sigma\rangle=3.24\pi\text{Å}^2$ and R=1.1 and 1.2. Here we have included all the $\underset{\approx}{\psi}_i$ expansion terms. Only the second-order results are shown, since the third-order contribution is at most only about 0.4% lower than the second-order, indicating that the convergence is very rapid. The fourth-order contribution from $\underset{\approx}{\psi}_5$ only raises the third-order contribution by at most 0.01%, so this term is neglible. The effect of $\underset{\approx}{\psi}_4$ is also very small. Its contribution is less than 1%, but it does make $\Delta\eta_1$ nonzero. However, this coefficient is a factor of 100 smaller than the maximum value of the other coefficients and would appear simply as $\Delta\eta_1=0$ on the graphical scale shown.

For this same expansion set we show in Figs. 18 and 19 the change in the bulk viscosity, $\Delta\kappa$, and the coupling coefficients as functions of the field. The convergence is not as rapid as with the shear viscosity. For $\Delta\kappa$ the third-order contribution lowers the second-order result by about 15%, while the fourth-order contribution from $\underset{\approx}{\psi}_5$ is graphically negligible on our scale. The third-order contribution tends to destroy a "hump" present in the second-order expressions for the coupling coefficients, and it lowers the second-order contribution by about 10%.

In Figs. 20 and 21 we show the results of the shear viscosity using the additional Sonine polynomials. Only the dominant, second-order contribution is shown. We see that the additional polynomials have little effect as was also found in the rough-sphere model calculations of McCourt, Knaap, and Moraal (14). Hence we are unable to improve the agreement between experiment and theory by enlarging the expansion set. The dominant $\underset{\approx}{\psi}_3$ term has no large spherical contribution associated with its collision integrals. Presumably, this means that a better molecular interaction model is required to obtain satisfactory agreement, and hence that the viscosity offers a critical test of the model.

In Fig. 22 we compare the shear viscosity of CO for the electric and magnetic field cases. We only plot the exact solution since for the graphical scale used, it is indistinguishable from the second-order solution. We use the same R and $\langle\sigma\rangle$ values as for the thermal conductivity. We do not expect these results to agree with experiment for reasons discussed previously. However, the magnitude could be fit experimentally for CO but not the half-saturation value of β. Finally we note that the order in which $\Delta\eta_2$ and $\Delta\eta_3$ reach saturation is reversed from the order found in a magnetic field.

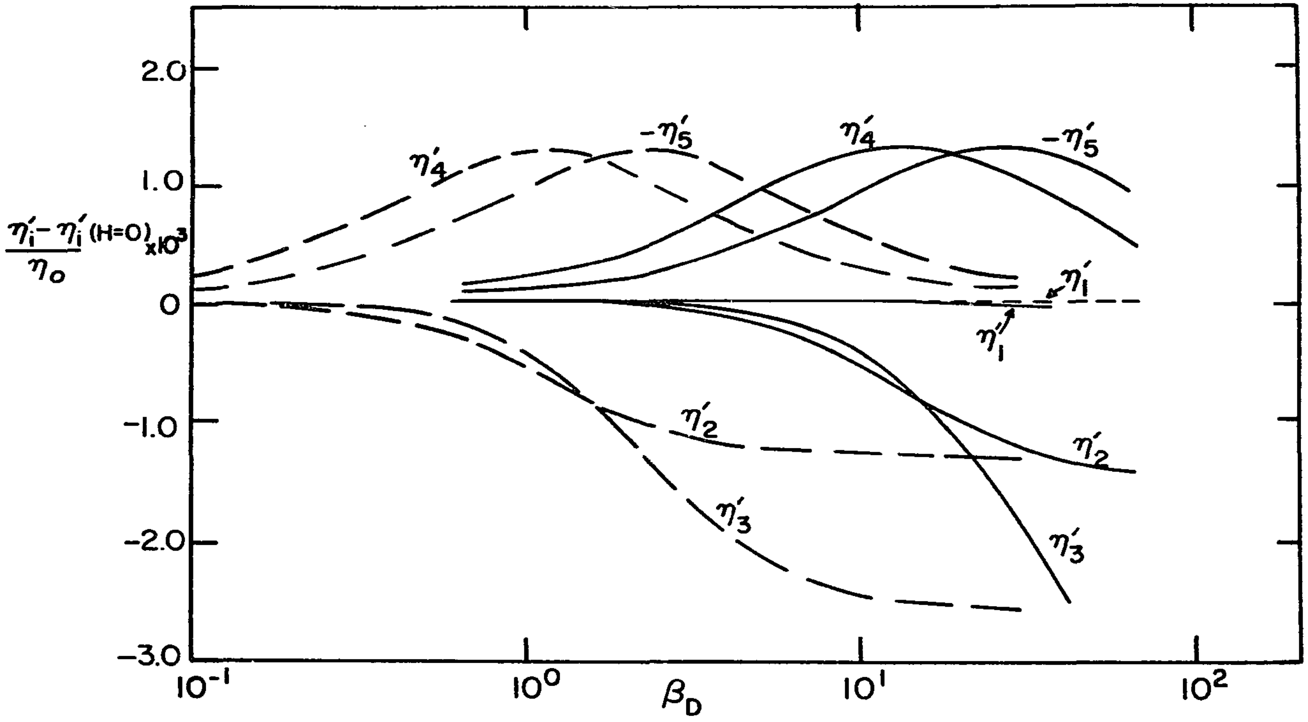


Fig. 15. The dashed curves are the calculated values of the five shear viscosity coefficients as functions of β_D. The solid curves are the experimental viscosity coefficients.

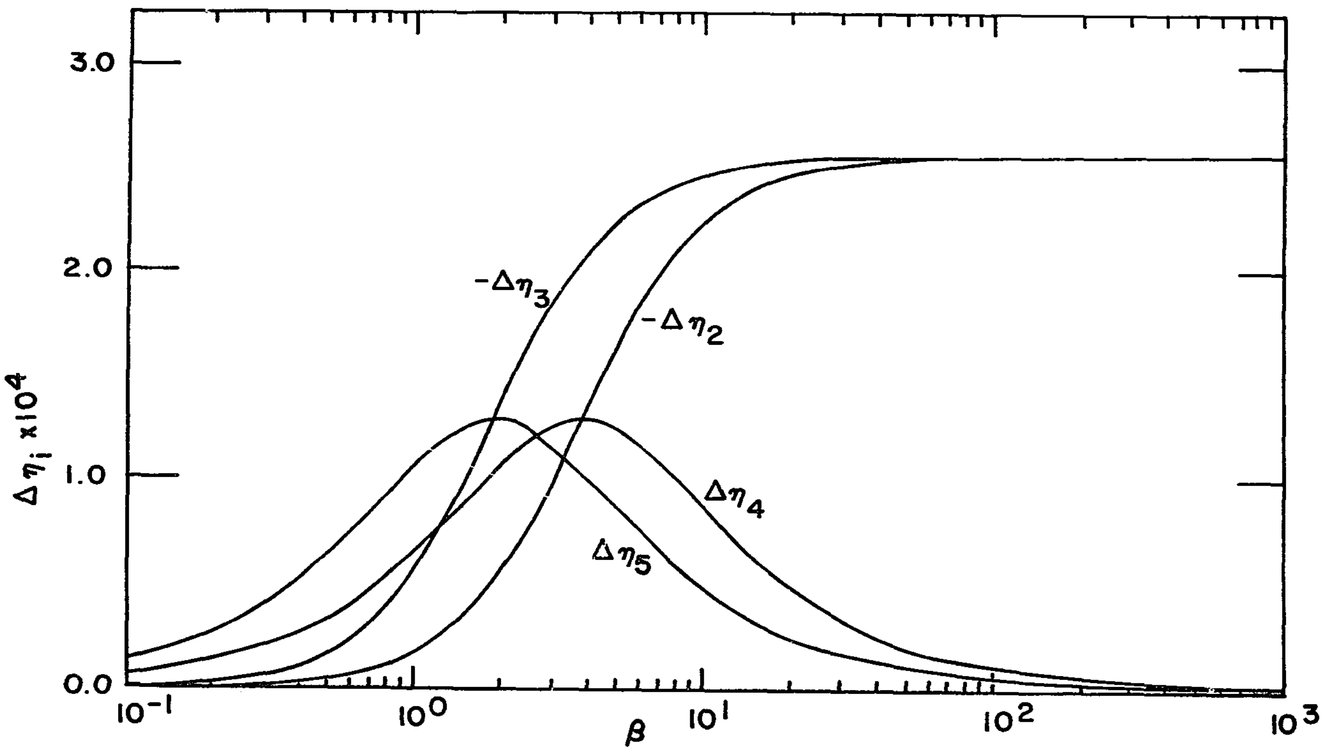


Fig. 16. The change in the shear viscosity, $\Delta\eta_i$, is in units of $(mkT/\pi)^{1/2}/2d^2$ and R=1.1.

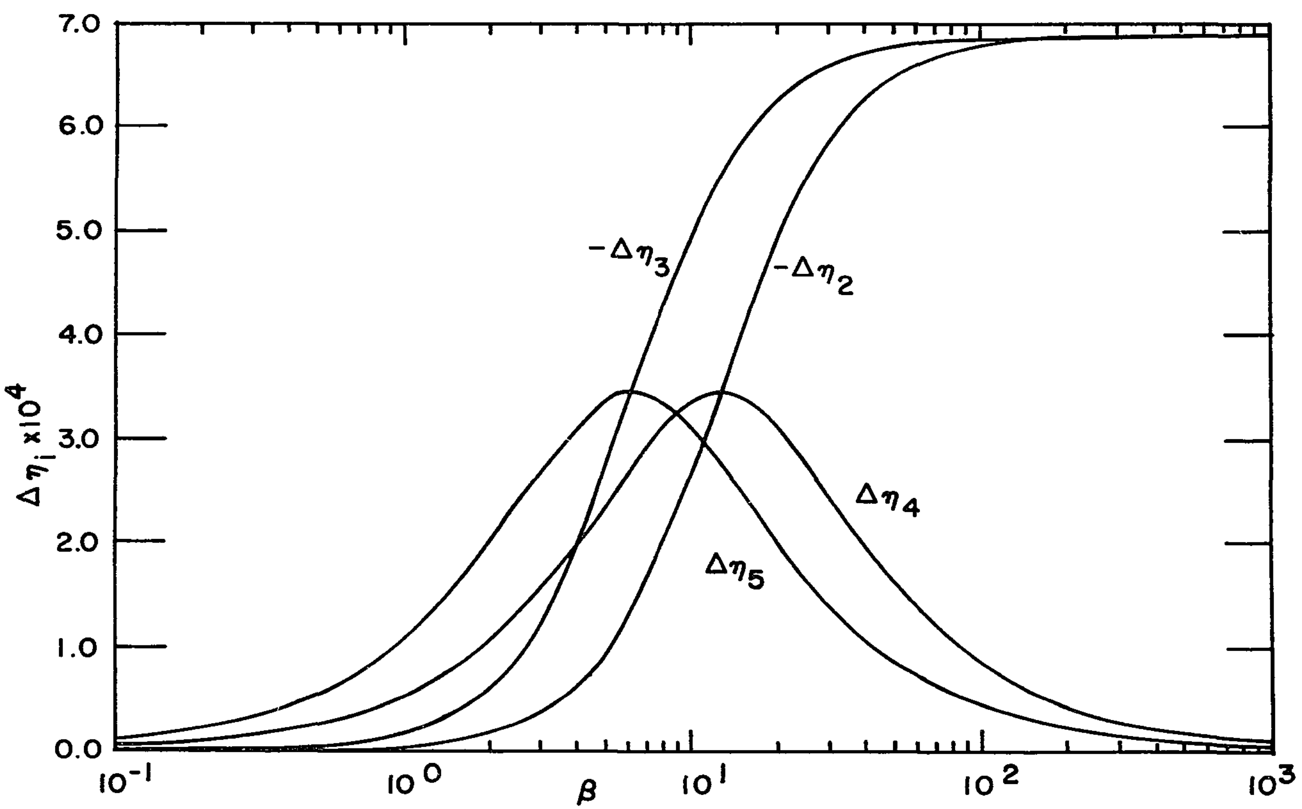


Fig. 17. The shear viscosity is for R=1.2.

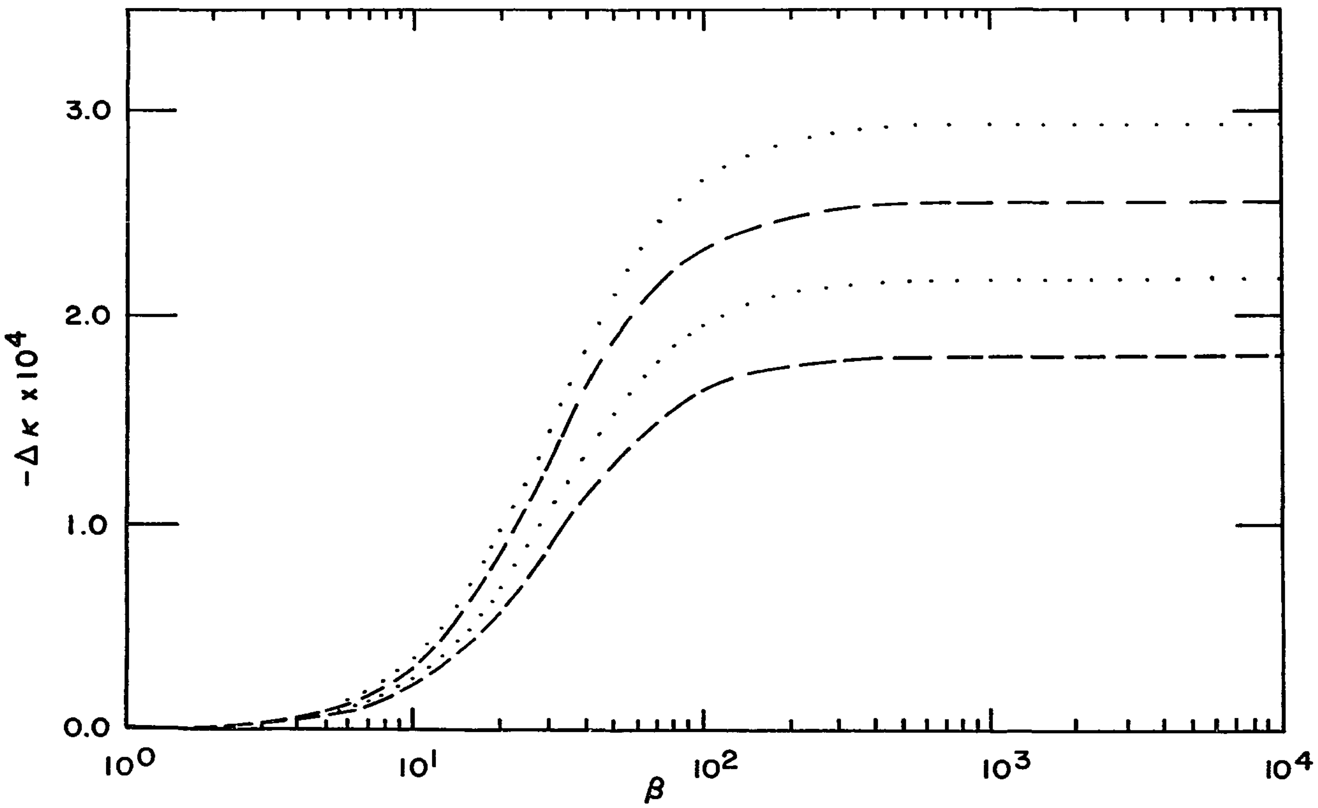


Fig. 18. The bulk viscosity is given in units of $(mkT/\pi)^{1/2}/2d^2$. The upper curves are for R=1.1 and the lower curves are for R=1.2. The dotted curves are the second-order calculations and the dashed curves are the third-order calculations.

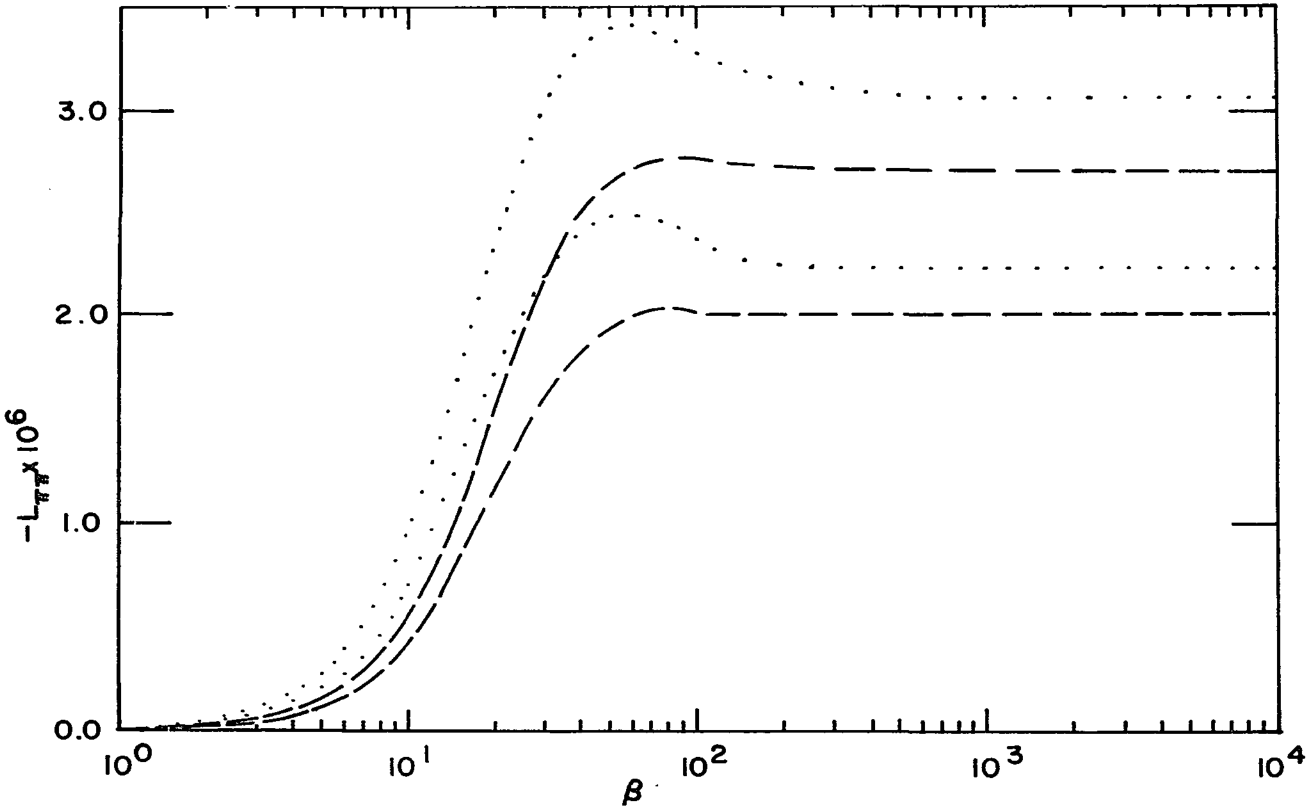


Fig. 19. The coupling coefficient is in units of $(mkT/\pi)^{1/2}/2d^2$. The upper curves are for R=1.2 and the lower curves are for R=1.1. The dotted curves are the second-order calculations and the dashed curves are the third-order calculations.

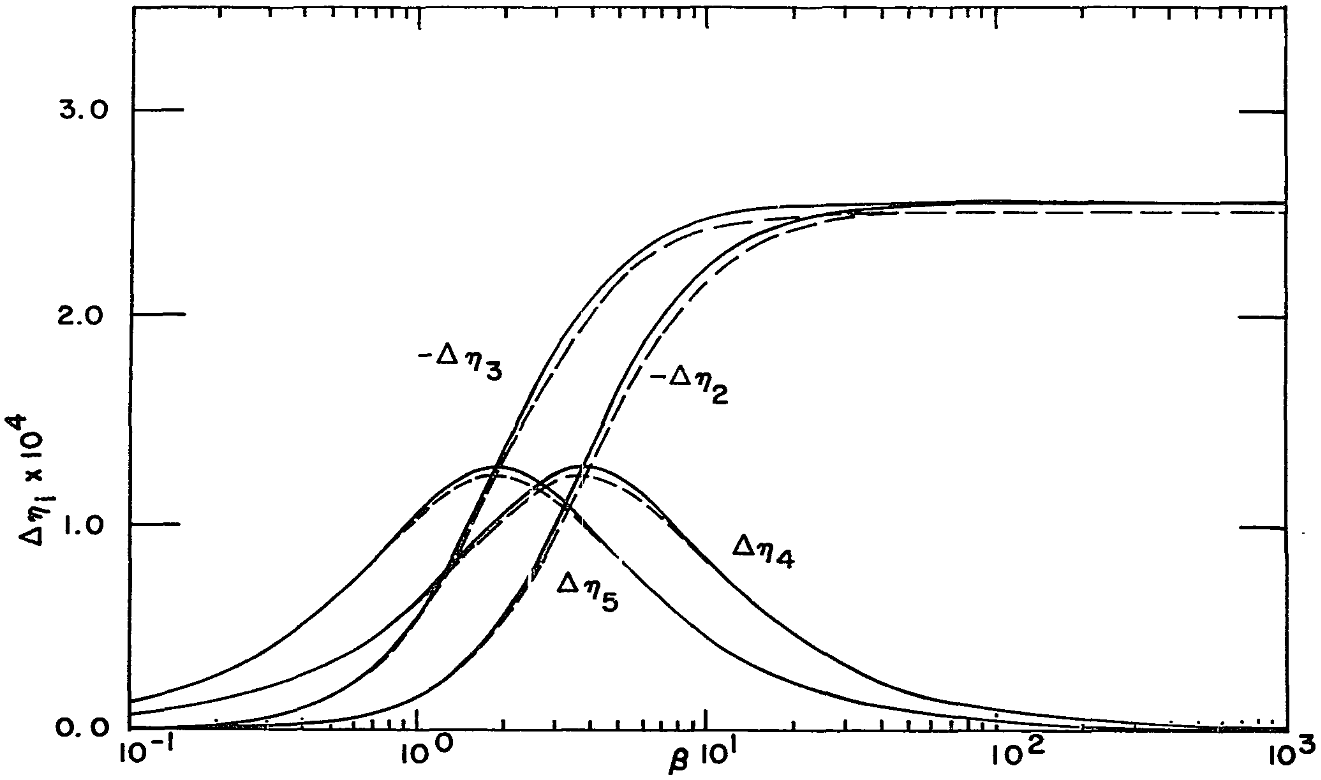


Fig. 20. The shear viscosity is given for R=1.1. The dashed curves are coefficients calculated using the additional Sonine polynomials in W^2 and Q^2 and the solid curves are without these polynomials.

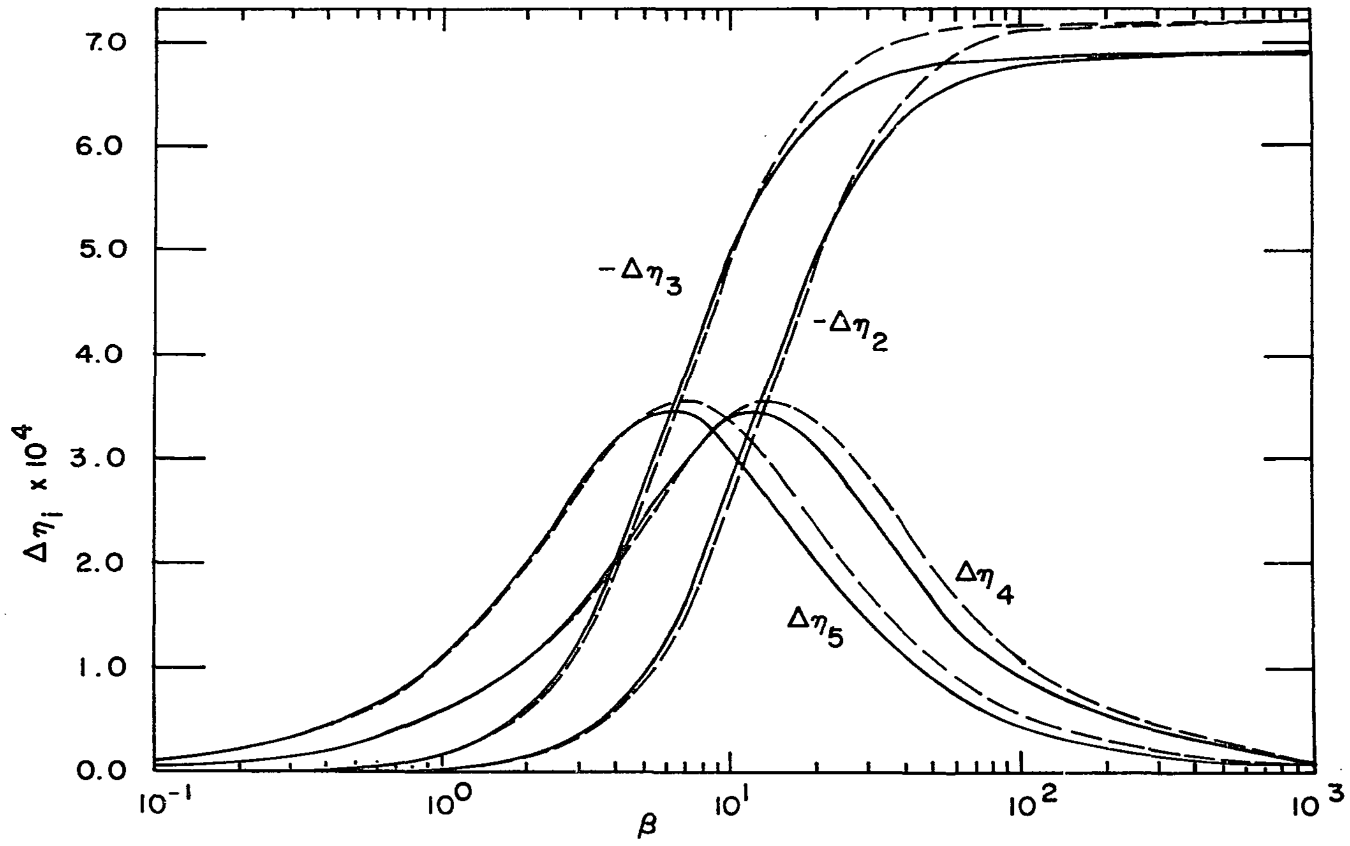


Fig. 21. The shear viscosity is given for R=1.2. The curve identification is the same as for Fig. 20.

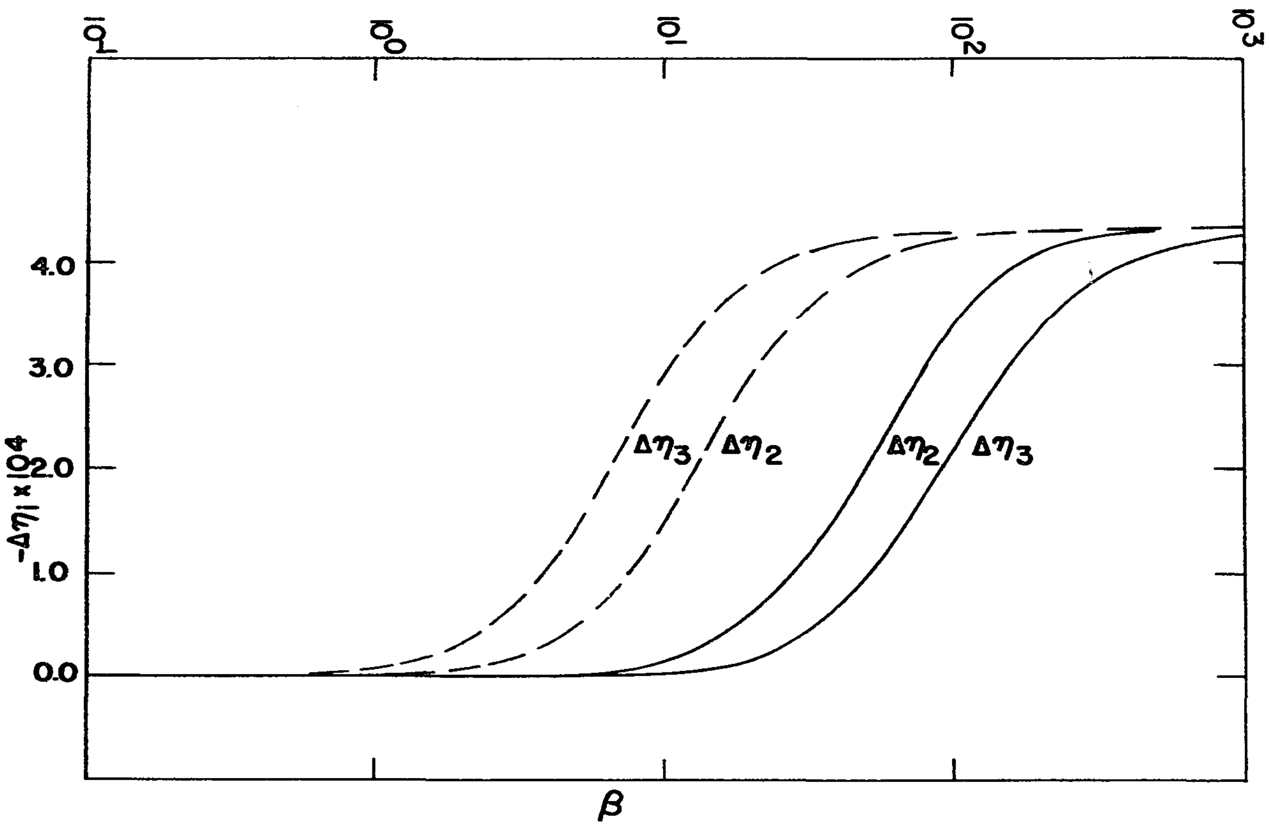


Fig. 22. The dashed curves are the magnetic field viscosity coefficients and the solid curves are the electric field coefficients.

APPENDIX A. COLLISION INTEGRALS

Here we outline the procedure for performing the angle and surface integrations of the collision integrals for the ellipsoid and spherocylinder models. The collision integrals $(\underset{\approx}{\Psi}^i, \underset{\approx}{\Psi}^j)$, representing $\underset{\approx}{h}_{ij}$ or $\underset{\approx}{b}_{ij}$, are defined by

$$(\underset{\approx}{\Psi}^i, \underset{\approx}{\Psi}^j) = \int d\hat{e}_1 d\hat{e}_2 \int d\hat{k}\, \delta(\hat{k}, \hat{e}_1, \hat{e}_2) \underset{\approx}{\ell}^{(i,j)}, \qquad \text{A.1}$$

where

$$\underset{\approx}{\ell}^{(i,j)} = -(2\pi n)^{-2} \int d\underset{\sim}{c}_1 d\underset{\sim}{c}_2 f_1^{(0)} f_2^{(0)} \delta(\hat{M}_1 \cdot \hat{e}_1) \delta(\hat{M}_2 \cdot \hat{e}_2) \hat{k} \cdot \underset{\sim}{g} \underset{\approx}{\Psi}^{it}$$
$$\times [\underset{\hat{k}\cdot \underset{\sim}{g}>0}{\underset{\approx}{\Psi}_1'^j + \underset{\approx}{\Psi}_2'^j} + \underset{\hat{k}\cdot \underset{\sim}{g}<0}{\underset{\approx}{\Psi}_1^j + \underset{\approx}{\Psi}_2^j}].$$

A prescription for evaluating the $\underset{\approx}{\ell}^{(i,j)}$ has been given by Hoffman (20), and hence will not be given here. First we discuss the geometry of rigid convex bodies and then that of spherocylinders. This will allow us to obtain explicit expressions for the surface and orientation integrations. Lastly we tabulate all the collision integrals in terms of their integrands, which are obtained by taking certain contractions of the $\underset{\approx}{\ell}^{(i,j)}$.

Geometry of Rigid Convex Molecules

A point on the surface of a specified convex body of fixed orientation is uniquely determined by the unit vector

$\hat{k}$, which is normal to the surface at the point. We define the supporting function $h(\hat{k})$ by

$$h(\hat{k}) = \rho \cdot \hat{k}, \qquad \text{A.2}$$

where ρ is a vector from the origin (arbitrarily chosen) to the point on the surface. If we let θ and ϕ be the usual spherical polar angles of $\hat{k}$, defined with respect to some z-axis in the direction of a unit vector $\hat{e}$, then

$$\frac{\partial h}{\partial \theta} = \frac{\partial \rho}{\partial \theta} \cdot \hat{k} + \rho \cdot \frac{\partial \hat{k}}{\partial \theta} = \rho \cdot \frac{\partial \hat{k}}{\partial \theta} \qquad \text{A.3}$$

and

$$\frac{\partial h}{\partial \phi} = \frac{\partial \rho}{\partial \phi} \cdot \hat{k} + \rho \cdot \frac{\partial \hat{k}}{\partial \phi} = \rho \cdot \frac{\partial \hat{k}}{\partial \phi}, \qquad \text{A.4}$$

since any infinitesimal change in ρ is perpendicular to $\hat{k}$. Now $\frac{\partial \hat{k}}{\partial \theta} = \hat{\theta}$ and $\frac{\partial \hat{k}}{\partial \phi} = \hat{\phi} \sin\theta$, where $\hat{\theta}$ and $\hat{\phi}$ are unit vectors orthogonal to $\hat{k}$ and each other. Thus we can write ρ as

$$\rho = \hat{k}h + \hat{\theta}(\rho \cdot \hat{\theta}) + \hat{\phi}(\rho \cdot \hat{\phi}) = \hat{k}h + \hat{\theta}\frac{\partial h}{\partial \theta} + (\hat{\phi}/\sin\theta)\frac{\partial h}{\partial \phi} \qquad \text{A.5}$$

or

$$\rho = \hat{k}h + \frac{\partial h}{\partial \hat{k}}, \qquad \text{A.6}$$

where

$$\frac{\partial}{\partial \hat{k}} = \hat{\theta}\frac{\partial}{\partial \theta} + (\hat{\phi}/\sin\theta)\frac{\partial}{\partial \phi}.$$

The element of surface area, $S^{(2)}$, on the body is given per unit solid angle by the determinant of $\frac{\partial \rho}{\partial \hat{k}}$ in the subspace normal to $\hat{k}$. This quantity can be expressed as follows:

$$S^{(2)} = -(1/2)\underset{\approx}{G}\odot^{2}\underset{\approx}{G}, \qquad \text{A.7}$$

where

$$\underset{\approx}{G} = h\underset{\approx}{V}_{\hat{k}} + \frac{\partial^{2}h}{\partial\hat{k}^{2}}\cdot\underset{\approx}{V}_{\hat{k}} \qquad \text{A.8}$$

and

$$\underset{\approx}{V}_{\hat{k}} = \hat{\theta}\hat{\phi} - \hat{\phi}\hat{\theta} = -\hat{k}\times\underset{\approx}{\delta}^{(1)}. \qquad \text{A.9}$$

The criterion for convexity is that $S^{(2)}$ be nonzero.

At any given instant two rigid convex molecules can at most be in contact at a single point, and at that point their surface normals are antiparallel. The volume excluded to the center of mass of the second molecule by the presence of the first (both molecules held with fixed orientations) is itself a convex body. The vector, ρ_{x}, to a point on this surface, measured from the origin of the first molecule, is given by $\rho_{x} = \rho_{1} - \rho_{2}$. For convenience we have taken the origin of each body to be its mass center. The supporting function $h_{x}(\hat{k})$ (the normal to this excluded volume being parallel to $\hat{k}$) of the excluded volume is given by

$$h_{x}(\hat{k}) = h_{1}(\hat{k}) + h_{2}(-\hat{k}), \qquad \text{A.10}$$

where it is understood that these quantities are functions of orientation as well as of $\hat{k}$.

For molecular models with C_{∞} symmetry, the supporting function is only a function of the angle between $\hat{k}$ and the symmetry axis, since h, the projection of $\wp$ on $\hat{k}$, is invariant to rotations about the symmetry axis. Hence, if we choose $\hat{e}$ to be along the symmetry axis, then $\wp$ becomes

$$\wp = h(x)\hat{k} + \underset{\approx}{U}_{\hat{k}}^{(2)} \cdot \hat{e}h'(x), \qquad \text{A.11}$$

where $x=\hat{k}\cdot\hat{e}$, $\underset{\approx}{U}_{\hat{k}}^{(2)} = \underset{\approx}{\delta}^{(1)} - \hat{k}\hat{k}$, and $h'(x) = dh/dx$. The last term of equation A.11 arises from a change of variable,

$$\frac{\partial}{\partial \hat{k}} = \frac{\partial}{\partial \hat{k}}(\hat{k}\cdot\hat{e})\frac{\partial}{\partial(\hat{k}\cdot\hat{e})} = \underset{\approx}{U}_{\hat{k}}^{(2)} \cdot \hat{e}\frac{\partial}{\partial(\hat{k}\cdot\hat{e})}.$$

The supporting function for the excluded volume then becomes

$$h_x = h(x_1) + h(-x_2) = h_1 + h_2. \qquad \text{A.12}$$

If we now evaluate the surface element of the excluded volume, we obtain

$$S_x^{(2)} = -(1/2)\underset{\approx}{G}\odot^2\underset{\approx}{G} = g^2 + g[(1-x_1^2)h_1'' + (1-x_2^2)h_2''] +$$
$$(1-x_1^2)(1-x_2^2)\sin^2\alpha\, h_1''h_2'', \qquad \text{A.13}$$

where α is the angle between the projections of $\hat{e}_1$ and $\hat{e}_2$ in the plane perpendicular to $\hat{k}$, $g = h_x - x_1h_1' + x_2h_2'$, and $h''(x) = d^2h/dx^2$.

The projection of a convex body onto a plane is itself a convex figure. For bodies with C_∞ symmetry the supporting function, h_p, for this plane figure is given by

$$h_p(\hat{n}\cdot\hat{e}_\perp) = h(\hat{k}\cdot\hat{e})_{\hat{a}\cdot\hat{k}=0} = h((\hat{n}\cdot\hat{e}_\perp)(1 - (\hat{e}\cdot\hat{a})^2)^{1/2}), \qquad \text{A.14}$$

where $\hat{n}$ is a normal to the perimeter of the projection and equals $\hat{k}$ for all points on the body such that $\hat{k}\cdot\hat{a}=0$. Here $\hat{a}$ is a unit vector normal to the projection plane, and

$$\hat{e}_\perp = (\hat{e} - (\hat{e}\cdot\hat{a})\hat{a})/(1 - (\hat{e}\cdot\hat{a})^2)^{1/2}$$

is the unit vector along the projection of $\hat{e}$ in the plane. If ω is the angle between $\hat{n}$ and $\hat{e}$, then $\underset{\sim}{R}$, the projection of $\underset{\sim}{\rho}$ in the plane, is given by

$$\underset{\sim}{R} = \hat{n}h_p + \hat{\omega}\frac{\partial}{\partial\omega}h_p = \hat{n}h_p + \frac{\partial}{\partial\hat{n}}h_p. \qquad \text{A.15}$$

Thus the element of arc length, $S^{(1)}$, is given by the determinant of $\frac{\partial \underset{\sim}{R}}{\partial\hat{n}}$ in the subspace normal to $\hat{n}$, or by

$$S^{(1)} = h_p + \frac{\partial^2}{\partial\omega^2}h_p. \qquad \text{A.16}$$

The area, $\sigma(\hat{a})$, of the projection is given by

$$\sigma(\hat{a}) = (1/2)\int d\hat{n}S^{(1)}h_p, \qquad \text{A.17}$$

and the average cross-sectional area, $\langle\sigma\rangle$, is

$$\langle\sigma\rangle = (4\pi)^{-1}\int d\hat{a}\sigma(\hat{a}) = (8\pi)^{-1}\int d\hat{a}\int d\hat{k}\delta(\hat{a}\cdot\hat{k})h(x)[h(x) - xh'(x) + (1 - x^2 - (\hat{a}\cdot\hat{e})^2)h''(x)]. \qquad \text{A.18}$$

This expression can be simplified to give

$$\langle\sigma\rangle = (\pi/2)\int dxh(x)[h(x) - xh'(x) + (1/2)(1-x^2)h''(x)]. \qquad \text{A.19}$$

We are now in a position to carry out the surface and orientation integrations of the collision integrals for rigid, convex molecular models with C_∞ symmetry. The supporting function for the ellipsoid of revolution is

$$h(x) = [a^2 + x^2(b^2 - a^2)]^{1/2}, \qquad \text{A.20}$$

where b is the length of the major axis and a is the length of the minor axis. For a loaded ovaloid, i.e., the mass center is shifted along the symmetry axis from the geometrical center,

$$h_L(x) = h(x) + \delta x, \qquad \text{A.21}$$

where $\delta\hat{e}$ is the vector from the shifted center to the original center. The two molecular parameters, a and b, will often be replaced by $R = a/b$ and $\langle\sigma\rangle$ in our considerations, since R gives a measure of the nonsphericity and $\langle\sigma\rangle$ is a measure of the effective cross section or "size". For the prolate ellipsoid

$$\langle\sigma\rangle = \pi a^2/2 + \pi ab^2\tan^{-1}[(b^2-a^2)^{1/2}/a]/2(b^2-a^2)^{1/2}. \qquad \text{A.22}$$

Hence, for any desired "size" and nonsphericity, we can obtain the appropriate a and b.

Since $\underset{\approx}{\mathscr{F}}^{(i,j)} = \underset{\approx}{\mathscr{F}}^{(i,j)}(x_1,x_2,\alpha)$, we can rewrite $(\underset{\approx}{\Psi}^i,\underset{\approx}{\Psi}^j)$ as

$$(\underset{\approx}{\Psi}^i,\underset{\approx}{\Psi}^j) = 8\pi^2\int_{-1}^{1}dx_1\int_{-1}^{1}dx_2\int_{0}^{2\pi}d\alpha S_X^{(2)}(x_1,x_2,\alpha)\underset{\approx}{\mathscr{F}}^{(i,j)}(x_1,x_2,\alpha). \text{A.23}$$

The integration over α can be done analytically, since the supporting function does not depend on α. The remaining integral cannot, in general, be done analytically, and hence must be calculated numerically. A similar formula for $(\underset{\approx}{\Psi}^{i},\underset{\approx}{\Psi}^{j})$ can be obtained for the loaded spherocylinder. Since the spherocylinder and its excluded volume are not convex, the form of the equation is more complex. However, the resulting numerical calculations for the transport coefficients using the spherocylinder model are only slightly different from those using an ellipsoid of the same "size" and "nonsphericity". A detailed analysis of the spherocylinder collision integrals has already been given by Klein et al. (18), so the spherocylinder formula for $(\underset{\approx}{\Psi}^{i},\underset{\approx}{\Psi}^{j})$ will not be given here.

Tabulation of Collision Integrals

The tensors $\underset{\approx}{h}_{ij}$ and $\underset{\approx}{b}_{ij}$ are linear combinations of a set of linearly independent isotropic tensors. Here we give the required expansions along with explicit expressions for the expansion coefficients. The necessary isotropic tensors are given in the next section. The tensor integrals are related by $\underset{\approx}{h}_{ij}=\underset{\approx}{h}^{t}_{ij}$ and $\underset{\approx}{b}_{ij}=\underset{\approx}{b}^{t}_{ij}$, so only the integrals for $i \geq j$ will be given. This relationship differs from that of Hoffman and Dahler (17) in the definition of the transpose. For integrals odd in $\underset{\sim}{Q}$ they give the relationship with a minus sign.

The collision integrals are expanded in isotropic tensors as follows:

$$\underset{\approx}{h}_{ij} = h_{ij}\underset{\approx}{\delta}^{(1)} \qquad i,j=1,2,$$

$$\underset{\approx}{h}_{i4} = h_{i4}\,\underset{\approx}{\epsilon} \qquad i=1,2,$$

$$\underset{\approx}{h}_{i5} = 0 \qquad i=1,2,3,$$

$$\underset{\approx}{h}_{i3} = h_{i3}\underset{\approx}{\delta}^{(2)} \qquad i=1,2,$$

$$\underset{\approx}{h}_{33} = h^1_{33}\underset{\approx}{\delta}^{(1,2)} + h^2_{33}\underset{\approx}{T}_1^{(6)},$$

$$\underset{\approx}{h}_{34} = h_{34}\underset{\approx}{T}^{(5)},$$

$$\underset{\approx}{h}_{44} = h^1_{44}\underset{\approx}{\delta}^{(1,1)} + h^2_{44}\underset{\approx}{T}^{(4)},$$

$$\underset{\approx}{h}_{45} = h_{45}\underset{\approx}{\delta}^{(3)},$$

$$\underset{\approx}{h}_{55} = h_{55}\underset{\approx}{\delta}^{(1,3)},$$

$$\underset{\approx}{b}_{1i} = 0 \qquad i=2,3,5,$$

$$\underset{\approx}{b}_{14} = b_{14}\underset{\approx}{\delta}^{(2)},$$

$$\underset{\approx}{b}_{ij} = b_{ij}\underset{\approx}{\delta}^{(2)} \qquad i,j=2,3,$$

$$\underset{\approx}{b}_{i4} = b_{i4}\underset{\approx}{T}_1^{(6)} \qquad i=2,3,$$

$$\underset{\approx}{b}_{i5} = b_{i5}\underset{\approx}{T}_1^{(5)} \qquad i=2,3,$$

$$\underset{\approx}{b}_{44} = b^1_{44}\underset{\approx}{\delta}^{(2,2)} + b^2_{44}\underset{\approx}{T}_1^{(8)} + b^3_{44}\underset{\approx}{T}_2^{(8)} + b^4_{44}\underset{\approx}{T}_3^{(8)} + b^5_{44}\underset{\approx}{T}_4^{(8)},$$

$$\underset{\approx}{b}_{54} = b^1_{54}\underset{\approx}{T}_1^{(7)} + b^2_{54}\underset{\approx}{T}_2^{(7)} + b^3_{54}\underset{\approx}{T}_3^{(7)},$$

$$\underset{\approx}{b}_{55} = b^{1}_{55}\underset{\approx}{\delta}^{(2,1)} + b^{2}_{55}\underset{\approx}{T}{}'^{(6)}_{1},$$

$$\underset{\approx}{b}_{6i} = 0 \qquad i=2,3,7,$$

$$\underset{\approx}{b}_{66} = b_{66}\underset{\approx}{\delta}^{(1)},$$

$$\underset{\approx}{b}_{7i} = 0 \qquad i=2,3,6,$$

$$\underset{\approx}{b}_{77} = b_{77}\underset{\approx}{\delta}^{(3)},$$

and

$$\underset{\approx}{b}_{ij,km} = b_{ij,km}\underset{\approx}{\delta}^{(2)}.$$

The scalar parts of the collision integrals are linear combinations of the integrals

$$TI = (2\pi)^{-1}\int_{-1}^{1}dx_1\int_{-1}^{1}dx_2\int_{0}^{2\pi}d\alpha\, S_x^{(2)}(x_1,x_2,\alpha)\tilde{T}I, \qquad \text{A.24}$$

where

$$\tilde{T}1 = 1/D, \qquad \tilde{T}2 = 1/D^3,$$

$$\tilde{T}3 = a_1^2(\hat{k}\cdot\hat{e}_2)^2/D^5, \qquad \tilde{T}4 = a_1^2/D,$$

$$\tilde{T}5 = a_1^2/D^3, \qquad \tilde{T}6 = a_1^2/D^5,$$

$$\tilde{T}7 = (\underset{\sim}{a}_1\cdot\hat{e}_2)^2/D^5, \qquad \tilde{T}8 = a_1^4/D^3,$$

$$\tilde{T}9 = a_1^4/D^5, \qquad \tilde{T}10 = a_1^4/D^7,$$

$$\tilde{T}11 = (\underset{\sim}{a}_1\cdot\underset{\sim}{a}_2)^2/D^3, \qquad \tilde{T}12 = (\underset{\sim}{a}_1\cdot\underset{\sim}{a}_2)^2/D^5,$$

$\tilde{T}13 = (\underset{\sim}{a}_1 \cdot \underset{\sim}{a}_2)^2/D^7,$ $\tilde{T}14 = a_1^2 a_2^2/D^3,$

$\tilde{T}15 = a_1^2 a_2^2/D^5,$ $\tilde{T}16 = a_1^2 a_2^2/D^7,$

$\tilde{T}17 = (\hat{k} \cdot \hat{e}_1)^2/D,$ $\tilde{T}18 = (\hat{k} \cdot \hat{e}_2)^2/D^3,$

$\tilde{T}19 = (\hat{k} \cdot \hat{e}_1)^2 (\hat{k} \cdot \hat{e}_2)^2/D^3,$ $\tilde{T}20 = (\hat{k} \cdot \hat{e}_1)^4/D^3,$

$\tilde{T}21 = (\hat{k} \cdot \hat{e}_1)\hat{k} \cdot (\hat{e}_1 \times \underset{\sim}{a}_1)/D^4,$ $\tilde{T}22 = (\hat{e}_1 \cdot \hat{e}_2)^2/D^3,$

$\tilde{T}23 = (\underset{\sim}{a}_1 \cdot \hat{e}_2)^2/D^3,$ $\tilde{T}24 = a_1^2 (\hat{k} \cdot \hat{e}_1)^2/D^3,$

$\tilde{T}25 = a_1^2 (\hat{k} \cdot \hat{e}_1)^2/D^5,$ $\tilde{T}26 = a_1^2 (\hat{k} \cdot \hat{e}_2)^2/D^3,$

$\tilde{T}27 = (\hat{k} \cdot \hat{e}_1)\hat{k} \cdot (\hat{e}_1 \times \underset{\sim}{a}_1)/D^2,$ $\tilde{T}28 = 1/D^5,$

$\tilde{T}29 = (\hat{k} \cdot \hat{e}_1)^2 (\hat{k} \cdot \hat{e}_2)^2/D,$ $\tilde{T}30 = (\hat{e}_1 \cdot \hat{e}_2)^2/D,$

$\tilde{T}31 = 1/D^7,$ $\tilde{T}32 = (\underset{\sim}{a}_1 \cdot \hat{e}_2)^2/D,$

$\tilde{T}33 = (\hat{k} \cdot \hat{e}_1)^2/D^5,$ $\tilde{T}34 = a_1^2 a_2^2 (\hat{e}_1 \cdot \hat{e}_2)^2/D^3,$

$\tilde{T}35 = a_1^6/D^5,$ $\tilde{T}36 = a_1^2 (\underset{\sim}{a}_2 \cdot \hat{e}_1)^2/D^3,$

$\tilde{T}37 = a_1^4 (\hat{k} \cdot \hat{e}_1)^2/D^5,$ $\tilde{T}38 = a_1^6/D^7,$

$\tilde{T}39 = a_1^2 a_2^2 (\hat{k} \cdot \hat{e}_1)^2/D^5,$ $\tilde{T}40 = a_1^4 a_2^2/D^5,$

$\tilde{T}41 = a_1^4/D^7,$ $\tilde{T}42 = a_1^2 a_2^2 (\underset{\sim}{a}_1 \cdot \hat{e}_2)^2/D^5,$

$\tilde{T}43 = a_1^4 a_2^4/D^7,$ $\tilde{T}44 = a_1^2 a_2^2 (\underset{\sim}{a}_1 \cdot \underset{\sim}{a}_2)^2/D^7,$

$\tilde{T}45 = a_1^2 (\underset{\sim}{a}_2 \cdot \hat{e}_1)^2/D^5,$ $\tilde{T}46 = a_1^2 (\underset{\sim}{a}_1 \cdot \hat{e}_2)^2/D^5,$

$\tilde{T}47 = (\underset{\sim}{a}_1 \cdot \underset{\sim}{a}_2)^2/D,$ $\qquad$ $\tilde{T}48 = a_1^4 a_2^2/D^7,$

$\tilde{T}49 = (\underset{\sim}{a}_1 \cdot \hat{e}_2)(\underset{\sim}{a}_2 \cdot \hat{e}_1)(\hat{e}_1 \cdot \hat{e}_2)/D,$

$\tilde{T}50 = (\underset{\sim}{a}_1 \cdot \hat{e}_2)(\underset{\sim}{a}_2 \cdot \hat{e}_1)(\hat{e}_1\ \hat{e}_2)/D^3,$

$D = (1 + a_1^2 + a_2^2)^{1/2},$

and

$\underset{\sim}{a}_i = (m/2I)^{1/2} \rho_i \times \hat{k}.$

The collision integrals in units of $(\pi kT/m)^{1/2}$ are

$h_{11} = (15T1 - 11T2)/6,$

$h_{22} = (T1 + 6T4 - 6T8 - 4T5 + 27T9/4 - 27T15/4)/3,$

$h_{12} = -5T5/3,$

$h_{13} = -2T5/15,$

$h_{23} = -(T1/3 - T17 - .5T24 + .5T26 - 4.5T9 + 8T5/3 +$
$\quad 4.5T15)/10,$

$h_{14} = h_{24} = 0,$

$h_{33}^1 = (-12Z1 + 11Z2)/210,$

$Z1 = 14T4/3 + 19T1/18 - T17/3 - 8T8/3 - 26T5/9 + 7T24/3 -$
$\quad .5T29 - T26/3 + 1.5T9 - 1.5T15,$

$Z2 = 17T1/6 + 14T4 + 9T9 - 8T8 - 28T5/3 - 13.5T12 +$

$T23 - .5T30 + 4.5T15,$

$h^2_{33} = (6Z1 - 2Z2)/35,$

$h_{34} = (\pi)^{1/2}T27/30,$

$h^1_{44} = (2Z4 - Z3)/15,$

$Z3 = .5T1 - .5T17 + T4,$

$Z4 = T1 + 3T4 - 2T5,$

$h^2_{44} = (3Z3 - Z4)/15,$

$h_{45} = (.2T1 - .6T17 - .5T5 - 1.1T24 + .4T8)/7,$

$h_{55} = (18T4 + 2.4T1 - 17.1T8 - 11.4T5 + 19.05T9 + 8.1T35 -$

$12T38 + 3T50)/21,$

$b_{11} = 6.5(T1 - T2),$

$b_{14} = (-T1/3 + T2 - 2T28/3 + 2T17 - 2T18)/4,$

$b_{22} = 2T1/3 - 4T2/15,$

$b_{33} = (14T4/3 - 8T8/3 - 4T11 + 4T14/3)/5,$

$b_{23} = 2(T1 - T2)/15,$

$b_{24} = (7T1/6 - 7T5/6 - 3.5T17 - 2T2/3 + 2T18 + 4T6/3)/140,$

b_{34} = (2.5T5 - 5.5T24 - 2T23 + 4T9/3 + 4T12 - 8T15/3)/140,

$b_{25} = b^2_{54} = 0$,

$b_{35} = (\pi)^{1/2}$T27/60,

b^1_{44} = (13R1/24 + 5R2/3 - 5R3/24 - 2R4 - .5R5)/105,

b^2_{44} = (19R1/6 + 13(R2 + R3)/24 - 3.5(R4 + R5))/105,

b^3_{44} = (13R1/24 - 5R2/24 + 5R3/3 - .5R4 - 2R5)/105,

b^4_{44} = (-7R1/2 - R2/2 - 2R3 + 4R4 + 8R5)/105,

b^5_{44} = (-7R1/2 - 2R2 - R3/2 + 8R4 + 4R5)/105,

R1 = F1 - 2F2/3 + F3/9,

R2 = F4 - F5/3 + F3/9,

R3 = F9 - 2F6/3 + F3/9,

R4 = F11 + SB, R5 = F10 + SB,

SB = -2(F7 + F8)/3 + 2(F6 + F2)/9 + F5/9 - F3/9,

F1 = 8(T1 - T17 + T18) - 3T20 - T19 + 16(T4 - T5) + 12(T24 - T8) + 4(T26 - T14 - T2),

F2 = 8T1 - 8T17 + 20T4 - 6T2 - 20T8 + 6T18 - 16T5 -

12T14 + 4T24 + 6T26 - 4T9 - 4T6 + 2T25 + 2T3 - 4T15,

F3 = 16T1 + 6T4 - 12T2 - 60T5 - 60T8 - 36T14 + 30T9 +
11T6 - 24T15 - 60T16 - 60T10,

F4 = 32T1 + 90T4 - 9T2 - 90T5 - 60T8 - T22 + 4T23 -
12T11 + 32.5T6 + 100T9 - 8T12 + 4T7 - 60T10 - 60T13,

F51 = 16T1 + 90T4 - 9T2 - 50T5 - 60T8 - T22 + 12T23 -
36T11 + 32.5T6 + 30T9 - 60T10 - 60T13 + 4T7 - 24T12,

F52 = 32T1 + 60T4 - 12T2 - 60T5 - 60T8 - 12T14 + 100T9 +
11T6 - 8T15 - 60T10 - 60T16,

F5 = F51 + F52,

F6 = 8T1 - 8T17 + 2T4 - 20T8 - 6T2 - 4T5 + 6T18 - 12T14 -
2T24 - 4T9 - 4T6 + 2T25 + 2T3 - 4T15,

F7 = 8T1 - 8T17 + 30T4 - 5T2 - 6.5T5 + 6T18 - T19 +
2T23 - 9.5T24 - 20T8 - 12T11 + 27(T6 - T25)/4 -
4T9 - 4T12,

F8 = 14T1 - 10T17 + 20T4 - 6T2 + 3.5T18 - 7.5T5 + 6T24 +
6T26 - 20T8 - 4T14 - 27T9/4 - 4T6 + 2T25 + 2T3,

$F9 = 8T1 - 8T17 + 16T4 - 4T2 + 8T18 - 3T20 - T19 -$

$2T8 - 8T5 + 8T24 - 4T14,$

$F10 = 8T1 - 8T17 + 16T4 - 4T2 + 8T18 - 3T20 - T19 - 2T8 -$

$2T5 + 2T24 - 4T11,$

$F11 = 14T1 - 10T17 + 30T4 - 5T2 + 6T818 - T19 - 20T8 -$

$4T11 - 20T5 + 9T24 + 13.5T9 - 27T25/4 + 27T6/4,$

$b^1_{54} = -(\pi)^{1/2}(14T27/3 - 2T21)/70,$

$b^3_{54} = -b^1_{54},$

$b^1_{55} = (-12AS + 11AT)/210,$

$b^2_{55} = (6AS - 2AT)/35,$

$AS = 10T4/3 + 47T1/18 - 7T17/6 - 26T5/9 - 5T2/9 +$

$T18/3 + 0.75T6,$

$AT = 10T4 + 20T1/3 - 4T2/3 - 40T5/3 + 4.5T6,$

$b_{66} = 2T4/3,$

$b_{77} = (12T4 - 11.4T8 + 5.4T35 + 3T99)/7,$

$b_{21,22} = 3.5b_{22} - X1,$

$X1 = (35T1/3 - 3.5T2 - 2T28/3)/5,$

$$b_{21,32} = 1.5b_{23} - X2,$$

$$X2 = (7T1/3 - 5T2/3 - 2T28/3 - 2T17 + 2T18)/10,$$

$$b_{31,22} = 3.5b_{23} - X3,$$

$$X3 = (14T5 + 2T6)/15,$$

$$b_{31,32} = 1.5b_{33} - X4,$$

$$X4 = (14T4 + 2T23 - 8T8 - 12T11 + T5 - 8T9/3 - 4T12 + 4T14 + 4T15/3)/10,$$

$$b_{22,22} = 49b_{22}/4 - 7X1 + (385T1/6 - 91T2/3 + 185T28/24 - 8T31)/5,$$

$$b_{22,32} = 21b_{23}/4 - 3.5X2 - 1.5X3 + (7T1/6 - 3.5T17 - T2 + 3T18 + 49T4/6 - 7T5/6 + 5T6 - T28/6 + T33/2)/5,$$

$$b_{32,32} = 9b_{33}/4 - 3X4 + (F51 - F3)/5,$$

$$b_{21,23} = b_{22} - X5,$$

$$X5 = (25T1/3 - 17T2/3 + 4T28/3)10,$$

$$b_{21,33} = 3b_{23} - X6,$$

$$X6 = (10T4/3 + 2T24 + 4T9/3)/5,$$

$b_{31,23} = b_{23} - X7,$

$X7 = (2T5 + 4T9/3 + 4T15/3)/10$

$b_{31,33} = 3b_{33} - X8,$

$X8 = (44T4/3 - 5T8 - 8T35/3 + 10T14/3 + 4T15/3 -$

$14T11 + T12 + T36)/5,$

$b_{22,23} = 3.5b_{22} - X1 - 3.5X5 + (35T1/3 - 7T2/2 -$

$143T28/12 - 55T5/3 + 133T6/12 + 25T31/4)/5,$

$b_{22,33} = 10.5b_{23} - 3.5X6 - 3X3 + (35T5/3 + 7T24 +$

$5T6/3 + 7T9/3 + T25 + 5T10)/5,$

$b_{32,23} = 1.5b_{23} - 1.5X7 - X2 + 0.2(F6 - F3/3),$

$b_{32,33} = 4.5b_{33} - 1.5X8 - 3X4 + (22T4 - 5T5 - 23T8/3 +$

$229T9/12 - 4T35 - 20T38 + 3T23 - T30/4 - 15T11 +$

$5T14 + 3T36 - 3T12 + 5T15/3 + T45 + T46 - 3T47 +$

$15T12 + 2T4 + 10T48)/5,$

$b_{23,23} = b_{22} - 2X5 + 0.2(F52 - F3/3),$

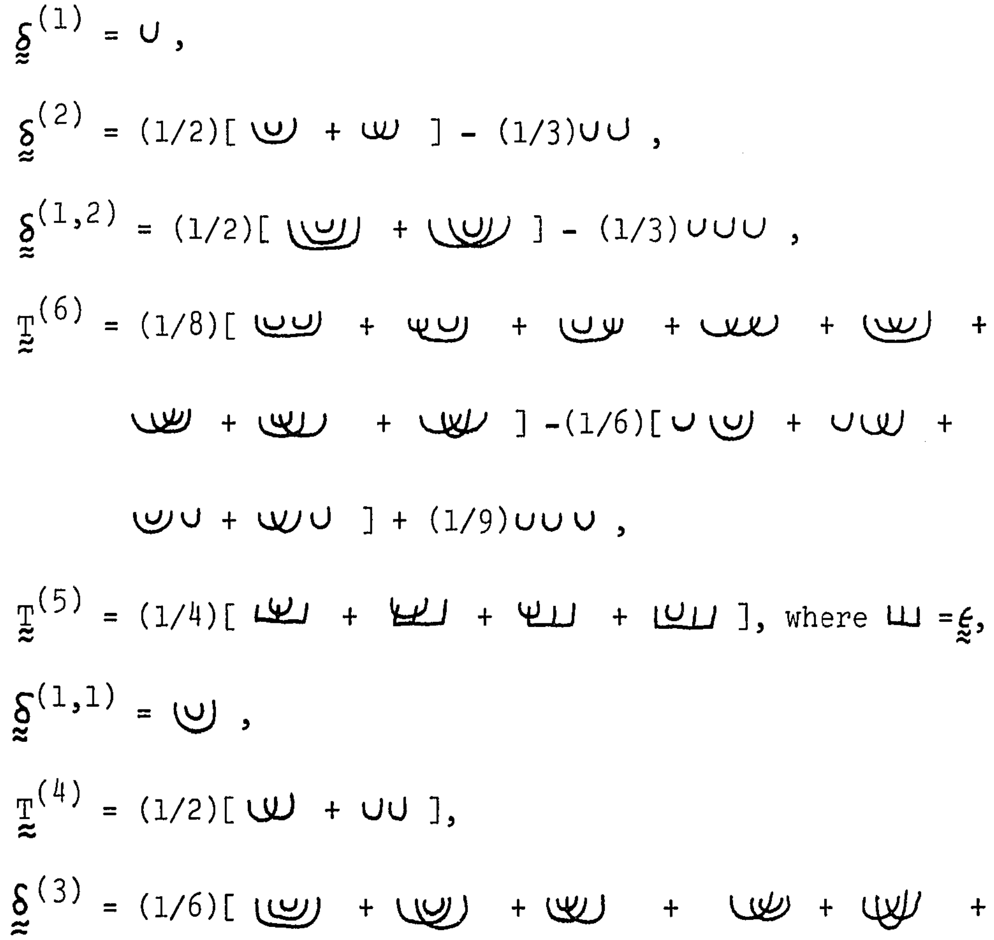
$b_{23,33} = 3b_{23} - X6 - 3X7 + (25T5/6 + 2.5T24 - 6T9 +$

$T37 + 10T38 + 5T15/3 + T39 + 10T48)/5,$

$$b_{33,33} = 9b_{33} - 6X8 + (76T4 - 218T8/3 + 409T35/6 - 40T41 + 25T14/3 + 6T36 - T34 - 48T11 + 12T12 + 20T40/3 + 4T42 - 60T44 + 20T43)/5.$$

Isotropic Tensors

Here we list the pertinent isotropic tensors needed for the collision integrals listed in the previous section. They are given in terms of $\cup$'s, where $\cup_{ij}=\delta_{ij}$. For example  $_{ijkm}=\delta_{im}\delta_{jk}$. The tensors are as follows:



 $] - (1/15)[$  $+$  $+$  $+$  $+$

 $+$  $+$  $+$  $+$  $],$

$\underset{\approx}{S}^{(1,3)} = (1/6)[$  $+$  $+$  $+$  $+$

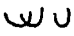
 $+$  $] - (1/15)[$  $+$  $+$

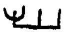
 $+$  $+$  $+$  $+$

 $+$  $+$  $],$

$\underset{\approx}{T}_1^{(6)} = (1/8)[$  $+$  $+$  $+$  $+$  $+$

 $+$  $+$  $] - (1/6)[$  $+$  $+$

 $+$  $+$  $+$  $] + (2/9)$  $,$

$\underset{\approx}{T}_1^{(5)} = (1/4)[$  $+$  $+$  $+$  $],$

$\underset{\approx}{S}^{(2,2)} = (1/4)[$  $+$  $+$  $+$  $] -$

$(1/6)[$  $+$  $+$  $+$  $] +$

$(1/9)$  $,$

$\underset{\approx}{T}_1^{(8)} = (1/4)[$  $+$  $+$  $+$  $] -$

$(1/6)[$  $+$  $+$  $+$  $] +$

$(1/9)$  $,$

$\underset{\approx}{T}_2^{(8)} = (1/4)[$  $+$  $+$  $+$  $] -$

(1/6)[ +  +  + ] +

(1/9)  ,

$\underset{\approx}{T}_3^{(8)}$ = (1/16)[ +  +  +  +

 +  +  +  +

 +  +  +  +

 +  +  + ] - $\underset{\approx}{T}$,

$\underset{\approx}{T}_4^{(8)}$ = (1/16)[ +  +  +  +

 +  +  +  +

 +  +  +  +

 +  +  + ] - $\underset{\approx}{T}$,

$\underset{\approx}{T}$ = (1/24)[ +  +  +  +

 +  +  +  +

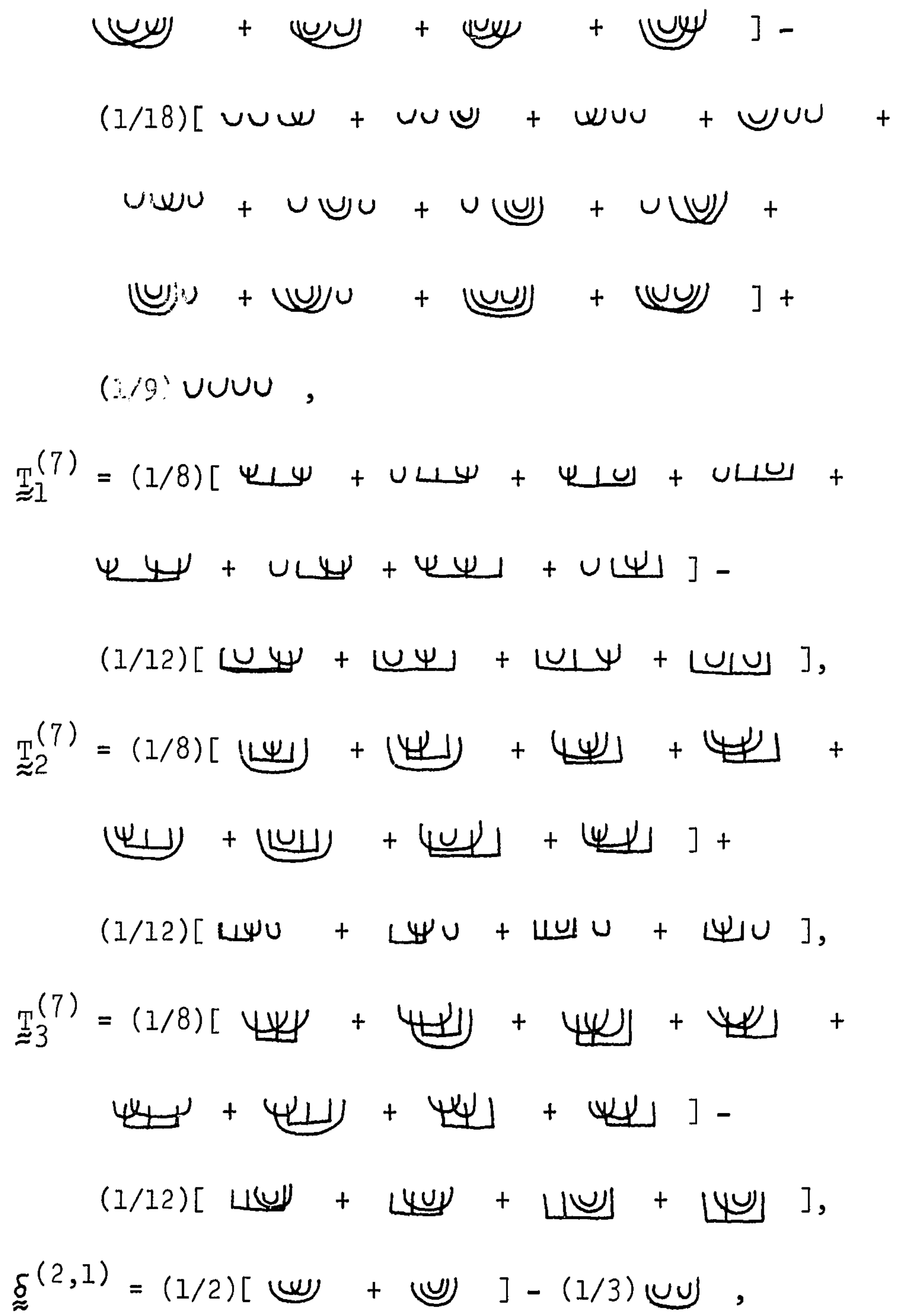
 +  +  +  +

 +  +  +  +

 +  +  +  +

 +  +  +  +

 +  +  +  +



and

$$(\underset{\approx}{T}_1'^{(6)})_{ijkmno} = (\underset{\approx}{T}_1^{(6)})_{jkiomn}.$$

APPENDIX B. SYMMETRY IMPLICATIONS

Here we examine the implications of various symmetries such as parity or reflection invariance to obtain the Onsager-Casimir relations. We begin by applying the parity operator $\hat{P}$ to the heat flux vector $\underset{\sim}{q}$ and to the viscous-pressure tensor $\underset{\approx}{\pi} = \underset{\approx}{P} - nkT\underset{\approx}{\delta}^{(1)}$. The fluxes are both polar quantities and hence exhibit the symmetry

$$\hat{P}\underset{\sim}{q} = -\underset{\sim}{q} \text{ and } \hat{P}\underset{\approx}{\pi} = \underset{\approx}{\pi}. \tag{B.1}$$

The most general form for these fluxes is

$$-\underset{\sim}{q} = \langle \underset{\sim}{D}, \underset{\sim}{A} \rangle \cdot \frac{\partial T}{\partial \underset{\sim}{r}} + \langle \underset{\sim}{D}, \underset{\approx}{B} \rangle \odot^{2} \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{r}} \tag{B.2}$$

and

$$-\underset{\approx}{\pi} = \langle D_1 \underset{\approx}{\delta}^{(1)} + \underset{\approx}{D}_2, \underset{\sim}{A} \rangle \cdot \frac{\partial T}{\partial \underset{\sim}{r}} + \langle D_1 \underset{\approx}{\delta}^{(1)} + \underset{\approx}{D}_2, \underset{\approx}{B} \rangle \odot^{2} \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{r}}. \tag{B.3}$$

If we apply $\hat{P}$ to $\underset{\sim}{q}$, we obtain the condition

$$-\underset{\sim}{q} = (\hat{P}\langle \underset{\sim}{D}, \underset{\sim}{A} \rangle) \cdot \frac{\partial T}{\partial \underset{\sim}{r}} - (\hat{P}\langle \underset{\sim}{D}, \underset{\approx}{B} \rangle) \odot^{2} \frac{\partial \underset{\sim}{u}}{\partial \underset{\sim}{r}}. \tag{B.4}$$

Therefore $\langle \underset{\sim}{D}, \underset{\sim}{A} \rangle$ must be even under $\hat{P}$ and $\langle \underset{\sim}{D}, \underset{\approx}{B} \rangle$ odd.

The tensors $\langle \underset{\sim}{D}, \underset{\sim}{A} \rangle$ and $\langle \underset{\sim}{D}, \underset{\approx}{B} \rangle$ are linear combinations of isotropic tensors formed from the unit vectors $\hat{E}$ or $\hat{H}$ and the tensors $\underset{\approx}{U}^{(2)}$ and $\underset{\approx}{V}$. Any second rank tensor so constructed will be even under $\hat{P}$, but only for the electric field case can we construct a third rank tensor odd under $\hat{P}$. This is because $\hat{P}\hat{E} = -\hat{E}$ and $\hat{P}\hat{H} = \hat{H}$. A similar argument can be given for $\hat{P}$ applied to $\underset{\approx}{\pi}$, and hence we can conclude that visco-thermal coupling can occur only for the electric field case.

For the linear ${}^1\Sigma$ molecules under consideration in this thesis, both the operators F and J are even under $\hat{P}$, and thus there can be no coupling of tensors with different parity. This means that if we divide $\underset{\approx}{B}$ into even and odd parity parts as $\underset{\approx}{B} = \underset{\approx}{B}_o + \underset{\approx}{B}_e$, the equation governing $\underset{\approx}{B}_o$ is

$$0 = f^{(0)}F(\underset{\approx}{B}_o) + J(\underset{\approx}{B}_o). \qquad \text{B.5}$$

Forming the moments, one obtains a set of scalar equations for which the only solution is zero, since the coefficient matrix is nonsingular. Therefore, we have no visco-thermal coupling for these molecules in an electric field. For symmetric top molecules, however, this is not the case (15).

We now consider the implications of the time reversal operator $\hat{T}$. Since $\hat{T}\underset{\sim}{D} = -\underset{\sim}{D}$, we have

$$\langle \hat{T}\underset{\sim}{D},\underset{\sim}{A}\rangle = -\underset{\approx}{\lambda} = \langle \hat{T}J(\underset{\sim}{A}),\underset{\sim}{A}\rangle + \langle \hat{T}F(\underset{\sim}{A}),\underset{\sim}{A}\rangle \qquad \text{B.6}$$

and

$$\langle \hat{T}\underset{\sim}{A},\underset{\sim}{D}\rangle = -\hat{T}\underset{\approx}{\lambda}^t = \langle \hat{T}\underset{\sim}{A},J(\underset{\sim}{A})\rangle + \langle \hat{T}\underset{\sim}{A},F(\underset{\sim}{A})\rangle . \qquad \text{B.7}$$

Subtracting equation B.7 from B.6 we obtain

$$-\underset{\approx}{\lambda} + \hat{T}\underset{\approx}{\lambda}^t = \langle \hat{T}J(\underset{\sim}{A}),\underset{\sim}{A}\rangle - \langle \hat{T}\underset{\sim}{A},J(\underset{\sim}{A})\rangle + \langle \hat{T}F(\underset{\sim}{A}),\underset{\sim}{A}\rangle -$$

$$\langle \hat{T}\underset{\sim}{A},F(\underset{\sim}{A})\rangle . \qquad \text{B.8}$$

In reference (17) it is shown that $\hat{T}J = J^{\dagger}\hat{T}$, and it is easily verified that $\hat{T}F = F^{\dagger}\hat{T}$. (Here $\langle \underset{\approx}{\psi}, J(\underset{\approx}{\phi})\rangle = \langle \underset{\approx}{\phi}, J^{\dagger}(\underset{\approx}{\psi})\rangle$.) Thus we have

$$\underset{\approx}{\lambda} = T\underset{\approx}{\lambda}^{t} \qquad \text{B.9}$$

or

$$\underset{\approx}{\lambda}(\underset{\sim}{H}) = \underset{\approx}{\lambda}^{t}(-\underset{\sim}{H}) \text{ and } \underset{\approx}{\lambda}(\underset{\sim}{E}) = \underset{\approx}{\lambda}^{t}(\underset{\sim}{E}). \qquad \text{B.10}$$

Since $\underset{\approx}{\lambda} = \lambda_0\underset{\approx}{\delta}^{(1)} + \Delta\lambda_1\underset{\approx}{B}_0^{(a)}(1) + \Delta\lambda_2\underset{\approx}{B}_1^{(a)}(1) + \Delta\lambda_3\underset{\approx}{B}_1^{(b)}(1)$ and $(\underset{\approx}{B}_1^{(b)}(1))^{t} = -\underset{\approx}{B}_1^{(b)}(1)$, we have the transverse coefficient $\Delta\lambda_3 = 0$ for the electric field case. A similar argument can be given to show that the transverse coefficients are also absent from the shear viscosity and to obtain the remaining Onsager-Casimir relations. These remaining relations are given in reference (11).

LIST OF SYMBOLS

h = Planck's constant

k = Boltzmann's constant

μ_B = Bohr magneton

μ_N = nuclear magneton

g_r = rotational g factor

d_E = magnitude of the dipole moment

d = internuclear distance

p = hydrostatic pressure

$\underset{\sim}{H}$ = magnetic field

$\underset{\sim}{E}$ = electric field

$f^{(N)}$ = N-particle distribution function (p. 7)

$\underset{\sim}{q}_i, \underset{\sim}{p}_i$ = generalized coordinates and momenta (p. 7)

$f^{(1)}$ = single-particle distribution function (p. 8)

$\underset{\sim}{r}_i, \underset{\sim}{v}_i$ = position and velocity of particle i

$\hat{k}$ = unit vector perpendicular to the excluded volume (p. 10)

$\underset{\sim}{\rho}_i$ = vector from the mass center to point of contact (p. 11)

$\underset{\sim}{\omega}_i$ = angular velocity of particle i

$\underset{\sim}{g}$ = relative velocity of two particles (p. 11)

$\underset{\sim}{M}$ = angular momentum

$\underset{\sim}{W} = (m/2kT)^{1/2}(\underset{\sim}{v} - \underset{\sim}{u})$

$\underset{\sim}{Q} = (2IkT)^{-1/2}\underset{\sim}{M}$

m = molecular mass

I = moment of inertia

n = number density (p. 14)

$\underset{\sim}{u}$ = stream velocity (p. 14)

T = temperature (p. 14)

F = magnetic or electric field operator (p. 13)

$f^{(0)}$ = local equilibrium distribution function (p. 14)

χ = distortion of local equilibrium distribution function (p. 15)

$\underset{\sim}{A}$ = thermal conductivity distortion (p. 15)

$\underset{\approx}{B}$ = viscosity distortion (p. 15)

$\underset{\approx}{J}_{ij}\left(\begin{matrix}p,q\\p',q'\end{matrix}\right)$ = matrix element of J (p. 17)

J = collision operator (p. 14)

$J^{(0)}$ = "spherical" part of J (p. 18)

$J^{(1)}$ = "nonspherical" part of J (p. 18)

$\mathcal{J}^{(0)} = n^{-1}f^{(0)}F - n^{-1}J^{(0)}$ (p. 19)

$\mathcal{J}^{(1)} = -n^{-1}J^{(1)}$ (p. 19)

$\underset{\approx}{\delta}^{(n)}$ and $\underset{\approx}{\delta}^{(p,q)}$ = isotropic tensors (p. 18)

$I^{(0)} = \mathcal{J}^{-1(0)}$ (p. 19)

$\underset{\approx}{J}_{ij}^{(0)}\left(\begin{matrix}p,q\\p,q\end{matrix}\right)$ = matrix element of $J^{(0)}$ (p. 20)

$\underset{\approx}{F}_{ij}\left(\begin{matrix}p,q\\p,q\end{matrix}\right)$ = matrix element of F (p. 20)

$\underset{\approx}{I}_{k}^{(0)}(p,q)$ = matrix element of $I^{(0)}$ (p. 21)

$\underset{\approx}{B}_{m}^{(a)}(q)$ and $\underset{\approx}{B}_{m}^{(b)}(q)$ = isotropic tensors (p. 21)

$\underset{\approx}{\tilde{B}}_{m}^{(a)}(q)$ and $\underset{\approx}{\tilde{B}}_{m}^{(b)}(q)$ = isotropic tensors (p. 23)

$\underset{\sim}{q}$ = heat flux vector (p. 26)

$\underset{\approx}{\lambda}$ = thermal conductivity tensor (p. 26)

$S_{m}^{(n)}(x)$ = Sonine polynomial (p. 26)

$\underset{\approx}{A}^{pqst}$ = thermal distortion expansion coefficients (p. 26)

$\underset{\sim}{D} = -f^{(0)}[(5/2-W^2) + (1-Q^2)]\underset{\sim}{W}$ (p. 27)

$\underset{\approx}{A}^{i}$ = thermal distortion expansion coefficients (p. 28)

$\underset{\approx}{h}_{ij}$ = thermal conductivity collision integral (p. 28)

$\beta_D = (mkT/\pi)^{1/2}(\mu_N g_r/d^2 h)(H/p)$

$\beta_P = (m/\pi kT)^{1/2}(\mu_B h/d^2 I)(H/p)$

$\beta_E = (d_E^2/d^2 kT)(m/2\pi I)^{1/2}(E^2/p)$

$\Delta\lambda_i$ = thermal conductivity coefficient (p. 31)

a = minor axis of an ellipsoid of revolution

b = major axis of an ellipsoid of revolution

R = b/a

$\langle\sigma\rangle$ = average cross-sectional area of a molecule

S,L = radius and length of the cylinder of a spherocylinder

$\Delta\lambda = (\Delta\lambda_1 + \Delta\lambda_2)/2$

$\beta_{1/2} = \beta_D, \beta_P$, or β_E at half-saturation

$\Delta\lambda_\perp = \Delta\lambda_2$

$\Delta\lambda_\parallel = \Delta\lambda_1$

$\lambda_{tr} = \Delta\lambda_3$

$\underset{\approx}{P}$ = pressure tensor (p. 59)

$D_1 = f^{(0)}(4W^2/15 - 2Q^2/5)$ (p. 59)

$\underset{\approx}{D}_2 = 2f^{(0)}\overset{\circ}{\underset{\approx}{W}\underset{\approx}{W}}$ (p. 59)

$\underset{\approx}{\eta}$ = shear viscosity tensor (p. 59)

κ = bulk viscosity (p. 59)

$\underset{\approx}{L}^{(02)}_{\pi\pi}$ and $\underset{\approx}{L}^{(20)}_{\pi\pi}$ = coupling coefficient for shear and bulk viscosities (p. 59)

$\underset{\approx}{B}^{pqst}$ = viscosity distortion expansion coefficients (p. 60)

$\underset{\approx}{b}_{ij}$ = viscosity collision integrals (p. 62)

$\Delta\eta_i$ = shear viscosity coefficient (p. 63)

$h(\hat{k})$ = molecular supporting function (p. 79)

$h_x(\hat{k})$ = excluded volume supporting function (p. 81)

$S_x^{(2)}$ = surface element of excluded volume (p. 81)

$\hat{P}$ = parity operator (p. 99)

$\hat{T}$ = time reversal operator (p. 100)

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