

effect, it is necessary to repeat the experiment in a truly uniform one-dimensional high Mach number flow, which was not attainable with the present UTIAS low-density facility.

The shock wave results indicate that shock curvature may produce very significant radial diffusion effects, resulting in an enrichment of the heavy gas on the centerline behind the shock. This effect might be used to explain, at least partially, the unrealistically large species separation observed when sampling tubes are introduced into a supersonic flow field.

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New Statistical Models for Kinetic Theory: Methods of Construction

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A statistical model of the collision term in the Boltzmann equation is introduced which is similar in concept to the well-known Krook model but yields the correct Prandtl number of $\frac{2}{3}$ for a monatomic gas. A new method for constructing kinetic models is presented which is based on the information theory concept of entropy or uncertainty. This method, which is applicable to quite general systems in nonequilibrium statistical mechanics, is used to construct statistical models for multicomponent gas mixtures and for gases consisting of molecules with internal degrees of freedom.

I. INTRODUCTION

DURING the past several years, the Krook statistical model¹ has been used by many authors as an approximation to the Boltzmann collision integral for solving problems in rarefied gas dynamics.² As was first pointed out by Krook,³ the model equation is particularly useful in a large class of problems for which explicit expressions for the distribution function $f(\mathbf{v})$ can be obtained in the form of integrals involving only a few low-order moments of $f(\mathbf{v})$. These integral equations can be solved numerically by an iteration procedure⁴ whose accuracy is only limited by the mesh sizes and number of iterations which are economically practical. Since the model equation shares many of the properties of the full

Boltzmann equation, these numerical results are useful for checking the validity of various approximation procedures whose accuracy would otherwise be unknown.⁵

In addition to providing a testing ground for approximation procedures which are to be applied to the Boltzmann equation, the model equation is a useful approximation to the Boltzmann equation in its own right. This is particularly important for problems, such as high-frequency sound waves,⁶ which involve large Knudsen numbers so that the classical expansion methods of Chapman-Enskog⁷

¹ D. G. Anderson and H. K. Macomber, in *Rarefied Gas Dynamics*, J. H. de Leeuw, Ed. (Academic Press Inc., New York, 1965), Vol. I.

² L. Sirovich and J. K. Thurber, in *Rarefied Gas Dynamics*, J. H. de Leeuw, Ed. (Academic Press Inc., New York, 1965), Vol. I; also, *J. Acoust. Soc. Am.* **37**, 329 (1965). These studies use an extension of the Krook model, based upon a linearization of the distribution function about a local Maxwellian, which was developed by E. P. Gross and E. A. Jackson [*Phys. Fluids* **2**, 432 (1959)] for Maxwell molecules and extended to an arbitrary force law by L. Sirovich [*Phys. Fluids* **5**, 908 (1962)]; the last paper also extends these techniques to multicomponent gas mixtures.

³ S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, London, 1952).

¹ P. L. Bhatnagar, E. P. Gross, and M. Krook, *Phys. Rev.* **94**, 511 (1964).

² For example, the Krook model is used in approximately 15 papers in *Rarefied Gas Dynamics* [J. H. de Leeuw, Ed. (Academic Press Inc., New York, 1965), Vol. I].

³ M. Krook, *Phys. Rev.* **99**, 1896 (1955).

⁴ H. W. Liepmann, R. Narasimha, and M. Chahine, *Phys. Fluids* **5**, 1313 (1962); D. G. Anderson, Ph.D. thesis, Harvard University (1963); H. K. Macomber, Ph.D. thesis, Harvard University (1965).

and Grad⁸ have little validity. For such problems, it will prove useful to have a more accurate model provided it does not sacrifice the simplicity of the Krook model.

In the hydrodynamic limit, the Chapman-Enskog method can be used to obtain the Navier-Stokes equations from a kinetic equation in which the Krook model is employed as the interaction term.⁹ This model contains an undetermined parameter which can be chosen phenomenologically to give the correct value for the coefficient of viscosity. However, the model predicts that the Prandtl number will be unity while the correct value for a monatomic gas is very nearly $Pr = \frac{2}{3}$. The aim of this paper is to propose a new model which retains much of the mathematical simplicity of the Krook model, but yields the correct Prandtl number and therefore has the same asymptotic solution as the Boltzmann equation in the hydrodynamic limit.

The term "statistical model" has been used by Krook to denote a general class of kinetic models. In a sense, the Boltzmann collision integral itself might be considered a statistical model, inasmuch as it involves the hypothesis of molecular chaos. However, the Boltzmann integral treats in detail the geometry of every possible binary molecular collision. The philosophy behind the statistical models is that the important properties of the collision operator can be described by taking a statistical average over all collisions without describing each collision individually. In this paper we combine this statistical viewpoint with certain concepts from information theory to obtain a new procedure for constructing statistical models.

The general form for a statistical model in a monatomic gas is discussed in Sec. II, and a method of constructing statistical models based on maximizing Shannon's measure of uncertainty is presented in Sec. III. The ellipsoidal statistical model for monatomic gases is developed in Sec. IV, and in Sec. V the Chapman-Enskog method is used to show that this model leads to the correct Navier-Stokes equations. New models for multicomponent gas mixtures and for gases with internal degrees of freedom are constructed in Secs. VI and VII.

II. THE FORM OF THE STATISTICAL MODEL

For single-component gases, the Boltzmann equation has the form

$$\frac{\partial}{\partial t}(nf) + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}}(nf) + \mathbf{a} \cdot \frac{\partial}{\partial \mathbf{v}}(nf) = \frac{\delta f}{\delta t}, \quad (1)$$

where $n(\mathbf{r}, t)f(\mathbf{v}, \mathbf{r}, t) d\mathbf{r} d\mathbf{v}$ is defined as the expected number of particles in the volume element $d\mathbf{r}$ about \mathbf{r} which have velocities in the range $d\mathbf{v}$ about \mathbf{v} at time t . For our purposes, it is convenient to normalize f so that $\int f(\mathbf{v}) d\mathbf{v} = 1$ and n is the number density. In Eq. (1), \mathbf{a} is the external force per unit mass and $\delta f/\delta t$ is the collision integral. In this paper we consider statistical models of the collision term which have the form

$$\delta f/\delta t = -n^2 K[f]\{f(\mathbf{v}) - \Psi[f]\}, \quad (2)$$

where $K[f]$ and $\Psi[f]$ are functionals of f which are as yet undetermined. The main task in this paper is to determine forms for K and Ψ that are simpler in the form than the Boltzmann collision integral, but provide good approximations to the important properties of the molecular interactions. The Boltzmann collision integral⁷ is

$$\frac{\delta f}{\delta t} = -n^2 \int [f(\mathbf{v})f(\mathbf{w}) - f(\mathbf{v}')f(\mathbf{w}')]gb db d\epsilon d\mathbf{w}, \quad (3)$$

where \mathbf{v}' and \mathbf{w}' are the velocities after collision of particles which initially had velocities \mathbf{v} and \mathbf{w} , $g = |\mathbf{v} - \mathbf{w}|$, b is the impact parameter, and ϵ is the angle specifying the orientation of the plane of the relative orbit. Equation (2) could be made formally identical with the Boltzmann integral, if we were to choose

$$K = \int f(\mathbf{w})gb db d\epsilon d\mathbf{w} \quad (4)$$

and make an obvious choice for Ψ . However, the integral of Eq. (4) does not exist unless there is a finite cutoff radius for the molecular force, and for a general force law there is no unambiguous way to choose such a cutoff. In fact, the magnitude of Eq. (4) would be strongly affected by changes in the cutoff parameter which are too small to have a significant effect on the transport properties of the system. Moreover, the velocity dependence of K would be different depending on whether we chose a maximum impact parameter or a minimum scattering angle as the cutoff parameter. Therefore, instead of identifying K with Eq. (4), we regard K as an undetermined functional of f which will later be chosen so as to represent the more important aspects of the intermolecular collisions correctly.

If K were chosen to satisfy Eq. (4), it would be a function of velocity unless the force law was taken to be Maxwellian and the cutoff parameter

⁸ H. Grad, Commun. Pure Appl. Math. 2, 331 (1949).

⁹ F. J. Fishman, Jr., Ph.D. thesis, Harvard University (1957).

was chosen to be a minimum scattering angle. However, a velocity-dependent K leads to a more complicated statistical model than is usually desirable, and in this paper we always assume K to be independent of velocity.

The Krook model is obtained from the general form for statistical models given by Eq. (2) by setting $\Psi = \Phi(\mathbf{v}, \mathbf{r}, t)$, where Φ is the local Maxwellian distribution

$$\Phi = (2\pi RT)^{-3/2} \exp - [(\mathbf{v} - \mathbf{u})^2/2RT]. \quad (5)$$

In Eq. (5) the gas constant $R = k/m$, where m is the mass of the molecule and k is Boltzmann's constant. Also, the flow velocity is defined as $\mathbf{u}(\mathbf{r}, t) = \int \mathbf{v} f(\mathbf{v}) d\mathbf{v}$. The second-order moments of f are

$$M_{ij}(\mathbf{r}, t) = \int (v_i - u_i)(v_j - u_j) f(\mathbf{v}) d\mathbf{v}, \quad (6)$$

and the kinetic temperature is defined at every point in space by the relation $3RT = M_{ii}$, where we use the summation convention for repeated Latin subscripts.

An interesting analogy exists between the Krook model of the Boltzmann equation and the radiation transport equation used in the study of stellar atmospheres.¹ In the latter equation, the emission and absorption of the continuous spectrum of radiation is approximated by a term which is similar in form to the Krook model except that Maxwell's equilibrium distribution for molecules is replaced by Planck's equilibrium distribution for black-body radiation at the local thermodynamic temperature.¹⁰ Another interesting and suggestive analogy can be made between the Krook model and the old mean-free-path formulations of kinetic theory. In the simple mean-free-path theory, it is assumed that molecules emerging from a collision have a Maxwellian distribution of velocities with the local temperature and flow velocity. Similarly, the emission term Φ , which describes the distribution of particles emerging from collisions in the Krook model, is the local Maxwell distribution. However, because the model is introduced in conjunction with the Boltzmann equation, we are able to take advantage of a more powerful mathematical formulation than that used in the mean-free-path theory.¹¹ The early at-

tempts to improve the simple mean-free-path theory led to the "persistence of velocity" theories which recognized that after a collision a molecule partially remembers its original velocity and energy. This suggests that the Krook model could also be improved by including "persistence of velocity" effects, and we attempt to do this by correlating $\Psi[f]$, the probability distribution for particles emerging from collision, with certain statistical properties of f , the particle distribution before collision.

A number of important properties of the Boltzmann collision integral are shared by the Krook model. These include: (i) The collision term drives the distribution function toward equilibrium and vanishes, if and only if, the distribution function $f(\mathbf{v})$ is equal to the local Maxwellian equilibrium function; (ii) the collision term conserves molecular mass, momentum, and kinetic energy; (iii) the collision term is a \mathbf{v} -functional of $f(\mathbf{v}, \mathbf{r}, t)$, i.e., it depends upon the values of f over the entire range of \mathbf{v} -space but only upon the values at single point in $\mathbf{r} - t$ space; (iv) the collision term is invariant in form under rotation or translation of coordinates.

The new statistical model to be developed in this paper will also be required to satisfy properties (i)-(iv). In addition, much of the usefulness of the Krook model for solving problems in kinetic theory is due to the fact that it only depends upon a few lower-order moments of $f(\mathbf{v})$, and we desire a similar dependence for the new model.

III. STATISTICAL ARGUMENTS

In the general form for a statistical model given by Eq. (2), the term $-n^2 K f(\mathbf{v}) d\mathbf{v} d\mathbf{r}$ is an "absorption" term which represents the number of particles removed by collisions from the velocity range $d\mathbf{v}$ about \mathbf{v} and the volume element $d\mathbf{r}$ about \mathbf{r} per unit time. Considering the normalization of $f(\mathbf{v})$ and our assumption that K is independent of velocity, it follows that $n^2 K$ is the total number of particles undergoing collision at a point $\mathbf{r} - t$ per unit volume per unit time. Because every particle which is absorbed must be reemitted after collision, it is necessary for the functional $\Psi[f]$ which appears in the "emission" term to satisfy

$$\int \Psi(\mathbf{v}, \mathbf{r}, t) d\mathbf{v} = 1. \quad (7)$$

¹⁰ For example, see V. V. Sobolev, *A Treatise on Radiative Transfer* (D. Van Nostrand, Inc., New York, 1963).

¹¹ The mean-free-path theory, however, leads to a Prandtl number of 5/3 while the Krook model gives the more accurate value of unity. According to E. H. Kennard [*Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 178] the correct Prandtl number of 2/3 is increased by a factor of 3/2 due to neglecting the greater persistence

of $\sum v_x v^2$ than of the quantity $\sum v_x v_y$ in the simple mean-free-path theory, while the remainder of the increase up to 5/3 is due to neglecting the correlation between high values of the kinetic energy, $\frac{1}{2} m v^2$, and high rates of convection for high values of v . Thus the Krook model corrects the latter deficiency but not the former.

The function Ψ therefore plays the role of a probability density such that $\Psi(\mathbf{v}, \mathbf{r}, t) d\mathbf{v}$ is the probability that a particle which has undergone a collision at the point $\mathbf{r} - t$ will emerge from the collision with a velocity in the range $d\mathbf{v}$ about \mathbf{v} . It is important to emphasize that we have not specified the velocity of the particle before collision in the definition of Ψ . In fact Ψ is to be considered as an average over initial velocities which are themselves random variables determined by the distribution function f .

The conservation of mass, momentum, and energy requires the collision term to satisfy five relations of the form $\int (\delta f / \delta t) \theta(\mathbf{v}) d\mathbf{v} = 0$, where $\theta(v) = 1, v_1, v_2, v_3$, or v^2 . Therefore, in addition to the normalization given in Eq. (7), Ψ must satisfy the moment relations

$$\int v_i \Psi(\mathbf{v}) d\mathbf{v} = u_i, \quad (8)$$

$$\int (v_i - u_i)(v_j - u_j) \Psi(\mathbf{v}) d\mathbf{v} = 3RT, \quad (9)$$

where u_i is the j th component of the flow velocity and T is the temperature.

Our next task will be to determine $\Psi(\mathbf{v})$ subject to the requirements of Eqs. (7)–(9), but there are obviously an infinite number of choices for $\Psi(\mathbf{v})$ which accomplish this. For example, we could choose

$$\Psi(\mathbf{v}) = \frac{1}{2}[\delta(\mathbf{v} - \mathbf{u} + \mathbf{a}) + \delta(\mathbf{v} - \mathbf{u} - \mathbf{a})],$$

where \mathbf{a} is any vector whose magnitude is $(3RT)^{1/2}$ and $\delta(\mathbf{x}) = \delta(x_1) \delta(x_2) \delta(x_3)$ is the three-dimensional delta-function. However, it is intuitively obvious that this is a poor choice for the probability density Ψ because it assumes that it is *absolutely certain* that a particle will emerge from a collision with either a velocity $\mathbf{u} + \mathbf{a}$ or a velocity $\mathbf{u} - \mathbf{a}$. In fact, the conditions imposed by Eqs. (7)–(9) give only a limited amount of information about the velocity distribution, and an arbitrary assignment of the probability density can introduce an unjustified bias towards certain velocities. In order to avoid such a bias, we should assign a probability density Ψ which gives the maximum possible uncertainty about the velocity with which a particle will emerge from collision, subject to the conditions given by Eqs. (7)–(9).

First let us consider a finite scheme in which there are n possible outcomes A_1, \dots, A_n which occur with probabilities p_1, \dots, p_n . In his development of information theory, Shannon¹² introduced the entropy

¹² C. E. Shannon, Bell System Tech. J. **27**, 379, 623 (1948).

$$S = - \sum_{i=1}^n p_i \ln p_i,$$

which has been demonstrated to provide a unique measure of the “amount of uncertainty” which satisfies certain conditions necessary for consistency.¹³

To generalize S to the continuous distribution Ψ , let us assume that \mathbf{v} can take on only the discrete values

$$\mathbf{v} = \delta(k\hat{i}_x + l\hat{i}_y + m\hat{i}_z),$$

where k, l , and m are integers and δ will ultimately be allowed to approach zero.¹⁴

Let $\Delta\mathbf{v}$ be an element of volume whose linear dimensions are large compared to δ but small enough so that the probability of each state within $\Delta\mathbf{v}$ can be assumed to have the common value p_Δ . Then the number of states with $\Delta\mathbf{v}$ is $N_\Delta = \delta^{-3} \Delta\mathbf{v}$. The probability that the particle will emerge with a velocity within $\Delta\mathbf{v}$ is $N_\Delta p_\Delta = \Psi(\mathbf{v}) \Delta\mathbf{v}$ so that $p_\Delta = \delta^3 \Psi(\mathbf{v})$ and the contribution of the states within $\Delta\mathbf{v}$ to the entropy is

$$\Delta S = - \sum_{\Delta} p_i \ln p_i = - \Psi \Delta\mathbf{v} \ln (\Psi \delta^3),$$

and the total entropy is

$$S = - \int \Psi(\mathbf{v}) \ln \Psi(\mathbf{v}) d\mathbf{v}, \quad (10)$$

where we have dropped a term $-3 \ln \delta$ which is simply an additive constant independent of Ψ .

We now argue that, if we are given no other information about Ψ beyond conditions (7)–(9), the best possible assignment of the probability density Ψ is the one which maximizes the uncertainty S subject to these conditions.¹⁵ An extremum of S can be obtained by the method of Lagrangian multipliers, and it is easily verified that the extremum is a maximum. Multiplying Eq. (7) by the Lagrangian multiplier α , Eq. (8) by α_i , and Eq. (9) by $\bar{\alpha}$, letting $\Psi \rightarrow \Psi + \delta\Psi$ in each equation and adding these equations to the variation of Eq. (10) yields

$$\delta S = - \int \delta\Psi [\ln \Psi + 1 - \alpha - \alpha_i v_i - \bar{\alpha}(v_i - u_i)(v_j - u_j)] d\mathbf{v}.$$

¹³ A. I. Khinchin, *Mathematical Foundations of Information Theory* (Dover Publications, Inc., New York, 1957).

¹⁴ This corresponds to choosing a uniform measure for the density of the discrete states. See E. T. Jaynes, in *Statistical Physics*, K. W. Ford, Ed. (W. A. Benjamin, Inc., New York, 1963).

¹⁵ For a discussion of similar uses of information theory in science and engineering, see Ref. 14 and M. Tribus, *Thermodynamics and Thermodynamics* (D. Von Nostrand Company, Inc., Princeton, New Jersey, 1961); E. T. Jaynes, Phys. Rev. **106**, 620 (1957); **108**, 171 (1957).

For a maximum, δS must vanish for an arbitrary $\delta \Psi$, so the bracket in the last equation is set equal to zero, yielding $\Psi = \exp[\alpha - 1 + \alpha_i v_i + \bar{\alpha}(v_i - u_i)(v_i - u_i)]$. The five Lagrangian multipliers are evaluated by requiring Ψ to satisfy Eqs. (7)–(9), and finally we obtain $\Psi = \Phi$, where Φ is just the equilibrium Maxwellian distribution used in the Krook model. Thus, if Eqs. (7)–(9) are the only information we have about Ψ , maximizing S does not give us a new model but simply allows us to see the Krook model from a new viewpoint. However, we can now attempt to acquire additional information about Ψ , and use the same technique for maximizing the uncertainty S to obtain a more accurate choice for Ψ .

IV. THE ELLIPSOIDAL STATISTICAL MODEL

Let λ_{ij} denote the second-order moments of $\Psi(\mathbf{v})$, so that

$$\lambda_{ij} = \int (v_i - u_i)(v_j - u_j) \Psi(\mathbf{v}) d\mathbf{v}. \quad (11)$$

We now assume that the λ_{ij} are known quantities; it is not necessary to discuss the precise method of determining the λ_{ij} at this point, and we reserve this discussion until later. As in the last section, we choose the probability distribution Ψ so that it will maximize the uncertainty S ; however, Ψ must now satisfy the conditions given by Eqs. (7), (8), and (11), and the additional information will improve our estimate of Ψ . Introducing the Lagrangian multipliers α , α_i , and α_{ij} into Eqs. (7), (8), and (17), respectively, the variation in S is

$$\delta S = - \int \delta \Psi [\log \Psi + 1 - \alpha - \alpha_i v_i - \alpha_{ij}(v_i - u_i)(v_j - u_j)] d\mathbf{v} = 0.$$

As before, the extremum is found by setting the bracket equal to zero and, after evaluating the Lagrangian multipliers, we obtain

$$\Psi(\mathbf{v}, \mathbf{r}, t) = (2\pi)^{-\frac{3}{2}} |\lambda|^{-\frac{1}{2}} \exp - \frac{1}{2} \epsilon_{ij}(v_i - u_i)(v_j - u_j), \quad (12)$$

where $|\lambda|$ is the determinant of λ , the tensor whose components are λ_{ij} and ϵ_{ij} denotes the components of $\epsilon = \lambda^{-1}$, the tensor inverse to λ . Since the probability distribution given by Eq. (12) is an ellipsoidal distribution in velocity space, the new statistical model will be called the ellipsoidal statistical model.

The additional information supplied by specifying λ_{ij} can only reduce the uncertainty about the velocity of a particle emerging from collision. It is easily verified that the uncertainty S obtained by

substituting Eq. (12) into Eq. (10) is always less than or equal to the value of S associated with $\Psi = \Phi$, with equality occurring only if $\lambda_{ij} = RT \delta_{ij}$.

The conservation of kinetic energy during a collision requires Eq. (9) to be satisfied so the spur of λ is

$$\lambda_{ij} = 3RT = M_{ij}. \quad (13)$$

In formulating a useful statistical model, we must assume the collision term can be approximated from the knowledge of relatively simple statistical properties of the distribution function. In particular, we shall choose λ_{ij} to be a linear function of the second-order moments of f ,

$$\lambda_{ij} = G_{ijkl} M_{kl},$$

where the linearity is suggested by Eq. (13). Since the Boltzmann collision integral is an isotropic operator, the statistical model must likewise be invariant in form under a rotation of the coordinate system, and therefore G_{ijkl} must be an isotropic tensor. The most general form for the isotropic tensor of fourth order, which involves three independent scalar parameters,¹⁶ is

$$G_{ijkl} = a \delta_{ij} \delta_{kl} + b(\delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk}) + \frac{1}{2} \lambda (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}),$$

and, since M_{ij} is symmetric, it follows that

$$\lambda_{ij} = a M_{kk} \delta_{ij} + \lambda M_{ij}. \quad (14)$$

The conservation of energy determines a when Eq. (14) is substituted into Eq. (12), yielding

$$\lambda_{ij} = (1 - \lambda) RT \delta_{ij} + \lambda M_{ij} = RT \delta_{ij} + \lambda \tilde{M}_{ij}, \quad (15)$$

where we have introduced the divergenceless symmetric tensor \tilde{M} , with components

$$\tilde{M}_{ij} = M_{ij} - \frac{1}{3} M_{kk} \delta_{ij} = M_{ij} - RT \delta_{ij}.$$

The ellipsoidal statistical model is now completely defined by Eqs. (2), (12), and (15), except for two undetermined quantities, the parameter λ and the functional $K[f]$. For simplicity, we assume that K depends only on the moments of f of order less than 3. Since K must be invariant in form under translation or rotation of coordinates, K must be independent of \mathbf{u} and depend only on the spur $M_{ii} = 3 RT$. Thus $K[f] = K(T)$ is a function of temperature alone.

It is clear that the quadratic form $\epsilon_{ij} v_i v_j$, which appears in the argument of exponential of the emis-

¹⁶ For example, see H. Jeffreys, *Cartesian Tensors* (Cambridge University Press, Cambridge, England, 1931).

sion term ψ , must be a positive definite form; otherwise there would be some direction in velocity space for which the emission term would increase without limit. It can be shown from Eq. (15) that the positive definiteness of ϵ_{ij} follows from the positive definiteness of M_{ij} provided $-\frac{1}{2} \leq \lambda \leq 1$, for all possible M_{ij} . It is also evident from Eq. (15) that, for the particular choice $\lambda = 0$, the ellipsoidal statistical model reduces to the Krook model.

V. THE DETERMINATION OF λ AND $K(T)$ BY THE CHAPMAN-ENSKOG PROCEDURE

A. Chapman-Enskog Solution

In this section we briefly outline a Chapman-Enskog derivation of the Navier-Stokes equations using the ellipsoidal statistical model for the collision term in the kinetic equation. A derivation of the Navier-Stokes equations from the Krook model was previously given by Fishman.⁹ Using the ellipsoidal statistical model as an intermediary allows us to evaluate Chapman and Cowling's first approximation⁷ to the coefficients of heat conduction and viscosity for an arbitrary molecular force law without the necessity of solving an integral equation or of introducing Sonine polynomial expansions. Thus it may be useful pedagogically to adopt this procedure for deriving the Navier-Stokes equations *ab initio*. However, our main objective here will be to obtain expressions for λ and $K(T)$ for an arbitrary force law.

Following Chapman and Cowling, we introduce the peculiar velocity $\mathbf{c} = \mathbf{v} - \mathbf{u}(\mathbf{r}, t)$ and write the distribution function in terms of \mathbf{c} as $F(\mathbf{c}, \mathbf{r}, t) = f(\mathbf{v} + \mathbf{u}, \mathbf{r}, t)$. Then the kinetic equation becomes

$$\mathfrak{D}(nF) = \frac{1}{\delta} n^2 K \left(\frac{\exp(-\frac{1}{2}\epsilon_{ij}c_i c_j)}{(2\pi)^{\frac{1}{2}} |\lambda|^{\frac{1}{2}}} - F \right), \quad (16)$$

where \mathfrak{D} is the operator,

$$\mathfrak{D} = \frac{D}{Dt} + c_i \frac{\partial}{\partial x_i} - \left(\frac{Du_i}{Dt} + c_i \frac{\partial u_i}{\partial x_i} \right) \frac{\partial}{\partial c_i},$$

and D/Dt is the Lagrangian derivative,

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + u_j \frac{\partial}{\partial x_j}.$$

The Chapman-Enskog expansion is an expansion in powers of the small dimensionless parameter $(nK\tau)^{-1}$, where τ is the macroscopic time required for significant changes in the distribution function and nK is the collision frequency. A concise formulation of this expansion is obtained by inserting the term $1/\delta$ into the collision term¹⁷ of Eq. (16) and

writing the distribution function in the form

$$F = F^{(0)}(1 + \delta F^{(1)} + \delta^2 F^{(2)} + \dots),$$

where δ is considered small during the expansion and ultimately allowed to approach unity.

Because of the term $1/\delta$, the collision term must be zero in lowest order, requiring $F^{(0)}$ to be a Maxwellian distribution, and we choose the temperature and flow velocity to be the exact local values, i.e.,

$$F^{(0)} = \Phi(\mathbf{v}, \mathbf{u}, T) = (2\pi RT)^{-\frac{3}{2}} \exp(-c^2/2RT). \quad (17)$$

The divergenceless tensor $\tilde{M}_{ij} = \tilde{M}_{ij}^{(0)} + \delta \tilde{M}_{ij}^{(1)} + \dots$, but from Eq. (17) $\tilde{M}_{ij}^{(0)} = 0$. Then the inverse of λ_{ij} is

$$\epsilon_{ij} = \delta_{ij}(RT)^{-1} - \delta \lambda \tilde{M}_{ij}^{(1)}(RT)^{-2} + O(\delta^2), \quad (18)$$

and the determinant of λ_{ij} is

$$|\lambda| = (RT)^3 + O(\delta^2). \quad (19)$$

Substituting Eqs. (17)–(19) into the right-hand side of Eq. (25) and neglecting terms of order δ , one obtains

$$\frac{1}{\delta} \frac{\delta f}{\delta t} = n^2 K \Phi \left(\frac{\lambda \tilde{M}_{ij}^{(1)} c_i c_j}{2(RT)^2} - F^{(1)} \right). \quad (20)$$

Neglecting terms of order δ , we substitute Eq. (17) into the left-hand side of Eq. (16) and eliminate the time derivatives by means of the zero-order Euler equations. This procedure, which is independent of the collision model, yields

$$\mathfrak{D}(nF^{(0)}) = n\Phi \left[\frac{1}{2} c_i \left(\frac{c^2}{RT} - 5 \right) \frac{\partial}{\partial x_i} \cdot \log T + \frac{1}{RT} c_i c_k \frac{\partial u_k}{\partial x_i} \right], \quad (21)$$

where we have introduced the notation

$$\frac{\partial u_k}{\partial x_i} = \frac{1}{2} \left(\frac{\partial u_k}{\partial x_i} + \frac{\partial u_i}{\partial x_k} \right) - \frac{1}{3} \frac{\partial u_i}{\partial x_i} \delta_{ki}.$$

Equating the expressions (20) and (21) yields the first-order correction to the distribution function

$$F^{(1)} = \frac{1}{RT} \left(\frac{\lambda}{2RT} \tilde{M}_{ij}^{(1)} - \frac{1}{nK} \frac{\partial u_i}{\partial x_j} \right) c_i c_j + \frac{1}{2nK} \frac{\partial \log T}{\partial x_i} \left(5 - \frac{c^2}{RT} \right) c_i, \quad (22)$$

which automatically satisfies the compatibility relations.

By definition,

$$\tilde{M}_{ij}^{(1)} = \int \Phi F^{(1)} (c_i c_j - \frac{1}{3} c^2 \delta_{ij}) dc = \int \Phi F^{(1)} c_i c_j dc,$$

¹⁷ H. Grad, in *Handbuch der Physik*, S. Flügge, Ed. (Springer-Verlag, Berlin, 1958), Vol. 12.

so that, from Eq. (22) we have

$$\tilde{M}_{ij}^{(1)} = \frac{2RT}{(1-\lambda)nK} \frac{\partial u_i}{\partial x_j}. \quad (23)$$

A simpler form for the Chapman-Enskog distribution $F^{(1)}$ can be obtained by substituting Eq. (23) into Eq. (22), yielding

$$F^{(1)} = -(nK)^{-1} \left[\frac{c_j c_k}{(1-\lambda)RT} \frac{\partial u_k}{\partial x_j} + \frac{1}{2} c_i \left(\frac{c^2}{RT} - 5 \right) \frac{\partial \log T}{\partial x_i} \right]. \quad (24)$$

The divergenceless pressure tensor is defined as

$$\tilde{p}_{ij} = p_{ij} - \frac{1}{3} p_{kk} \delta_{ij} = mn \tilde{M}_{ij},$$

and since \tilde{M}_{ij} is given by Eq. (23), we have

$$\tilde{p}_{ij} = -\frac{2kT}{(1-\lambda)K} \frac{\partial u_i}{\partial x_j}. \quad (25)$$

The last equation is identical with the Navier-Stokes expression for the divergenceless pressure tensor provided we identify the coefficient of viscosity as

$$\mu = kT/K(1-\lambda). \quad (26)$$

Let us define the contracted third-order tensor

$$M_{iii} = \int c_i c_j c_k F(\mathbf{c}) d\mathbf{c}.$$

Then, for the Chapman-Enskog distribution of Eq. (24),

$$M_{iii} = -(5R^2T/nK)(\partial T/\partial x_i). \quad (27)$$

The heat-conduction vector is defined as $h_i = \frac{1}{2} mn M_{iii}$, and from Eq. (27) we have

$$h_i = -(5mR^2T/2K)(\partial T/\partial x_i), \quad (28)$$

which is identical with the Navier-Stokes expression provided we identify the coefficient of heat conduction as

$$\kappa = 5mR^2T/2K. \quad (29)$$

The undetermined parameters in the ellipsoidal statistical model, as determined by Eqs. (26) and (29), are

$$\lambda = (\text{Pr} - 1)/\text{Pr}, \quad (30)$$

$$K = kT \text{Pr}/\mu, \quad (31)$$

where the Prandtl number is defined as

$$\text{Pr} = \mu c_p/\kappa = 5R\mu/2\kappa.$$

Thus λ and K can be determined phenomenologically by measuring μ and κ experimentally.

In theory, the differential scattering crosssection which appears in the Boltzmann collision integral can be calculated by quantum theory from first principles. However, in practice, a particular form is assumed for the intermolecular force law and certain parameters in this assumed form are fixed by choosing them so that the calculated viscosity agrees with the experimental viscosity measured over a range of temperatures. Thus, in a sense, both the ellipsoidal statistical model and the Boltzmann collision integral are phenomenological. Since the assumption of binary collisions was not crucial in the derivation of the ellipsoidal statistical model, the model may provide a phenomenological description for systems in which the binary collision model is not valid. [The only real use of the binary collision assumption was in the assumption that K was independent of n ; for a more general model, $K = K(n, T)$.]

B. Determination of Model Parameters from the Boltzmann Integral

In the last section a method was obtained for determining λ and K when the experimental values of μ and κ were known. However, when the molecular force law is known, it would be advantageous to have a method of determining λ and K directly from the Boltzmann integral.

First let us define the second-order interaction moments,

$$J_{ij} = \int c_i c_j \frac{\delta f}{\delta t} d\mathbf{c},$$

and the contracted third-order interaction moments,

$$J_{iii} = \int c_i c_j c_k \frac{\delta f}{\delta t} d\mathbf{c},$$

which are associated with the relaxation of the pressure tensor and the heat flux vector.

For the ellipsoidal statistical model, the interaction moments are easily shown to be

$$J_{ij} = -n^2 K (M_{ij} - \lambda_{ij}) = -n^2 K (1 - \lambda) \tilde{M}_{ij}, \quad (32)$$

$$J_{iii} = -n^2 K M_{iii}. \quad (33)$$

When the Chapman-Enskog distribution, as given by Eqs. (17) and (24), is substituted into Eqs. (32) and (33), the ellipsoidal statistical model interaction moments, which turn out to be independent of K and λ , become

$$J_{ij} = 2nRT \tilde{\partial} u_i / \partial x_j, \quad (34)$$

$$J_{iii} = 5nR^2T \partial T / \partial x_i. \quad (35)$$

However, these interaction moments can also be determined directly from the Boltzmann equation, and we determine K and λ by requiring that the ellipsoidal statistical model interaction moments are identical with the Boltzmann equation interaction moments.

For the Chapman-Enskog distribution, the Boltzmann collision integral becomes

$$\frac{\delta f}{\delta t} = n^2 \int \Phi(\mathbf{c})\Phi(\mathbf{c}_1)[F^{(1)}]gb \, db \, d\epsilon \, d\mathbf{c}_1, \quad (36)$$

where $F^{(1)}$ is given by Eq. (34), and we have introduced the notation

$$[G] = G(\mathbf{c}') + G(\mathbf{c}_1') - G(\mathbf{c}) - G(\mathbf{c}_1),$$

where G is any function of velocity and \mathbf{c}' and \mathbf{c}_1' are the velocity after collision of two particles which collide with initial velocities \mathbf{c} and \mathbf{c}_1 . Then

$$J_{ii} = n^2 \int \Phi(\mathbf{c})\Phi(\mathbf{c}_1)c_i c_i [F^{(1)}]gb \, db \, d\epsilon \, d\mathbf{c} \, d\mathbf{c}_1. \quad (37)$$

Substituting Eq. (24) into Eq. (37), the integration can be carried out after a somewhat lengthy algebraic manipulation to give

$$J_{ii} = \frac{16nRT}{5K(1-\lambda)} \Omega^2(2) \frac{\partial u_i}{\partial x_i}, \quad (38)$$

where $\Omega^2(2)$, an integral depending only on temperature which has been evaluated by Chapman and Cowling⁷ for many molecular force laws, is

$$\Omega^2(2) = \pi^{\frac{1}{2}} \int_0^\infty e^{-x^2} x^6 \phi^{(2)} [2x(RT)^{\frac{1}{2}}] \, dx,$$

where

$$\phi^{(2)}(g) = \int_0^\infty (1 - \cos^2 \chi) gb \, db.$$

Since the ellipsoidal statistical model result of Eq. (34) must equal Eq. (38), we require that

$$K(1-\lambda) = (8/5)\Omega^2(2). \quad (39)$$

The third-order moment J_{iii} is evaluated from the Boltzmann integral in a manner similar to the derivation of J_{ii} , and we obtain

$$J_{iii} = \frac{16nR^2T}{3K} \Omega^2(2) \frac{\partial T}{\partial x_i}. \quad (40)$$

If the ellipsoidal statistical model result of Eq. (35) is to agree with Eq. (40), we require

$$K = (16/15)\Omega^2(2), \quad (41)$$

and, from Eq. (39), the parameter λ is independent

of the molecular force law and has the universal value

$$\lambda = -\frac{1}{2}. \quad (42)$$

These values for K and λ can be substituted into Eqs. (26) and (28) to obtain the ellipsoidal statistical model expressions for the coefficients of viscosity and heat conduction

$$\mu = 5kT/8\Omega^2(2), \quad \text{Pr} = 2/3,$$

which are identical with what Chapman and Cowling call the first approximation⁷ to the transport coefficients. These expressions are exact for Maxwellian molecules and good approximations for any force law. In the Chapman-Enskog method of deriving the Navier-Stokes equations from the Boltzmann equation, it is necessary to solve an integral equation to obtain $F^{(1)}$, the first-order correction to the distribution function. In order to solve this integral equation, $F^{(1)}$ must be expanded in a series of Sonine polynomials. By using the ellipsoidal statistical model as an intermediary, the mathematical procedures are considerably simplified.

The arguments in Sec. IV required K to be a function of temperature alone, and this is satisfied by Eq. (41). Since K must depend only upon temperature, the value of K given by Eq. (41) will hold for highly nonequilibrium distributions, even though it was obtained by considering the near-equilibrium Chapman-Enskog solution. To verify this, we note that, with $\lambda = -\frac{1}{2}$ and K given by Eq. (41), the interaction moments given by Eqs. (32) and (33) are

$$J_{ii} = -(8/5)\Omega^2(2)n^2\tilde{M}_{ii}, \quad (43)$$

$$J_{iii} = -(16/15)\Omega^2(2)n^2M_{iii}. \quad (44)$$

Equations (43) and (44) are the exact results obtained from the Boltzmann collision integral for Maxwell molecules and an arbitrary distribution function. For other force laws, these equations correspond to the so called diagonal approximation which Grad considers a "good approximation in general."¹⁷ Since these are the same moments which appear in Grad's thirteen-moment method, the ellipsoidal statistical model gives the same result as the Boltzmann collision integral at the thirteen-moment level of approximation.

VI. MULTICOMPONENT GAS MIXTURES

In this section the idea of maximizing the uncertainty S will be used to construct a statistical model for a gas mixture. Let $n_a(\mathbf{r}, t)$ denote the number density of particles of type "a" and

$n_a(\mathbf{r}, t)f_a(\mathbf{v}, \mathbf{r}, t)d\mathbf{v}$ denote the expected number of particles of type "a" in the volume element $d\mathbf{r}$ about the position $\mathbf{r} = (x_1, x_2, x_3)$ with velocities in the range $d\mathbf{v}$ about $\mathbf{v} = (v_1, v_2, v_3)$. Neglecting external forces, the Boltzmann equation for the a th component of the gas has the form

$$\frac{\partial}{\partial t}(n_a f_a) + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}}(n_a f_a) = \frac{\delta f_a}{\delta t} = \sum_b \frac{\delta f_{ab}}{\delta t}. \quad (45)$$

The ellipsoidal statistical model developed in the previous section can be used without change as a model for the self-collision term $\delta f_{aa}/\delta t$. Therefore, we concentrate on the cross-collision term $\delta f_{ab}/\delta t$ which describes the rate of change of the a th distribution function due to collisions with particles of type "b." An inspection of the Boltzmann collision integral for mixed binary collisions suggests a model having the form

$$\delta f_{ab}/\delta t = -n_a n_b K_{ab}(f_a - \psi_{ab}), \quad (46)$$

where K_{ab} and ψ_{ab} should clearly be independent of n_a and n_b . Here, $n_a n_b K_{ab} d\mathbf{r} dt$ represents the total number of molecules of type "a" in the volume element $d\mathbf{r}$ which undergo collisions with molecules of type "b" in the time interval dt . Assuming that particles are neither created or destroyed, $\int \psi_{ab} d\mathbf{v} = 1$, where $\psi_{ab}(\mathbf{v}, \mathbf{r}, t) d\mathbf{v}$ is the probability that an "a" particle will emerge from a collision with a velocity in the range $d\mathbf{v}$ about \mathbf{v} . Now we assume that in some manner we can determine the mean velocity and the mean energy with which "a" particles emerge from collisions with "b" particles. That is, we assume that the quantities

$$\mathbf{u}^{ab} = \int \mathbf{v} \psi_{ab} d\mathbf{v}, \quad (47)$$

$$3 \frac{k}{m_a} T_{ab} = \int (\mathbf{v} - \mathbf{u}^{ab})^2 \psi_{ab} d\mathbf{v} \quad (48)$$

are known functions of \mathbf{r} and t .

As usual, the functional $\psi_{ab}[f_a, f_b]$ will be determined by maximizing the uncertainty $S = -\int \psi_{ab} \ln \psi_{ab} d\mathbf{v}$, subject to the restrictions given by Eqs. (47)–(48). The mathematics is essentially identical with that of Sec. III, and we obtain

$$\psi_{ab} = (m_a/2\pi k T_{ab})^{3/2} \exp - [m_a(\mathbf{v} - \mathbf{u}^{ab})^2/2kT_{ab}], \quad (49)$$

which is the same model for gas mixtures which was originally introduced by Gross and Krook.¹⁸

In order to obtain an improved approximation for the collision term, we must specify further in-

formation about the probability distribution ψ_{ab} . Therefore, let us assume that all of the second-order moments,

$$\lambda_{ij}(a, b) = \int (v_i - u_i^{ab})(v_j - u_j^{ab}) \psi_{ab} d\mathbf{v}, \quad (50)$$

are known, in addition to Eqs. (47) and (48). Maximizing S subject to these restrictions leads to the expression

$$\psi_{ab} = (2\pi)^{-3} |\lambda|^{-1/2} \exp - \frac{1}{2} \epsilon_{ij} (v_i - u_i^{ab})(v_j - u_j^{ab}), \quad (51)$$

where ϵ_{ij} is the ij th component of the tensor inverse to λ_{ij} and $|\lambda|$ is the determinant of λ_{ij} . For notational simplicity, λ_{ij} is always to be understood as $\lambda_{ij}(a, b)$ unless otherwise specified; this should cause no confusion but note that $\lambda_{ij}(a, b) \neq \lambda_{ij}(b, a)$.

The ellipsoidal statistical model for cross-collisions will be completely described by Eqs. (46) and (51) once the parameters \mathbf{u}^{ab} and λ_{ij} are determined. As with the Gross-Krook model,⁹ the conservation of total momentum and energy place certain restrictions on \mathbf{u}^{ab} and λ_{ij} . For our purposes, it is convenient to choose these parameters by requiring the model to give the same results for the rate of change of certain lower-order moments as the Boltzmann integral for the Maxwell force law; the conservation requirements are then automatically satisfied.

Let the mean flow velocity of the a th species be denoted by

$$\mathbf{u}^a = \int f_a \mathbf{v} d\mathbf{v},$$

and the second-order moments by

$$M_{ii}^a = \int f_a (v_i - u_i^a)(v_i - u_i^a) d\mathbf{v},$$

where the temperature is defined as $T_a = (m_a/3k)M_{ii}^a$. Also the contracted third-order tensor related to heat transfer is denoted by

$$Q_i^a = \int (v_i - u_i^a)(\mathbf{v} - \mathbf{u}^a) f_a d\mathbf{v};$$

the notation is defined similarly for "b" particles.

Now consider the collision moments of the form

$$J_{ab}[g(\mathbf{v})] = \int g(\mathbf{v}) \frac{\delta f_{ab}}{\delta t} d\mathbf{v}.$$

It is well known that low-order collision moments can be simply expressed in terms of low-order moments of the distribution functions, when the collision term is taken to be the Boltzmann collision

¹⁸ E. P. Gross and M. Krook, Phys. Rev. **102**, 593 (1956).

integral for Maxwell molecules, and we simply write the results here.¹⁹

$$J_{ab}[\mathbf{v}] = -2n_a n_b \pi \phi_{ab}^{(1)} (m_b/m_0) (\mathbf{u}^a - \mathbf{u}^b), \quad (52)$$

where

$$\phi_{ab}^{(i)} = \int (1 - \cos^i \chi) g b db = (m_0 t_{ab}/m_a m_b)^{1/2} A_i \quad (53)$$

and $m_0 = m_a + m_b$, the force law is $F = t_{ab} r^{-5}$ and A_i is a numerical constant of order unity with $A_1 = 0.422$ and $A_2 = 0.436$.⁷ For either the Gross-Krook or the ellipsoidal statistical model, we have

$$J_{ab}[\mathbf{v}] = -n_a n_b K_{ab} [\mathbf{u}^a - \mathbf{u}^{ab}]. \quad (54)$$

Equations (52) and (54) will be equal if we choose

$$\mathbf{u}^{ab} = \mathbf{u}^a + \alpha (m_b/m_0) \mathbf{u}^*, \quad (55)$$

where $\mathbf{u}^* = \mathbf{u}^b - \mathbf{u}^a$ and we have introduced the undetermined constant $\alpha = 2\pi\phi_{ab}^{(1)}/K_{ab}$.

Next consider the second-order moments for the Boltzmann equation

$$\begin{aligned} J_{ab}[(v_i - u_i^a)(v_j - u_j^a)] &= -4n_a n_b \pi (m_b/m_0)^2 \\ &\cdot \{ \phi_{ab}^{(1)} [(m_a/m_b) M_{ij}^a - M_{ij}^b - u_i^* u_j^*] \\ &- \frac{1}{4} \phi_{ab}^{(2)} [(M_{kk}^a + M_{kk}^b + \mathbf{u}^{*2}) \delta_{ij} \\ &- 3(M_{ij}^a + M_{ij}^b + u_i^* u_j^*)] \}. \end{aligned} \quad (56)$$

The second-order moments for the ellipsoidal statistical model equation are

$$\begin{aligned} J_{ab}[(v_i - u_i^a)(v_j - u_j^a)] \\ = -n_a n_b K_{ab} [M_{ij}^a - \lambda_{ij} - \alpha^2 (m_b/m_0)^2 u_i^* u_j^*], \end{aligned} \quad (57)$$

and, if the collision moments of Eqs. (56) and (57) are to be equal, we require that

$$\begin{aligned} \lambda_{ij} &= M_{ij}^a \left(1 - \frac{2\alpha m_a m_b}{m_0^2} \right) + 2\alpha \left(\frac{m_b}{m_0} \right)^2 M_{ij}^b \\ &+ \alpha(2 - \alpha) \left(\frac{m_b}{m_0} \right)^2 u_i^* u_j^* + \frac{1}{2} \alpha \frac{A_2}{A_1} \left(\frac{m_b}{m_0} \right)^2 \\ &\cdot [(M_{kk}^a + M_{kk}^b + \mathbf{u}^{*2}) \delta_{ij} \\ &- 3(M_{ij}^a + M_{ij}^b + u_i^* u_j^*)]. \end{aligned} \quad (58)$$

With \mathbf{u}^{ab} and T_{ab} given by Eqs. (54) and (58), the ellipsoidal statistical model gives the exact values for the relaxation of \mathbf{u}_a and M_{ij}^a , regardless of the particular value chosen for α . One would like to evaluate α so that the relaxation of Q_a^* , the heat flux moment, would be given exactly; however, this is not generally possible because relaxation of Q_a^*

depends partly upon Q_a^b , which does not appear in the ellipsoidal statistical model for cross-collisions. The following argument can be used to evaluate α : first we note that all of the arguments for the term $\delta f_{ab}/\delta t$ are valid when the "b" particles are actually "a" particles. Then $m_b = m_a$, $M_{ij}^b = M_{ij}^a$, $\mathbf{u}^b = \mathbf{u}^a$, and Eq. (58) becomes

$$\lambda_{ij} = M_{ij}^a (1 - 3\alpha A_2/4A_1) + (\alpha A_2/4A_1) M_{kk}^a \delta_{ij}. \quad (59)$$

But Eq. (59) should agree with Eq. (15) for self-collisions, and with $\lambda = -\frac{1}{2}$, Eq. (15) is

$$\lambda_{ij} = (\frac{1}{2})(M_{kk}^a \delta_{ij} - M_{ij}^a), \quad (60)$$

and therefore

$$\alpha = 2A_1/A_2. \quad (61)$$

Actually, α could be a function of m_b/m_a , in which case Eq. (61) would be the value of α only for $m_b = m_a$. Equation (61) implies that $K_{ab} = \pi\phi_{ab}^{(2)}(g) = (16/15)\Omega_{ab}^2(2)$, in agreement with the self-collision model of Sec. IV.

For the Gross-Krook model, Hamel²⁰ and Morse²¹ have used the choice $\alpha = 1$. This has at least two advantages: (1) then $n_b K_{ab} = 2\pi n_b \phi_{ab}^{(1)}$, which is agreeable intuitively because this, is usually defined as the collision frequency for momentum transfer; (2) then $\mathbf{u}^{ab} = (m_a \mathbf{u}^a + m_b \mathbf{u}^b)/m_0$, which would be the correct form if the scattering were spherically symmetric in the center of mass system. However, since scattering is not spherically symmetric for Maxwell molecules, these advantages are not decisive. Basically, the choice for the parameter α remains arbitrary, and this arbitrariness may prove advantageous for special problems, such as when large mass ratios are involved.

It is worth noting that, if we replace λ_{ij} by its contracted form, $\frac{1}{3}\lambda_{kk} \delta_{ij}$, the ellipsoidal statistical model reduces to the Gross-Krook model with

$$\begin{aligned} T_{ab} &= \frac{m_a}{3k} \lambda_{kk} \\ &= T_a + \frac{2\alpha m_a m_b}{m_0^2} (T_b - T_a) + \alpha(2 - \alpha) \frac{m_a m_b^2}{3k m_0^2} u^{*2}, \end{aligned} \quad (62)$$

which would agree with values for T_{ab} given by Hamel²⁰ and Morse,²¹ if α were taken to be unity.

For non-Maxwellian force laws, the ellipsoidal statistical model no longer gives the exact equations for the relaxation of \mathbf{u}_a and T_a . However, as shown by Morse^{19,21} and by Tanenbaum,¹⁹ the relaxation equations take the form similar to the equations

¹⁹ See, for example, T. F. Morse, Phys. Fluids **6**, 1420 (1963), or B. S. Tanenbaum, Phys. Fluids **8**, 683 (1965).

²⁰ B. B. Hamel, Phys. Fluids **8**, 418 (1964).

²¹ T. F. Morse, Phys. Fluids **7**, 2012 (1964).

for Maxwell force laws if $(\mathbf{u}^a - \mathbf{u}^b)^2 \ll a_0^2$ where $a_0^2 = 2k[(T_a/m_a) + (T_b/m_b)]$ and if both f_a and f_b do not differ greatly from a Maxwellian. By comparison with these results, a model for a non-Maxwellian force law is obtained by choosing

$$\alpha K_{ab} = (16/3)\Omega_{ab}^{(1)}(1)\{a_0\}, \quad (63)$$

where

$$\Omega_{ab}^{(s)}(r)\{a_0\} = \pi^{\frac{1}{2}} \int e^{-x^2} x^{2r+2} \phi_{ab}^{(s)}(a_0) dx.$$

Equation (58) is slightly changed to give

$$\begin{aligned} \lambda_{ii} = & M_{ii}^a \left(1 - \frac{2\alpha m_a m_b}{m_0^2}\right) \\ & + 2\alpha \left(\frac{m_b}{m_0}\right)^2 M_{ii}^b + \alpha(2 - \alpha) \left(\frac{m_b}{m_0}\right)^2 u_i^* u_i^* \\ & + \frac{1}{2} \alpha \frac{\Omega_{ab}^{(2)}(2)}{\Omega_{ab}^{(1)}(1)} \left(\frac{m_b}{m_0}\right)^2 [(M_{kk}^a + M_{kk}^b + \mathbf{u}^{*2}) \delta_{ii} \\ & - 3(M_{ii}^a + M_{ii}^b + u_i^* u_i^*)], \end{aligned} \quad (64)$$

and in order to obtain agreement with the self-collision term, we choose

$$\alpha = 5\Omega_{ab}^{(1)}(1)/\Omega_{ab}^{(2)}(2). \quad (65)$$

For inverse power laws ($F = t_{ab}/r^s$), α becomes

$$\alpha = 5A_1(s)/A_2(s)[3 - 2/(s-1)], \quad (66)$$

where $A_1(s)$ are evaluated in Ref. 7. K_{ab} becomes

$$K_{ab} = \frac{8}{15} \pi^{\frac{1}{2}} a_0^{(s-5)/(s-1)} \left(\frac{m_0 t_{ab}}{m_a m_b}\right)^{2/(s-1)} A_2(s) \Gamma\left(4 - \frac{2}{s-1}\right). \quad (67)$$

For rigid spheres, the limit as $s \rightarrow \infty$, $\alpha = 5/2$, and

$$K_{ab} = (16/15)\pi^{\frac{1}{2}} a_0 \sigma^2, \quad (68)$$

where $\sigma = r_1 + r_2$.

Finally, for a Coulomb force with a Debye cutoff chosen in the usual way,¹⁹ $\alpha = 5/2$, and

$$K_{ab} = (2/15)(m_0/m_a m_b)^2 (e^4 \ln \Lambda / \pi^{\frac{1}{2}} a_0^3). \quad (69)$$

For all force laws, the cross-collision model agrees with the self-collision ellipsoidal statistical model when the "b" particles are identical with the "a" particles, and also agrees with the approximate relaxation equations for \mathbf{u}_a and T_a which were obtained from Boltzmann equation by Morse¹⁹ and by Tanenbaum.¹⁹

VII. STATISTICAL MODELS FOR GASES WITH INTERNAL ENERGY STATES

As a final example of the use of the maximum uncertainty principle to construct a collision model, we consider a gas whose molecules possess internal degrees of freedom. Let the number density for each quantum state l be $n_l(\mathbf{r}, t)$, where the single index l refers to the entire set of quantum numbers $\{l\} = l_1, l_2, l_3, \dots$ necessary to specify the internal state of the molecule. Also, let $n_l(\mathbf{r}, t) f_l(\mathbf{v}, \mathbf{r}, t) d\mathbf{v} d\mathbf{r}$ be the expected number of molecules in the quantum state l in the volume element $d\mathbf{r}$ about \mathbf{r} with velocities in the range $d\mathbf{v}$ about \mathbf{v} , so that $\int f_l d\mathbf{v} = 1$.

The Boltzmann equation for $n_l f_l$ has the form

$$\frac{\partial(n_l f_l)}{\partial t} + \mathbf{v} \cdot \frac{\partial(n_l f_l)}{\partial \mathbf{x}} = \frac{\delta f_l}{\delta t} = \left(\frac{\delta f_l}{\delta t}\right)_{e1} + \left(\frac{\delta f_l}{\delta t}\right)_{in}, \quad (70)$$

where we have broken up the collision term into two parts: (1) the elastic collision term $(\delta f_l/\delta t)_{e1}$ representing the rate of change of $n_l f_l$ due to collisions in which no change occurs in the internal energy of the colliding molecules; (2) the inelastic term $(\delta f_l/\delta t)_{in}$ representing collisions in which at least one of the colliding molecules changes its internal energy state. Clearly such a breakup of the collision term is always possible; a method of writing the breakup in terms of Wang Chang and Uhlenbeck's formal expression²² which generalized the Boltzmann collision integral to include internal degrees of freedom has been given by Morse.²³ An advantage of breaking up the collision term is that elastic collisions normally occur much more frequently than inelastic collisions.

A. Elastic Collision Term

For elastic collisions, the form of the collision term must be unaffected by the existence of internal energy states, which only determine the labeling of particles. Therefore, one could use the multicomponent model developed in the last section, i.e.,

$$\left(\frac{\delta f_l}{\delta t}\right)_{e1} = -n_l \sum_a n_a K_{la}(f_l - \psi_{la}).$$

However, there are usually a large number of energy states so that a simplification is desirable. If the force law causing the elastic deflection is sensibly independent of the internal energy states of the colliding particles, we may assume $K_{la} = K_{e1}$ independent of l and a .²⁴ Then the number of particles

²² C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan Report CM-681 (1951).

²³ T. F. Morse, Phys. Fluids 7, 159 (1964).

²⁴ Strictly speaking, K_{la} should depend on the kinetic temperature of the "q" and "a" particles individually, except for the Maxwell force law.

in state l in the volume element $d\mathbf{r}$ which undergo collision per unit time is $-n_l n K_{e1} d\mathbf{r}$ where $n = \sum_a n_a$ and the appropriate form for the statistical model is

$$(\delta f_l / \delta t)_{e1} = -n_l n K_{e1} (f_l - \psi_l^{(e1)}), \quad (71)$$

where

$$\psi_l^{(e1)} = \frac{1}{n} \sum_a n_a \psi_{la}, \quad (72)$$

and an explicit form for ψ_{la} is given in the last section. Clearly, $\psi_l^{(e1)}(\mathbf{v}, \mathbf{r}, t) d\mathbf{v}$ is the probability that a particle in quantum state l which has suffered an *elastic* collision at point \mathbf{r} and time t will emerge from the collision with a velocity in the range $d\mathbf{v}$ about \mathbf{v} . Although Eq. (72) gives an explicit form for $\psi_l^{(e1)}$, a simpler form would be desirable.

Let the mean flow velocity \mathbf{u}^a for the quantum state a and the total flow velocity \mathbf{u} be defined by

$$n\mathbf{u} = \sum_a n_a \mathbf{u}^a = \sum_a n_a \int \mathbf{v} f_a(\mathbf{v}) d\mathbf{v},$$

where we have implicitly assumed that the molecular mass m is not sensibly changed by a change in quantum state. Similarly, we define the total translational temperature $T^{(tr)}$ by

$$3nRT^{(tr)} = \sum_a n_a \int |\mathbf{v} - \mathbf{u}|^2 f_a(\mathbf{v}) d\mathbf{v},$$

and $T_a^{(tr)}$, the translational temperature for molecules in quantum state a , by

$$\begin{aligned} \sum_a n_a T_a^{(tr)} &= \left(\frac{1}{3R} \right) \sum_a n_a \int |\mathbf{v} - \mathbf{u}^a|^2 f_a(\mathbf{v}) d\mathbf{v} \\ &= nT^{(tr)} + \left(\frac{1}{3R} \right) (nu^2 - \sum_a n_a u_a^2). \end{aligned}$$

From Eq. (72) we can now calculate

$$\mathbf{U}^l = \int \mathbf{v} \psi_l^{(e1)} d\mathbf{v} = (1 - \frac{1}{2}\alpha) \mathbf{u}^l + \frac{1}{2}\alpha \mathbf{u}, \quad (73)$$

where we have used Eq. (55) and α is the undetermined parameter in the multicomponent model. Similarly, we find

$$\begin{aligned} 3RT_l^* &= \int |\mathbf{v} - \mathbf{U}^l|^2 \psi_l^{(e1)} d\mathbf{v} \\ &= 3RT^{(tr)} \frac{1}{2}\alpha + 3R(1 - \frac{1}{2}\alpha) T_l^{(tr)} \\ &\quad + \frac{1}{2}\alpha(1 - \frac{1}{2}\alpha) |\mathbf{u}^l - \mathbf{u}|^2, \end{aligned} \quad (74)$$

where Eqs. (55), (62), and (73) have been used.

The uncertainty S associated with $\psi_l^{(e1)}$ is

$$S = - \int \psi_l^{(e1)} \ln \psi_l^{(e1)} d\mathbf{v}.$$

Next we maximize S , assuming that the only information we have about $\psi_l^{(e1)}$ is Eqs. (73) and (74), to obtain

$$\begin{aligned} \psi_l^{(e1)} &= \Phi(\mathbf{v}, \mathbf{U}^l, T_l^*) \\ &= (2\pi k T_l^*)^{-\frac{3}{2}} \exp - \frac{|\mathbf{v} - \mathbf{U}^l|^2}{2RT_l^*}, \end{aligned} \quad (75)$$

as an approximation to Eq. (72).

In Sec. VI the parameter α which appears in Eqs. (73) and (74) was taken to be $\alpha = 2A_1/A_2 = 1.93$ for Maxwell molecules. If, instead, we choose $\alpha = 2$ then $\mathbf{U}^l = \mathbf{u}$ and $T_l^* = T^{(tr)}$. This leads to the simplified form of the model

$$(\delta f_l / \delta t)_{e1} = -n_l n K_{e1} [f_l - \Phi(\mathbf{v}, \mathbf{u}, T^{(tr)})]. \quad (76)$$

Regardless of our choice for α , it is easily verified that $\psi_l^{(e1)}$ as given by Eq. (72) is exactly equal to $\Phi(\mathbf{v}, \mathbf{u}, T^{(tr)})$ whenever $\mathbf{u}^a = \mathbf{u}$ and $T_a^{(tr)} = T^{(tr)}$ for all a , that is, whenever there is no correlation between the quantum state and the distribution in velocity space. Therefore, we consider Eq. (76) to be the appropriate model for the elastic collisions. If we sum Eq. (76) over all l and let $n f = \sum_l n_l f_l$, it reduces to the Krook model, $(\delta f / \delta t)_{e1} = -n^2 K_{e1} [f - \Phi(\mathbf{v}, \mathbf{u}, T)]$. From the arguments in the previous sections, it is apparent that, if we require the correct Prandtl number, the emission term $\psi_l^{(e1)} = \Phi(\mathbf{v}, \mathbf{u}, T)$ in Eq. (76) must be changed to an ellipsoidal statistical model where

$$\psi_l^{(e1)} = \frac{\exp - \frac{1}{2} \epsilon_{ij} (v_i - u_i)(v_j - u_j)}{(2\pi)^{\frac{3}{2}} |\boldsymbol{\lambda}|^{\frac{1}{2}}}, \quad (77)$$

and, from Eq. (15),

$$\lambda_{ij} = \frac{1}{2} (M_{kk}^{(tr)} \delta_{ij} - M_{ij}^{(tr)}), \quad (78)$$

where

$$nM_{ij}^{(tr)} = \sum_a n_a \int (v_i - u_i)(v_j - u_j) f_a(\mathbf{v}) d\mathbf{v}.$$

It is easily verified that either Eq. (76) or Eq. (77) will satisfy all the collisional invariants required for an elastic model, i.e., the conservation of number of particles in state l ,

$$\int \left(\frac{\delta f_l}{\delta t} \right)_{e1} d\mathbf{v} = 0,$$

the conservation of *total* momentum

$$\sum_l \int \mathbf{v} \left(\frac{\delta f_l}{\delta t} \right)_{e1} d\mathbf{v} = 0,$$

and the conservation of kinetic energy

$$\sum_l \int v^2 \left(\frac{\delta f_l}{\delta t} \right)_{e1} d\mathbf{v} = 0.$$

B. Inelastic Collision Term

For the inelastic collision term, we assume that the number of particles in state "l", in volume element $d\mathbf{r}$ about \mathbf{r} and with velocities in the range $d\mathbf{v}$ about \mathbf{v} which undergo inelastic collisions per unit time is $n(\mathbf{r}, t)K_{in}(\mathbf{r}, t)n_l(\mathbf{r}, t)f_l(\mathbf{v}, \mathbf{r}, t) d\mathbf{r} d\mathbf{v}$. The total number of particles in the volume element $d\mathbf{r}$ which undergo inelastic collisions per unit time is therefore $n^2 K_{in} d\mathbf{r}$. Therefore, an appropriate model for the inelastic collision term is

$$(\delta f_l / \delta t)_{el} = n K_{in} (n \psi_l^{(in)} - n_l f_l), \quad (79)$$

where $\psi_l^{(in)} d\mathbf{v}$ is the probability that, given a particle which has undergone an inelastic collision, it will emerge in quantum state "l" with a velocity in the range $d\mathbf{v}$ about \mathbf{v} .

The conservation requirements for the inelastic collisions are the conservation of *total* number of particles

$$\sum_l \int \left(\frac{\delta f_l}{\delta t} \right)_{in} d\mathbf{v} = 0,$$

the conservation of total momentum

$$\sum_l \int \left(\frac{\delta f_l}{\delta t} \right)_{in} d\mathbf{v} = 0,$$

and the conservation of total energy

$$\sum_l \int \left(\frac{1}{2} m v^2 + E_l \right) \frac{\delta f_l}{\delta t} d\mathbf{v} = 0.$$

The conservation laws lead to the following requirements on $\psi_l^{(in)}$:

$$\sum_l \int \psi_l^{(in)} d\mathbf{v} = 1, \quad (80a)$$

$$\sum_l \int \mathbf{v} \psi_l^{(in)} d\mathbf{v} = \mathbf{u}, \quad (80b)$$

$$\sum_l \int \left(\frac{1}{2} m |\mathbf{v} - \mathbf{u}|^2 + E_l \right) \psi_l^{(in)} d\mathbf{v} = \bar{E} + \frac{3}{2} k T^{(tr)}, \quad (80c)$$

where we have denoted the average internal energy per molecule by \bar{E} where

$$n\bar{E} = \sum_n n_n E_n.$$

In contrast to $\psi_l^{(el)}$, which was defined over a continuum \mathbf{v} , the probability density $\psi_l^{(in)}$ is defined over the discrete states l and, for each value of l , over a continuum \mathbf{v} . The appropriate uncertainty measure is therefore

$$S = - \sum_l \int \psi_l^{(in)} \ln \psi_l^{(in)} d\mathbf{v}. \quad (81)$$

Multiplying Eqs. (80a-c) by the Lagrangian multipliers λ , $\boldsymbol{\lambda}$, and $\bar{\lambda}$, taking the variation $\psi_l^{(in)} \rightarrow \psi_l^{(in)} + \delta \psi_l^{(in)}$, and adding to the variation of Eq. (81) yields

$$\delta S = - \sum_l \int \delta \psi_l^{(in)} [\ln \psi_l^{(in)} + 1 - \lambda - \boldsymbol{\lambda} \cdot \mathbf{v} - \bar{\lambda} (\frac{1}{2} m |\mathbf{v} - \mathbf{u}|^2 + E_l)] d\mathbf{v}.$$

The maximum of S occurs when the parenthesis vanishes, and after evaluating the Lagrangian multipliers from Eqs. (80a-c), we obtain

$$\psi_l^{(in)} = \Phi(\mathbf{v}, \mathbf{u}, T_\infty) \frac{\exp - (E_l / k T_\infty)}{\sum_n \exp - (E_n / k T_\infty)}, \quad (82)$$

where T_∞ is defined *implicitly* by the equation

$$\frac{3}{2} k T_\infty + \frac{\sum_n E_n \exp - (E_n / k T_\infty)}{\sum_n \exp - (E_n / k T_\infty)} = \frac{3}{2} k T^{(tr)} + \bar{E}, \quad (83)$$

and Φ is the Maxwellian with flow velocity \mathbf{u} and temperature T_∞ . The inelastic collision model is therefore specified by Eqs. (79), (82), and (83), where K_{in} is a phenomenological constant which is a function of temperature and possibly number density.

C. Applications to a Diatomic Gas

For a diatomic gas with rotational and vibrational degrees of freedom, the energy levels, measured from the ground state, are

$$E_l = \hbar \omega s + (\hbar^2 / 2I) r(r+1) = \hbar \omega s + e,$$

where s and r are the vibrational and rotational quantum numbers, respectively.

In most cases of practical interest, $kT \gg \hbar^2 / 2I$ and the rotational energy can be treated classically. In this case, it is convenient to introduce the notation $n_s(e, \mathbf{r}, t) f_s(\mathbf{v}, e, \mathbf{r}, t) d\mathbf{e} d\mathbf{v} d\mathbf{r}$, which represents the number of particles in vibrational state s with rotational energy between e and $e + de$ in the volume element $d\mathbf{r}$ about \mathbf{r} with velocities in the range $d\mathbf{v}$ about \mathbf{v} at time t . The summation in Eqs. (82) and (83) becomes

$$\begin{aligned} & \sum_n \exp - \left(\frac{E_n}{k T_\infty} \right) \\ &= \sum_{r=0}^{\infty} (2r+1) e^{-\hbar^2 r(r+1)/2IkT_\infty} \sum_{s=0}^{\infty} e^{-\hbar \omega s / k T_\infty} \\ &= (1 - e^{-\hbar \omega / k T_\infty})^{-1} \sum_{r=0}^{\infty} (2r+1) e^{-\hbar^2 r(r+1)/2IkT_\infty}, \end{aligned} \quad (84)$$

where there is a degeneracy of order $(2r+1)$ in

the r th rotational state. For $kT_\infty \gg \hbar^2/2I$, the important contributions to the final summation in Eq. (84) occur when $r \gg 1$, and the summation can be replaced by an integration,

$$\sum_{r=0}^{\infty} \rightarrow \int_0^{\infty} \frac{2I}{\hbar^2} \exp\left(\frac{-e}{kT_\infty}\right) de = \frac{2IkT_\infty}{\hbar^2}.$$

In this limit, the equation defining T_∞ becomes

$$\bar{E} + \frac{3}{2}kT^{(tr)} = \frac{5}{2}kT_\infty + \hbar\omega/(e^{\hbar\omega/kT_\infty} - 1), \quad (85)$$

where

$$n\bar{E} = \sum_{s=0}^{\infty} \int_0^{\infty} (\hbar\omega s + e)n_s(e) de, \quad n = \sum_{s=0}^{\infty} \int_0^{\infty} n_s(e) de.$$

The emission term $\psi_i^{(in)}(\mathbf{v})$ becomes

$$\psi_i^{(in)}(e, \mathbf{v}) = (kT_\infty)^{-1} \Phi(\mathbf{v}, \mathbf{u}, T_\infty) e^{-e/kT_\infty} \cdot (1 - e^{-\hbar\omega/kT_\infty}) e^{-\hbar\omega s/kT_\infty}, \quad (86)$$

and the inelastic collision term is

$$(\delta f_s(e, \mathbf{v})/\delta t)_{in} = -nK_{in}[n_s(e)f_s(e) - n\psi_s^{(in)}]. \quad (87)$$

In this notation, the kinetic equation is

$$\begin{aligned} \frac{\partial n_s(e)f_s(e, \mathbf{v})}{\partial t} + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{x}} [n_s(e)f_s(e, \mathbf{v})] \\ = \left(\frac{\delta f_s(e, \mathbf{v})}{\delta t} \right)_{e1} + \left(\frac{\delta f_s(e, \mathbf{v})}{\delta t} \right)_{in} + \left(\frac{\delta f_s}{\delta t} \right)_{rot}. \end{aligned} \quad (88)$$

The final term in Eq. (88) has been added to take account of inelastic collisions in which there is an energy exchange between rotational and translational degrees of freedom while the vibrational state is unchanged. The derivation of this term is similar to the full inelastic term and yields

$$(\delta f_s/\delta t)_{rot} = -nK_{rot}[n_s f_s(e, \mathbf{v}) - \bar{n}_s \psi_s^{(rot)}], \quad (89)$$

where the \bar{n}_s is the total number density of particles in state s , $\bar{n}_s = \int_0^{\infty} n_s(e) de$, and

$$\psi_s^{(rot)} = (kT_{rot})^{-1} \Phi(\mathbf{v}, \mathbf{u}, T_{rot}) \exp - (e/kT_{rot}), \quad (90)$$

$$\frac{5}{2}kT_{rot} = \frac{3}{2}kT^{(tr)} + \bar{e}, \quad (91)$$

where the average rotational energy \bar{e} is defined as

$$n\bar{e} = \sum_{s=0}^{\infty} \int_0^{\infty} en_s(e) de.$$

The elastic, rotational, and vibrational collision frequencies are normally ordered so that $nK_{e1} > nK_{rot} > nK_{in}$. For the moment, let us assume that they are separated by orders of magnitude although this may not be very well satisfied for the rotational and vibrational collision frequencies. Now consider the spatially homogeneous relaxation problem where

$n_s(e, 0)f_s(v, e, 0)$ can be specified arbitrarily. This specification determines the initial values for $T^{(tr)}(0)$, $T_{rot}(0)$, $T_\infty(0)$, $\mathbf{u}(0)$, $n_s(0)$, and $n(0)$. Then, during the translational epoch as $t \rightarrow t_1$, where $(nK_{e1})^{-1} \ll t_1 \ll (nK_{rot})^{-1}$, the distribution function

$$n_s(e, t)f_s(\mathbf{v}, e, t) \rightarrow n_s(e, 0)\Phi[\mathbf{v}, \mathbf{u}, T^{(tr)}(0)].$$

During the rotational epoch $t \rightarrow t_2$, where $(nK_{rot})^{-1} \ll t_2 \ll (nK_{in})^{-1}$, and

$$\begin{aligned} n_s(e, t)f_s(\mathbf{v}, e, t) \rightarrow \frac{\bar{n}_s(0)}{kT_{rot}(0)} \\ \cdot \exp - \left[\frac{e}{kT_{rot}(0)} \right] \Phi[\mathbf{v}, \mathbf{u}, T_{rot}(0)]. \end{aligned}$$

At this point, the rotational and translational degrees of freedom have come to equilibrium while all molecules remain in their initial vibrational state. During the final epoch, $t \rightarrow t_3$ where $t_3 \gg (nK_{in})^{-1}$ and the distribution function approaches its final equilibrium value

$$\begin{aligned} n_s(e, t)f_s(\mathbf{v}, e, t) \rightarrow \frac{n}{kT_\infty} \\ \cdot \exp - \left(\frac{e + \hbar\omega s}{kT_\infty} \right) \left[1 - \exp - \left(\frac{\hbar\omega}{kT_\infty} \right) \right] \Phi(\mathbf{v}, \mathbf{u}, T_\infty). \end{aligned}$$

The quantities n , \mathbf{u} , and T_∞ are constant during the whole relaxation process, $T^{(tr)}$ and $n_s(e)$ are constant during the translational epoch, and T_{rot} and \bar{n}_s are constant during the translational and rotational epochs.

D. Discussion

Although the kinetic theory of diatomic gases with internal energy states is potentially important for problems involving shock waves and hypersonic reentry, relatively little work has been published along these lines. A major obstacle has been the fact that, although a formal Boltzmann collision integral can be written down for these processes,²² the collision integral has never been evaluated for any realistic molecular model. In this situation the statistical model may provide a useful approximate method for studying these processes. The relaxation times $(nK_{e1})^{-1}$ and $(nK_{in})^{-1}$ must be chosen phenomenologically; a statistical model at this level of approximation is very convenient because these relaxation times are the parameters which are usually known experimentally.

The statistical model developed here is similar to a model for internal degrees of freedom introduced earlier by Morse,²³ but there are some differences which are worth noting. For the *elastic* collision

term $(\delta f_i/\delta t)_{e1}$, Morse uses the emission term $n^2 K_{e1} \Phi(\mathbf{v}, \mathbf{u}, T^{(tr)})$

$$\cdot \exp - (E_i/kT_i) \left[\sum_a \exp - (E_a/kT_i) \right]^{-1}$$

in place of the term $n K_{e1} n_i \Phi(\mathbf{v}, \mathbf{u}, T^{(tr)})$ given by our Eq. (76). The emission term used here is simpler and satisfies the requirement for conservation of particles in state i , $\int (\delta f_i/\delta t)_{e1} d\mathbf{v} = 0$, which is required for elastic collisions, while the Morse model satisfies only the weaker condition

$$\sum_i \int (\delta f_i/\delta t)_{e1} d\mathbf{v} = 0.$$

The Morse model allows transitions between internal energy states during the translational epoch, without however changing the *total* amount of energy locked in the internal degrees of freedom. Morse's inelastic collision term $(\delta f_i/\delta t)_{in}$ is the same as ours except that our T_∞ , which was defined by Eq. (83), is replaced by T_r defined (in our notation) by $c_r T_r = \frac{3}{2} k T^{(tr)} + \bar{E}$. Basically, this is a high-temperature approximation to our T_∞ , valid when kT is much greater than the spacing between energy levels. For example, when $kT \gg \hbar\omega$ for a diatomic gas, our Eq. (85) becomes

$$\frac{1}{2} k T_\infty = \frac{3}{2} k T^{(tr)} + \bar{E},$$

which is identical with Morse's equation for T_r with $c_r = \frac{1}{2} k$. Our Eq. (83) may equivalently be written as $\int_0^{T_\infty} c_e(T') dT' = \frac{3}{2} k T^{(tr)} + \bar{E}$, where $c_e(T)$ is in general a function of temperature.

VIII. CONCLUSION

A key step in constructing a statistical model of the collision term is the assignment of a probability distribution $\psi(\mathbf{v})$ for the velocities of molecules emerging from collision, about which we have only a limited amount of information in the form of a few lower-order moments. This is basically a problem in probability theory, and the variational method of maximizing Shannon's information measure allows us to obtain a "least-biased" assignment of ψ for any given state of knowledge.^{14,15} This method has the merit of allowing us to systematically improve the model by specifying additional moments of the collision term. The statistical models obtained at each step of this process describe a relaxation to the correct equilibrium distribution function. (Obtaining the maximum of the information theory entropy is straightforward when the method of Lagrangian multipliers can be used, but it should

be remarked that the Lagrangian multipliers are not applicable to every possible case.)

The ellipsoidal statistical model developed in this paper for a simple gas leads to the correct Prandtl number in the continuum limit, and therefore can be compared directly with the Navier-Stokes equations without the necessity of introducing a fictitious value for the coefficient of heat conductivity. The information theory entropy technique can be generalized to construct statistical models for quite general systems in nonequilibrium statistical mechanics as we have illustrated by considering gas mixtures and gases with internal degrees of freedom.

In this paper we have only considered models in which the collision parameter K was assumed to be independent of velocity. Although a model with a velocity-dependent $K(\mathbf{v})$ is more complicated to use in specific problems, it may be preferable in some cases, particularly if we were to generalize the model to systems with ionization and dissociation where a velocity cutoff is important. The information theory entropy is applicable to such models provided that in passing from Shannon's entropy for discrete states to a continuum we use $K(\mathbf{v})$ as a measure¹⁴ instead of the uniform measure used in Sec. III. Then the entropy measure becomes

$$S = - \int \psi \ln \left[\frac{\psi}{K(\mathbf{v})} \right]$$

for a simple gas. In lowest order, this measure leads to Krook's velocity-dependent model.

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APPENDIX . THE H -THEOREM FOR AN ELLIPSOIDAL STATISTICAL MODEL

According to Boltzmann's H -theorem for a simple gas, the quantity

$$H = \int n f \log n f d\mathbf{v}$$

satisfies the inequality $\partial H/\partial t \leq 0$ for a spatially homogeneous distribution, where the equality holds only if $f = \Phi$, the Maxwellian distribution. It is well known that the Krook model satisfies the

H -theorem, and we now consider the ellipsoidal statistical model, for which

$$\begin{aligned}\frac{\partial H}{\partial t} &= \int \frac{\delta f}{\delta t} (\log n f + 1) d\mathbf{v} \\ &= -n^2 K \int \log f(f - \Psi) d\mathbf{v}.\end{aligned}\quad (\text{A1})$$

Then a proof of the H -theorem is equivalent to showing $A = \int \log f(f - \Psi) d\mathbf{v}$ is positive-semidefinite for every function f . The quantity A can be put in the form $A = B + C$, where

$$B = \int \log \left(\frac{f}{\Psi} \right) (f - \Psi) d\mathbf{v} \geq 0, \quad (\text{A2})$$

$$C = \int \log \Psi (f - \Psi) d\mathbf{v}. \quad (\text{A3})$$

B is obviously positive-semidefinite and equals zero if and only if $f = \Psi$, which considering Eq. (15), requires Ψ to be the Maxwellian distribution.

Using Eqs. (12), (15), and the collisional invariants, C can be shown to equal

$$C = [(1 - \lambda)/6\lambda](\lambda_{kk}\epsilon_{ij} - 9). \quad (\text{A4})$$

Since ϵ_{ij} is the inverse of λ_{ij} , a positive-definite matrix, the product of the spurs $\epsilon_{ij}\lambda_{kk} \geq 9$ with equality occurring only if the distribution function is such that $\lambda_{ij} = RT\delta_{ij}$. However, $\lambda \cong -\frac{1}{2}$ so that C is negative-semidefinite and equal to zero only if $M_{ij} = RT\delta_{ij}$.

The H -theorem would be proved if one showed that $B \geq -C$, with equality occurring only when $f = \Phi$, so that $B = C = 0$. No general proof of

this has been found so that the existence of an H -theorem for the ellipsoidal statistical model remains an open question. On the other hand, we have not been able to find any function f which provides a counterexample to the H -theorem. For example, if f is the anisotropic Gaussian $f = a \exp -\frac{1}{2}\gamma_{ij}v_i v_j$, it is not difficult to show that $A = \frac{1}{6}(1 - \lambda) \cdot (M_{ij}\gamma_{ij} - 9)$; and since M_{ij} and γ_{ij} are positive-definite inverse matrices, $A \geq 0$ and the H -theorem is obeyed. The difficulty of finding a counterexample to the H -theorem can be appreciated by writing A in the form

$$A = \int \log \left(\frac{f}{\Phi} \right) (f - \Psi) d\mathbf{v},$$

where the integrand is negative only when the magnitude of f lies between the magnitudes of Φ and Ψ .

Although an H -theorem has not been demonstrated, it is not difficult to show that any distribution function in a spatially homogeneous problem always relaxes to equilibrium. If the ellipsoidal statistical model equation is multiplied by $v_i v_j - \frac{1}{3}v^2\delta_{ij}$ and integrated over velocity, the result is

$$\partial \tilde{M}_{ij} / \partial t = -nK(1 - \lambda)\tilde{M}_{ij},$$

so that

$$\tilde{M}_{ij}(t) = \tilde{M}_{ij}(0)e^{-nK(1-\lambda)t}. \quad (\text{A5})$$

From Eqs. (15) and (A5) one finds that $\lambda_{ij} \rightarrow 3RT$ and $\epsilon_{ij} \rightarrow 3/RT$, so that from Eq. (A4), $C \rightarrow 0$, leaving $A = B \geq 0$. Thus H continues to decrease until $B = 0$ which occurs only when f is the equilibrium Maxwell distribution.