

## Equations for Gas Mixtures

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Starting with the exact Boltzmann equations for gas mixtures with arbitrary intermolecular potentials, a macroscopic theory of mixtures is obtained. For a binary gas with masses  $m_\alpha$ ,  $m_\beta$  total number density  $n$ , viscosity  $\mu$ , and diffusion coefficient  $D_{\alpha\beta}$ , it is shown that the classical Chapman-Enskog theory of mixtures holds when  $C = 2\mu/[(m_\alpha + m_\beta)nD_{\alpha\beta}]$  (which is related to the Schmidt number) is near unity. This criterion delimits the region of validity of the Chapman-Enskog equations. For situations outside the Chapman-Enskog range a new system of equations, referred to as the two-temperature theory, is shown to be valid. The latter includes a new diffusion effect which involves temperature differences. The temperature difference in the Chapman-Enskog regime which becomes higher order is also explicitly obtained. For problems widely removed from equilibrium a two-fluid theory is advanced. The last has the Chapman-Enskog and two-temperature theories as limiting forms in near equilibrium situations. A heat flow problem illustrating the new equations is discussed.

### I. INTRODUCTION

CONSIDERATION of a multi-component gas must begin with an analysis of the associated Boltzmann equations. For any except the simplest problems, such a program is unfeasible. Fortunately, in most situations of interest, simpler equations may be shown to apply (under appropriate conditions, an example is the equations which follow from the Chapman-Enskog procedure). The analysis of the gas-mixture equations is, in part, more formidable than the comparable simple gas (i.e., single component) theory because of the many different scales which now enter in the approach to equilibrium.

The approach to equilibrium can be divided roughly into two processes. There is the approach of the distribution function to a Maxwellian distribution (referred to as Maxwellization); and, in addition, there is the equilibration of the species (i.e., the vanishing of differences in velocity and temperature among the species). Although the Maxwellization of a species itself can take place in a variety of ways, a suitable measure of this Maxwellization is the scale on which the stress of that species becomes isotropic (or, equivalently, the scale on which the heat conduction relaxes). Maxwellization can occur due to self-collisions alone, (e.g., the light gas in a binary mixture with disparate masses but equal mass densities), or due to cross collisions alone, (e.g., the heavy gas in the same mixture), or due to a combination of these events, (e.g., the light gas in a mixture with disparate masses but equal number densities).<sup>1</sup>

The equilibration of the species also does not take place with a definite pattern. Velocity and temperature differences may equilibrate on vastly different scales, (e.g., the second mentioned mixture above), or on the same scale, (e.g., the first mixture above). Moreover, the events just discussed need not occur sequentially but can occur concomitantly.

In the classical Chapman-Enskog procedure for a simple gas, one examines the Boltzmann equation for scales that are large compared with the mean free path (or mean time of flight). An analogous procedure for a mixture becomes difficult because of the multiplicity of length scales. Furthermore, equations resulting from such a program may apply only to one particular gas because account must be taken of the specific relative scalings contained in the Maxwellization and equilibration processes. In examining the classical Chapman-Enskog procedure for a binary gas (see Chapman and Cowling<sup>2</sup>), it becomes clear that the procedure is developed under the assumption that all scales are roughly the same order or that the phenomena to be examined is smooth with respect to all collisional scales. In the present study we present a method which is applicable to any gas mixture, and which considerably relaxes the latter requirement.

Our analysis is performed in two stages. We first consider the evolution of the mixture Boltzmann equations under the Maxwellization process. This leads to a system of equations in the density, temperature, and velocity of each species. This form is only an intermediate step in the perturbation procedure since equilibration effects are not yet

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<sup>1</sup> The validity of these statements, as well as additional examples will be demonstrated in later sections.

<sup>2</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1960).

included. (These equations are shown to be appropriate to situations widely removed from equilibrium.) The second and final step in the perturbation procedure takes into account the equilibration of the gas species. This results in a further reduction of the equations notably by the introduction of a diffusion equation. This contains, in addition to the usual diffusion effects, a term depending on temperature differences. Only under very special circumstances do we recover the Chapman-Enskog equations for gas mixtures. For a binary mixture, the criteria for Chapman-Enskog to hold is stated in the abstract. Even for mixtures with equal mass densities we find that a significant portion of the cases exhibit multiple temperature effects. Despite this delimitation of the Chapman-Enskog equations, it is also found that some fairly extreme situations fall into the Chapman-Enskog framework. This is discussed in Sec. IV.

In the final section we apply the new equations to heat flow in a binary mixture. It is found that slip boundary conditions for the individual species must be considered. For example, under proper conditions, only one species of a mixture may exhibit a significant slip. This leads naturally to the notion of relative slip for gas mixtures.

II. THE CONSERVATION EQUATIONS

In the interest of space and simplicity, the following analysis will deal only with binary mixtures. This does not restrict the generality of the results because the complexity of an *n*-component mixture is contained in a summation of terms each of which represents the effect of a binary collision.

We write the species number density distribution function as *f*<sub>α</sub> and the corresponding Maxwellian as<sup>3</sup>

$$f_{0\alpha} = n_\alpha \left( \frac{m_\alpha}{2\pi kT_\alpha} \right)^{3/2} \exp \left( \frac{-m_\alpha C_\alpha^2}{2kT_\alpha} \right), \quad (1)$$

where

$$C_\alpha = \xi - U_\alpha, \quad (2)$$

$$\rho_\alpha = m_\alpha n_\alpha = \int_{-\infty}^{\infty} m_\alpha f_\alpha d\xi, \quad (3)$$

$$U_{\alpha i} = \frac{1}{\rho_\alpha} \int_{-\infty}^{\infty} m_\alpha \xi_i f_\alpha d\xi, \quad (4)$$

$$\begin{aligned} \rho_\alpha e_\alpha &= \frac{3}{2} p_\alpha = \frac{3}{2} n_\alpha k T_\alpha \\ &= \int_{-\infty}^{\infty} m_\alpha \frac{(\xi - U_\alpha)^2}{2} f_\alpha d\xi. \end{aligned} \quad (5)$$

<sup>3</sup> Only equations for the α gas will be presented if the corresponding β gas equations can be obtained by a simple interchange of Greek subscripts.

The species stress and heat conduction are defined by

$$\begin{aligned} P_\alpha^{ij} &= \{P_\alpha^{ij}\} + \delta_{ij} p_\alpha \\ &= \int_{-\infty}^{\infty} m_\alpha (\xi - U_\alpha)_i (\xi - U_\alpha)_j f_\alpha d\xi, \end{aligned} \quad (6)$$

and

$$Q_{\alpha i} = \frac{1}{2} \int_{-\infty}^{\infty} m_\alpha (\xi - U_\alpha)_i (\xi - U_\alpha)^2 f_\alpha d\xi. \quad (7)$$

The following conventions are used: Greek subscripts denote components of the mixture, and Latin subscripts (and superscripts) denote vector components (the summation convention applies only to the Latin scripts). The brackets, { }, denote the symmetrized traceless portion of a second-order tensor.

The Boltzmann equation for one component of the mixture is

$$Df_\alpha = J_{\alpha\alpha} + J_{\alpha\beta} = J_\alpha, \quad (8)$$

where, using customary notation,<sup>2</sup>

$$D = \frac{\partial}{\partial t} + \xi_i \frac{\partial}{\partial x_i},$$

$$J_{\alpha\beta}(f_\alpha, f_\beta) = \int_{-\infty}^{\infty} (f'_\alpha f'_\beta - f_\alpha f_\beta) B^{\alpha\beta}(\theta, V) d\Omega d\xi_1, \quad (9)$$

and

$$V = |\xi_1 - \xi|.$$

From the properties of the collisional invariants, we have

$$\int_{-\infty}^{\infty} m_\alpha J_{\alpha\alpha} \begin{bmatrix} 1 \\ \xi_i \\ \xi^2/2 \end{bmatrix} d\xi = 0, \quad (10)$$

$$\int_{-\infty}^{\infty} m_\alpha J_{\alpha\beta} d\xi = 0, \quad (11)$$

and

$$\int_{-\infty}^{\infty} \left( m_\alpha J_{\alpha\beta} \begin{bmatrix} \xi_i \\ \xi^2/2 \end{bmatrix} + m_\beta J_{\beta\alpha} \begin{bmatrix} \xi_i \\ \xi^2/2 \end{bmatrix} \right) d\xi = 0. \quad (12)$$

Using these, the mass, momentum, and energy moments of the Boltzmann equation yield

$$\frac{\partial}{\partial t} \rho_\alpha + \frac{\partial}{\partial x_i} \rho_\alpha U_{\alpha i} = 0, \quad (13)$$

$$\begin{aligned} \frac{\partial}{\partial t} \rho_\alpha U_{\alpha i} + \frac{\partial}{\partial x_j} (\rho_\alpha U_{\alpha i} U_{\alpha j} + P_\alpha^{ij}) \\ = \int_{-\infty}^{\infty} m_\alpha \xi_i J_{\alpha\beta} d\xi, \end{aligned} \quad (14)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \rho_\alpha \left( e_\alpha + \frac{U_\alpha^2}{2} \right) &+ \frac{\partial}{\partial x_i} \left[ \rho_\alpha U_{\alpha i} \left( e_\alpha + \frac{U_\alpha^2}{2} \right) + Q_{\alpha i} + P^{ij}_\alpha U_{\alpha j} \right] \\ &= \int_{-\infty}^{\infty} m_\alpha \frac{\xi^2}{2} J_{\alpha\beta} d\xi. \end{aligned} \tag{15}$$

Since we are considering component equations, the right-hand sides of Eqs. (14) and (15) are not zero, and the equations are not in conservation form. We nevertheless, refer to these as component conservation equations.

The transfer terms on the right-hand sides of these equations are evaluated in two parts, first for Maxwell molecules and then for non-Maxwell molecules. As in the case of a simple gas, it is found that moments of the collision integrals for Maxwell molecules [i.e.,  $B^{\alpha\beta} = B^{\alpha\beta}(\theta)$  in Eq. (9)] can be evaluated without a specific knowledge of the distribution functions. Employing standard methods, we find,

$$\int_{-\infty}^{\infty} m_\alpha \xi_i J_{\alpha\beta} d\xi = -A \rho_\alpha \rho_\beta (U_\alpha - U_\beta)_i, \tag{16}$$

$$\begin{aligned} \int_{-\infty}^{\infty} m_\alpha \frac{\xi^2}{2} J_{\alpha\beta} d\xi &= - \left[ U_{\alpha i} (U_\alpha - U_\beta)_i \right. \\ &\left. + \frac{3k(T_\alpha - T_\beta)}{m_\alpha + m_\beta} - m_{\beta 0} (U_\alpha - U_\beta)^2 \right] A \rho_\alpha \rho_\beta, \end{aligned} \tag{17}$$

where

$$A = \frac{8(\pi)^{\frac{1}{2}}}{3} \Gamma(\frac{5}{2}) \mathcal{Q}_1 (m_\alpha + m_\beta)^{-1} \left( \frac{\chi_{\alpha\beta}}{m_\beta m_{\alpha 0}} \right)^{\frac{1}{2}}, \tag{18}$$

and

$$m_{\alpha 0} = m_\alpha / (m_\alpha + m_\beta);$$

$\chi_{\alpha\beta}$  is the constant of proportionality in the force law and  $\mathcal{Q}_1$  is a collision cross section.<sup>4</sup> For later purposes, it is convenient to list the additional two moments

$$\begin{aligned} \int_{-\infty}^{\infty} m_\alpha \{ \xi_i \xi_j \} J_{\alpha\beta} d\xi &= -(2m_{\alpha 0} A + 3m_{\beta 0} B) \rho_\beta \{ P^{ij}_\beta \} \\ &- (-2m_{\beta 0} A + 3m_{\beta 0} B) \rho_\alpha \{ P^{ij}_\alpha \} \\ &- \left( 2A \left[ m_{\alpha 0} \frac{\rho_\beta}{\rho} - m_{\beta 0} \frac{\rho_\alpha}{\rho} \right] + 3m_{\beta 0} B \right) \rho_\alpha \rho_\beta \\ &\cdot \{ (U_\alpha - U_\beta)_i (U_\alpha - U_\beta)_j \} \end{aligned} \tag{19}$$

<sup>4</sup>  $\mathcal{Q}_1(\eta)$  and  $\mathcal{Q}_2(\eta)$  are tabulated on p. 172 of Ref. (2).  $\eta$  is defined by Eq. (24).

and

$$\begin{aligned} \int_{-\infty}^{\infty} m_\alpha \xi_i \frac{\xi^2}{2} J_{\alpha\beta} d\xi &= -[(3m_{\alpha 0}^2 + m_{\beta 0}^2) A \\ &+ 4m_{\alpha 0} m_{\beta 0} B] \rho_\beta Q_{\alpha i} + 4m_{\beta 0}^2 (A - B) \rho_\alpha Q_{\beta i} \\ &- \frac{5kT}{2} \frac{A \rho_\alpha \rho_\beta}{m_\alpha} (U_\alpha - U_\beta)_i - \frac{5}{2} \frac{\rho_\alpha \rho_\beta}{m_\alpha + m_\beta} \\ &\cdot \left\{ 2 \left( m_{\alpha 0} \frac{\rho_\beta}{\rho} - m_{\beta 0} \frac{\rho_\alpha}{\rho} \right) \right. \\ &\left. + (m_{\alpha 0} - m_{\beta 0}) + \frac{\rho_\alpha - \rho_\beta}{m_\alpha n} \right\} A + 4m_{\beta 0} B \Big] \\ &\cdot (U_\alpha - U_\beta)_i (T_\alpha - T_\beta), \end{aligned} \tag{20}$$

$$B = \frac{1}{2} (\mathcal{Q}_2 / \mathcal{Q}_1) A. \tag{21}$$

It should be noted that, in contrast to the following, the evaluations above are exact.

For non-Maxwell molecules, moments of the collision integrals will involve the entire distribution function. To obtain a theory with wider applicability than just for Maxwell molecules, we now introduce approximate forms for these moments.

For power law molecules, Kolodner<sup>5</sup> has obtained certain finite expansions for the required moments of the collision integrals. We could, in fact, incorporate his expansions directly into the conservation equations (13)-(15), but this would lead to expressions that are too unwieldy for practical application. Instead, only those portions of the expansions which correspond to the terms for Maxwell molecules will be used. The neglected terms, which we refer to as off-diagonal terms, are quadratic in the higher moments, and, in addition, have coefficients that are relatively small. (One result of this approximation is the loss of the thermodiffusion effect. This is small except under extreme conditions.)

The coefficients of the diagonal terms are functions of the temperature difference and velocity difference squared, and may be expanded in powers of these differences. We make a further approximation in retaining only the first term in each of these expansions. This does not imply that the equations are applicable only to low-speed phenomena because the velocity and temperature differences appear naturally in a form normalized with respect to a sound speed and a temperature. It is only at exceedingly high Mach numbers that such terms might become important.

Under these approximations, Kolodner's expressions reduce to Eqs. (16), (17), (19), and (20)

<sup>5</sup> I. Kolodner, New York University Report 7980 (1957).

where now<sup>5</sup>

$$A = \frac{8(\pi)^{\frac{1}{2}}}{3} \Gamma\left(\frac{5+\eta}{2}\right) \mathcal{G}_1(\eta) (m_\alpha + m_\beta)^{-1} \cdot \left(\frac{\chi_{\alpha\beta}}{m_\beta m_{\alpha 0}}\right)^{(1-\eta)/2} \left(\frac{2kT_\alpha}{m_\alpha} + \frac{2kT_\beta}{m_\beta}\right)^{\eta/2} \quad (22)$$

and

$$B = \frac{5+\eta}{10} \frac{\mathcal{G}_2(\eta)}{\mathcal{G}_1(\eta)} A. \quad (23)$$

In these expressions, the molecules obey the force law

$$F_{\alpha\beta} = \frac{\chi_{\alpha\beta}}{r^\mu}, \quad \eta = \frac{\mu-5}{\mu-1}. \quad (24)$$

Note that Eqs. (22) and (23) reduce to Eqs. (18) and (21) for Maxwell molecules. Then the expressions (16), (17), (19), (20), (22), and (23) are exact for Maxwell molecules; for non-Maxwell molecules, they correspond to what Chapman and Cowling<sup>2</sup> call the first approximation in the determination of the transport coefficients.

For intermolecular potentials other than power laws, no general expressions for *A* and *B* appear to have been calculated. Although these, no doubt, lead to more complicated forms for *A* and *B* we anticipate that our considerations still apply.

Substituting Eqs. (19) and (20) into Eqs. (14) and (15) we obtain

$$\frac{\partial}{\partial t} \rho_\alpha U_{\alpha i} + \frac{\partial}{\partial x_i} (\rho_\alpha U_{\alpha i} U_{\alpha i} + P^{ij}) = -A \rho_\alpha \rho_\beta (U_\alpha - U_\beta)_i \quad (25)$$

and

$$\frac{\partial}{\partial t} \rho_\alpha e_\alpha + \frac{\partial}{\partial x_i} [\rho_\alpha U_{\alpha i} e_\alpha + Q_{\alpha i}] + P^{ij}_\alpha \frac{\partial U_{\alpha j}}{\partial x_i} = -A \rho_\alpha \rho_\beta \left[ \frac{3k(T_\alpha - T_\beta)}{m_\alpha + m_\beta} - m_{\beta 0} (U_\alpha - U_\beta)^2 \right]. \quad (26)$$

The "mechanical energy" equation has been eliminated in Eq. (26). We repeat that these equations are exact for Maxwell molecules and constitute the diagonal approximation for non-Maxwell molecules.

Alternate expressions for the conservation equations are developed by considering the mixture as a composite fluid. Adding the component continuity, momentum, and energy equations, respectively, we obtain

$$\frac{\partial}{\partial t} \rho + \frac{\partial}{\partial x_i} \rho U_i = 0, \quad (27)$$

$$\frac{\partial}{\partial t} \rho U_i + \frac{\partial}{\partial x_i} [\rho U_i U_i + P^{ij}] = 0, \quad (28)$$

$$\frac{\partial}{\partial t} \rho (e + U^2/2) + \frac{\partial}{\partial x_i} [\rho U_i (e + U^2/2) + U_i P^{ij} + Q_i] = 0, \quad (29)$$

where

$$\rho = \rho_\alpha + \rho_\beta, \quad n = n_\alpha + n_\beta, \quad (30)$$

$$U = (\rho_\alpha U_\alpha + \rho_\beta U_\beta) / (\rho_\alpha + \rho_\beta), \quad (31)$$

$$\rho e = \frac{1}{2} \int_{-\infty}^{\infty} [m_\alpha f_\alpha + m_\beta f_\beta] (\xi - U)^2 d\xi = \rho_\alpha e_\alpha + \rho_\beta e_\beta + \frac{\rho_\alpha \rho_\beta}{2\rho} (U_\alpha - U_\beta)^2, \quad (32)$$

$$P^{ij} = \int_{-\infty}^{\infty} (m_\alpha f_\alpha + m_\beta f_\beta) (\xi - U)_i (\xi - U)_j d\xi = \{P^{ij}_\alpha\} + \{P^{ij}_\beta\} + \frac{\rho_\alpha \rho_\beta}{\rho} \{(U_\alpha - U_\beta)_i (U_\alpha - U_\beta)_j\} + \delta_{ij} \left[ p_\alpha + p_\beta + \frac{\rho_\alpha \rho_\beta}{3\rho} (U_\alpha - U_\beta)^2 \right], \quad (33)$$

$$Q_i = \frac{1}{2} \int_{-\infty}^{\infty} [m_\alpha f_\alpha + m_\beta f_\beta] (\xi - U)_i (\xi - U)^2 d\xi = Q_{\alpha i} + Q_{\beta i} + \frac{5}{2} kT \frac{n_\alpha n_\beta}{\rho} (m_\beta - m_\alpha) (U_\alpha - U_\beta)_i + \frac{5}{2} \frac{n_\alpha n_\beta k}{n} (T_\alpha - T_\beta) (U_\alpha - U_\beta)_i + \frac{\rho_\alpha \rho_\beta}{2\rho} \left[ \frac{\rho_\beta^2 - \rho_\alpha^2}{\rho^2} - \frac{5}{3} \frac{n_\alpha n_\beta (m_\beta - m_\alpha)}{n\rho} \right] \cdot (U_\alpha - U_\beta)^2 (U_\alpha - U_\beta)_i + \left[ \frac{\rho_\beta}{\rho} \{P^{ij}_\alpha\} - \frac{\rho_\alpha}{\rho} \{P^{ij}_\beta\} \right] (U_\alpha - U_\beta)_i. \quad (34)$$

These equations are exact for all molecular force laws by virtue of the collisional invariants (10)–(12). The expressions for *P<sup>ij</sup>*, *Q<sub>i</sub>*, and *e* are dictated by general continuum theory.

### III. TWO-FLUID THEORY

Although the various processes of Maxwellization and equilibration can occur on a variety of scales, it is possible to easily estimate these scales by considering an associated relaxation problem. Referring

to Eq. (19), we see that the stress relaxation equation is given by

$$\frac{\partial}{\partial t} \begin{bmatrix} \{P_\alpha^{ij}\} \\ \{P_\beta^{ij}\} \end{bmatrix} = \begin{bmatrix} [(-3B_{\alpha\alpha}\rho_\alpha) + (-2m_{\alpha 0}A - 3m_{\beta 0}B)\rho_\beta] & [(2m_{\beta 0}A - 3m_{\beta 0}B)\rho_\alpha] \\ [(2m_{\alpha 0}A - 3m_{\alpha 0}B)\rho_\beta] & [(-3B_{\beta\beta}\rho_\beta) + (-2m_{\beta 0}A - 3m_{\alpha 0}B)\rho_\alpha] \end{bmatrix} \begin{bmatrix} \{P_\alpha^{ij}\} \\ \{P_\beta^{ij}\} \end{bmatrix} \\ = - \begin{bmatrix} \lambda_{\alpha\alpha}^\alpha + \lambda_{\alpha\alpha}^\beta & \lambda_{\alpha\alpha}^\alpha \\ \lambda_{\alpha\alpha}^\beta & \lambda_{\alpha\alpha}^\alpha + \lambda_{\alpha\alpha}^\beta \end{bmatrix} \begin{bmatrix} \{P_\alpha^{ij}\} \\ \{P_\beta^{ij}\} \end{bmatrix}, \tag{35}$$

where  $B_{\alpha\alpha}$ ,  $B_{\beta\beta}$  are given by Eqs. (22) and (23) with  $\beta = \alpha$  and with  $\alpha = \beta$ , respectively. The  $\lambda$ 's appearing in the last matrix are defined by direct identification with the quantities of the previous matrix. A driving term, quadratic in velocity differences, has been neglected in (35). As seen in the next section, this contributes negligibly in estimating the relaxation scale. Regarding (35) [and also referring to Eq. (19)] we see that these terms have their origin in three different effects:  $\lambda_{\alpha\alpha}^\alpha$  (self-self), due to self-collisions of the  $\alpha$  gas;  $\lambda_{\alpha\alpha}^\beta$  (self-cross), due to collisions of the  $\alpha$  gas with the  $\beta$  gas;  $\lambda_{\alpha\alpha}^\alpha$  (cross-cross), due to cross collisions of the  $\beta$  gas with the  $\alpha$  gas, but appearing in the  $\alpha$  gas equation. Corresponding remarks apply to the  $\beta$  gas frequencies.

The relaxation frequencies are given by the eigenvalues of the matrix in (35). These are

$$\lambda^\pm = \frac{1}{2} \{ (\lambda_\alpha^\alpha + \lambda_\beta^\beta) \pm [(\lambda_\alpha^\alpha - \lambda_\beta^\beta)^2 + 4\lambda_{\alpha\alpha}^\beta \lambda_{\alpha\alpha}^\alpha]^{1/2} \} \tag{36}$$

with

$$\lambda^{\alpha,\beta} = \lambda_{\alpha\alpha}^{\alpha,\beta} + \lambda_{\alpha\alpha}^{\beta,\alpha}. \tag{37}$$

The branch of the radical is chosen such that  $\lambda^-$  is the smallest eigenvalue (note, both eigenvalues are positive). In the Appendix we demonstrate that the heat conduction as well as all higher moments have relaxation frequencies which are of  $O(\lambda^-)$  or larger. It is therefore the case that  $\lambda^-$  provides a measure of the scale of Maxwellization of both gases.

We now consider situations for which temporal and spatial variations, i.e.,  $Df_{\alpha,\beta}$ , are slowly varying compared to the scale of Maxwellization. Then, clearly,  $f_\alpha$  and  $f_\beta$  are to lowest order just Maxwellians. Depending on the relationship between the (various) scales of equilibration and of Maxwellization, these Maxwellians can depend on composite or species quantities. For the moment we defer a discussion of these relative magnitudes, and allow ourselves the most latitude by basing the Maxwellians on species variables [see Eq. (1)].

Writing  $f = f_{0\alpha} + \epsilon f_\alpha^{(1)}$  and carrying terms to first order, we obtain

$$\left( \frac{\partial}{\partial t} + \xi_i \frac{\partial}{\partial x_i} \right) f_{0\alpha} \\ = J_{\alpha\alpha}(f_{0\alpha}, f_\alpha^{(1)}) + J_{\alpha\alpha}(f_\alpha^{(1)}, f_{0\alpha}) + J_{\alpha\beta}(f_{0\alpha}, f_{0\beta}) \\ + J_{\alpha\beta}(f_{0\alpha}, f_\beta^{(1)}) + J_{\alpha\beta}(f_\beta^{(1)}, f_{0\beta}). \tag{38}$$

$f_\alpha^{(1)}$  does not appear on the left-hand side because  $D$  by assumption is a higher-order operator. In writing Eq. (38) we recognize that  $J_{\alpha\beta}(f_{0\alpha}, f_{0\beta})$  may force certain terms into a higher order. This portion of the discussion is deferred to the next section and in the present section we consider only the significant nonconservation moments of (38). By standard manipulations<sup>2</sup> and substitution of the conservation equations, the left-hand side becomes

$$Df_{0\alpha} = f_{0\alpha} \left[ \left( \frac{m_\alpha C_\alpha^2}{2kT_\alpha} - \frac{5}{2} \right) C_{\alpha i} \frac{\partial \ln T_\alpha}{\partial x_i} \right. \\ + \frac{m_\alpha}{kT_\alpha} \{ C_{\alpha i} C_{\alpha j} \} : \left\{ \frac{\partial U_{\alpha i}}{\partial x_j} \right\} - \frac{C_{\alpha i}}{p_\alpha} \\ \cdot \left[ \frac{\partial}{\partial x_j} \{ P^{ij} \} + A \rho_\alpha \rho_\beta (U_\alpha - U_\beta)_i \right] \\ + \frac{1}{p_\alpha} \left( \frac{m_\alpha C_\alpha^2}{3kT_\alpha} - 1 \right) \left( \frac{\partial}{\partial x_i} Q_{\alpha i} + \{ P_\alpha^{ij} \} \frac{\partial U_{\alpha i}}{\partial x_j} \right. \\ \left. + \left[ \frac{3k(T_\alpha - T_\beta)}{m_\alpha + m_\beta} - m_{\beta 0} (U_\alpha - U_\beta)^2 \right] A \rho_\alpha \rho_\beta \right) \left. \right]. \tag{39}$$

It is clear that the stress and heat conduction are higher order compared to the other terms in this expression.

Taking the stress moment,  $m_\alpha \{ (\xi - U_\alpha)_i (\xi - U_\alpha)_j \}$ , and heat conduction moment,  $\frac{1}{2} m_\alpha (\xi - U_\alpha)_i (\xi - U_\alpha)^2$ , of Eq. (38) with the expression (39) [also using Eqs. (19) and (20)] yields

$$- \left\{ \begin{bmatrix} \lambda_{\alpha\alpha}^\alpha & 0 \\ 0 & \lambda_{\alpha\alpha}^\beta \end{bmatrix} + \begin{bmatrix} \lambda_{\alpha\alpha}^\alpha & \lambda_{\alpha\alpha}^\beta \\ \lambda_{\alpha\alpha}^\beta & \lambda_{\alpha\alpha}^\alpha \end{bmatrix} \right\} \begin{bmatrix} \{P_\alpha^{ij}\} \\ \{P_\beta^{ij}\} \end{bmatrix} \\ = 2 \begin{bmatrix} p_\alpha \{ \partial U_{\alpha i} / \partial x_j \} \\ p_\beta \{ \partial U_{\beta i} / \partial x_j \} \end{bmatrix} + \begin{bmatrix} [-2A + 3B] m_{\beta 0} \\ [-2A + 3B] m_{\alpha 0} \end{bmatrix} \\ \cdot \rho_\alpha \rho_\beta \{ (U_\alpha - U_\beta)_i (U_\alpha - U_\beta)_j \}. \tag{40}$$

$$\left\{ \begin{bmatrix} 2B_{\alpha\alpha}\rho_\alpha & 0 \\ 0 & 2B_{\beta\beta}\rho_\beta \end{bmatrix} + \begin{bmatrix} ((3m_{\alpha 0}^2 + m_{\beta 0}^2)A + 4m_{\alpha 0}m_{\beta 0}B)\rho_\beta & -4m_{\beta 0}^2(A - B)\rho_\alpha \\ -4m_{\alpha 0}^2(A - B)\rho_\beta & ((3m_{\beta 0}^2 + m_{\alpha 0}^2)A + 4m_{\alpha 0}m_{\beta 0}B)\rho_\alpha \end{bmatrix} \right\} \begin{bmatrix} Q_{\alpha i} \\ Q_{\beta i} \end{bmatrix} \\ = - \begin{bmatrix} \frac{5p_\alpha k}{2m_\alpha} \frac{\partial T_\alpha}{\partial x_i} \\ \frac{5p_\beta k}{2m_\beta} \frac{\partial T_\beta}{\partial x_i} \end{bmatrix} - \begin{bmatrix} \left\{ 2\left(m_{\alpha 0} \frac{\rho_\beta}{\rho} - m_{\beta 0} \frac{\rho_\alpha}{\rho}\right) + (m_{\alpha 0} - m_{\beta 0}) + \frac{\rho_\alpha - \rho_\beta}{m_\alpha n} \right\} A + 4m_{\beta 0} B \\ \left\{ 2\left(m_{\beta 0} \frac{\rho_\alpha}{\rho} - m_{\alpha 0} \frac{\rho_\beta}{\rho}\right) + (m_{\beta 0} - m_{\alpha 0}) + \frac{\rho_\beta - \rho_\alpha}{m_\beta n} \right\} A + 4m_{\alpha 0} B \end{bmatrix} \\ \frac{5}{2} \frac{\rho_\alpha \rho_\beta}{m_\alpha + m_\beta} (U_\alpha - U_\beta)_i (T_\alpha - T_\beta). \tag{41}$$

There are then solved for the stress and heat conduction to give the constitutive relations

$$\{P_\alpha^{ij}\} = -[\det S]^{-1} \left[ \left( 1 + \left( \frac{2}{3} m_{\beta 0} \frac{A}{B_{\beta\beta}} + m_{\alpha 0} \frac{B}{B_{\beta\beta}} \right) \frac{\rho_\alpha}{\rho_\beta} \right) 2\mu_\alpha \left\{ \frac{\partial U_{\alpha i}}{\partial x_j} \right\} - \left( -\frac{2}{3} m_{\beta 0} \frac{A}{B_{\alpha\alpha}} + m_{\beta 0} \frac{B}{B_{\alpha\alpha}} \right) 2\mu_\beta \left\{ \frac{\partial U_{\beta i}}{\partial x_j} \right\} \right. \\ \left. + \left[ \left( 1 + \left( \frac{2}{3} m_{\beta 0} \frac{A}{B_{\beta\beta}} + m_{\alpha 0} \frac{B}{B_{\beta\beta}} \right) \frac{\rho_\alpha}{\rho_\beta} \right) \left( -\frac{2A}{3B_{\alpha\alpha}} + \frac{B}{B_{\alpha\alpha}} \right) m_{\beta 0} \rho_\beta \right. \right. \\ \left. \left. - \left( -\frac{2}{3} m_{\beta 0} \frac{A}{B_{\alpha\alpha}} + m_{\beta 0} \frac{B}{B_{\alpha\alpha}} \right) \left( -\frac{2A}{3B_{\beta\beta}} + \frac{B}{B_{\beta\beta}} \right) m_{\alpha 0} \rho_\alpha \right] \{ (U_\alpha - U_\beta)_i (U_\alpha - U_\beta)_j \} \right] \\ = -2\tilde{\mu}_{\alpha\alpha} \left\{ \frac{\partial U_{\alpha i}}{\partial x_j} \right\} - 2\tilde{\mu}_{\alpha\beta} \left\{ \frac{\partial U_{\beta i}}{\partial x_j} \right\} + \tau_{\alpha\beta} \{ (U_\alpha - U_\beta)_i (U_\alpha - U_\beta)_j \}, \tag{42}$$

$$Q_{\alpha i} = -[\det H]^{-1} \left\{ \left[ 1 + \left( \left( \frac{3}{2} m_{\beta 0}^2 + \frac{1}{2} m_{\alpha 0}^2 \right) \frac{A}{B_{\beta\beta}} + 2m_{\alpha 0}m_{\beta 0} \frac{B}{B_{\beta\beta}} \right) \frac{\rho_\alpha}{\rho_\beta} \right] \kappa_\alpha \frac{\partial T_\alpha}{\partial x_i} + 2m_{\beta 0}^2 m_{\alpha 0}^2 \frac{A - B}{B_{\alpha\alpha}} \frac{\partial T_\beta}{\partial x_i} \right. \\ \left. + \left[ 1 + \left( \left( \frac{3}{2} m_{\beta 0}^2 + \frac{1}{2} m_{\alpha 0}^2 \right) \frac{A}{B_{\alpha\alpha}} + 2m_{\alpha 0}m_{\beta 0} \frac{B}{B_{\alpha\alpha}} \right) \frac{\rho_\alpha}{\rho_\beta} \right] \left[ \left( m_{\beta 0} + \frac{4}{5} \frac{\rho_\beta}{\rho} \right) \frac{A}{B_{\alpha\alpha}} \rho_\beta \right. \right. \\ \left. \left. - 2m_{\beta 0}^2 m_{\alpha 0}^2 \frac{A - B}{B_{\alpha\alpha}} \left( m_{\alpha 0} + \frac{4}{5} \frac{\rho_\alpha}{\rho} \right) \frac{A}{B_{\beta\beta}} \rho_\alpha \right] \frac{5k}{m_\alpha + m_\beta} (U_\alpha - U_\beta)_i (T_\alpha - T_\beta) \right\} \\ = -\tilde{\kappa}_{\alpha\alpha} \frac{\partial T_\alpha}{\partial x_i} - \tilde{\kappa}_{\alpha\beta} \frac{\partial T_\beta}{\partial x_i} + \sigma_{\alpha\beta} (T_\alpha - T_\beta) (U_\alpha - U_\beta)_i, \tag{43}$$

where

$$\det S = 1 + \left( \frac{2}{3} m_{\beta 0} \frac{A}{B_{\beta\beta}} + m_{\alpha 0} \frac{B}{B_{\beta\beta}} \right) \frac{\rho_\alpha}{\rho_\beta} + \left( \frac{2}{3} m_{\alpha 0} \frac{A}{B_{\alpha\alpha}} + m_{\beta 0} \frac{B}{B_{\alpha\alpha}} \right) \frac{\rho_\beta}{\rho_\alpha} + \frac{2}{3} \frac{AB}{B_{\alpha\alpha} B_{\beta\beta}},$$

$$\det H = 1 + \left[ \left( \frac{3}{2} m_{\beta 0}^2 + \frac{1}{2} m_{\alpha 0}^2 \right) \frac{A}{B_{\beta\beta}} + 2m_{\alpha 0}m_{\beta 0} \frac{B}{B_{\beta\beta}} \right] \frac{\rho_\alpha}{\rho_\beta} \\ + \left[ \left( \frac{3}{2} m_{\alpha 0}^2 + \frac{1}{2} m_{\beta 0}^2 \right) \frac{A}{B_{\alpha\alpha}} + 2m_{\alpha 0}m_{\beta 0} \frac{B}{B_{\alpha\alpha}} \right] \frac{\rho_\beta}{\rho_\alpha} + \frac{3}{4} (m_{\alpha 0}^2 - m_{\beta 0}^2) \frac{A^2}{B_{\alpha\alpha} B_{\beta\beta}} + 4m_{\alpha 0}m_{\beta 0} \frac{AB}{B_{\alpha\alpha} B_{\beta\beta}},$$

and

$$\mu_\alpha = p_\alpha / (3B_{\alpha\alpha}\rho_\alpha), \quad \kappa_\alpha = 5p_\alpha k / (4m_\alpha B_{\alpha\alpha}\rho_\alpha). \tag{44}$$

$\mu_\alpha$  and  $\kappa_\alpha$  are the ordinary viscosity and thermal conductivity of the  $\alpha$  gas.<sup>2</sup> The corresponding expressions for the  $\beta$  gas follow by interchanging  $\alpha$  and  $\beta$ .

Considering Eqs. (13), (25), (26), (42), (43), and their  $\beta$  gas counterparts, we obtain a determinate system of equations. We refer to these as the two-fluid equations.

#### IV. GENERALIZED CHAPMAN-ENSKOG PROCEDURE

The two-fluid equations derived in the previous section furnish a self-contained description of a binary gas. From the point of view of the perturbation procedure employed in obtaining them, the two-fluid equations are only an intermediate step. This is so because the relative scales of equilibration have not yet been introduced. We find in this section that within the framework of the perturbation procedure, the equilibration scales can modify

the two-fluid equations. We show, however, that the two-fluid equations themselves are more useful in situations widely removed from equilibrium.

The Maxwellization scale,  $\lambda_s$ ,

$$\lambda_s = \lambda^-$$

is given by Eq. (36). One may show<sup>6</sup>

$$|\lambda_{cc}^\alpha|/\lambda_s^\alpha, \quad |\lambda_{cc}^\beta|/\lambda_s^\beta < \frac{1}{5},$$

from which we get

$$\lambda_s \approx \min(\lambda_s^\alpha, \lambda_s^\beta). \quad (45)$$

This proves useful in future estimates.

In order to consider the effect of equilibration we must consider the behavior of  $(\mathbf{U}_\alpha - \mathbf{U}_\beta)$  and  $(T_\alpha - T_\beta)$ . We consider the "diffusion" first. Taking appropriate differences of the momentum equations (25), we obtain after some manipulation,

$$\begin{aligned} -\lambda_U(U_\alpha - U_\beta) = & \left\{ \frac{\partial}{\partial t} (U_\alpha - U_\beta)_i + \frac{1}{2}(U_\alpha + U_\beta)_i \frac{\partial}{\partial x_j} (U_\alpha - U_\beta)_i + (U_\alpha - U_\beta)_i \frac{\partial}{\partial x_j} \frac{1}{2} (U_\alpha + U_\beta)_i \right\} \\ & + \left[ \frac{1}{\rho_\alpha} \frac{\partial}{\partial x_j} \{P_\beta^{ij}\} - \frac{1}{\rho_\beta} \frac{\partial}{\partial x_j} \{P_\alpha^{ij}\} + \frac{n_\beta n_\alpha (m_\beta - m_\alpha)}{\rho p n} \frac{\partial}{\partial x_j} \left( \frac{\rho_\alpha \rho_\beta (\mathbf{U}_\alpha - \mathbf{U}_\beta)^2}{3\rho} \right) \right] \\ & + \frac{\rho p}{\rho_\alpha \rho_\beta} \left[ \frac{\partial}{\partial x_i} \left( \frac{n_\alpha}{n} \right) + \frac{1}{p} \frac{\partial}{\partial x_i} \left( \frac{n_\alpha n_\beta k (T_\alpha - T_\beta)}{n} \right) + \frac{n_\alpha n_\beta (m_\beta - m_\alpha)}{\rho n} \frac{\partial}{\partial x_i} \ln p \right], \quad (46) \end{aligned}$$

where

$$\lambda_U = A\rho. \quad (47)$$

It has already been assumed in the derivation of the two-fluid equations that derivatives are slowly varying on the scale of  $\lambda_s$ . Therefore to compare the curly-bracket term with the left-hand side of Eq. (46) we must compare the velocity relaxation frequency with the Maxwellization frequency. One easily shows that

$$\lambda_U/\lambda_s > 1$$

and hence, velocity relaxation takes place at least as rapidly as Maxwellization. Next from the derivation of  $\{P_{\alpha,\beta}^{ij}\}$  it is clear that the square bracket term in Eq. (46) is small compared with the last term, and therefore to lowest order,

$$\begin{aligned} (U_\alpha - U_\beta)_i = & -\frac{n^2}{n_\alpha n_\beta} D_{\alpha\beta} \left[ \frac{\partial}{\partial x_i} \left( \frac{n_\alpha}{n} \right) \right. \\ & + \frac{n_\alpha n_\beta}{\rho n} (m_\beta - m_\alpha) \frac{\partial}{\partial x_i} \ln p \\ & \left. + \frac{1}{p} \frac{\partial}{\partial x_i} \left( \frac{n_\alpha n_\beta k (T_\alpha - T_\beta)}{n} \right) \right]. \quad (48) \end{aligned}$$

$D_{\alpha\beta}$  is the coefficient of binary diffusion given by

$$D_{\alpha\beta} = kT/(m_\alpha m_\beta n A). \quad (49)$$

The thermo-diffusion effect does not appear in Eq. (48) since, as pointed out earlier, it vanishes for

<sup>6</sup> We continue to use Maxwell molecules to estimate relative scales. In support of this we consider Eq. (22). For purposes of estimates it is plausible to take the temperature of each component as being the same. This results in a form which is identical to the Maxwell molecule case for all mass ratios.

Maxwell molecules and is lost in the diagonal approximation for non-Maxwell molecules. A more elaborate derivation would furnish the thermo-diffusion effect and it seems justifiable to merely include it in Eq. (48) in situations which require it. Note that Eq. (48) contains a new diffusion effect due to temperature differences.

Although spacial derivatives are formally regarded as slowly varying [they are  $O(\epsilon)$  in the symbolism of the previous section], it is not necessarily the case that  $(U_\alpha - U_\beta)_i$  is also  $O(\epsilon)$ . (This is implicitly assumed in the Chapman-Enskog theory.<sup>2</sup>) Due to the presence of possibly large coefficients, this term may in fact be large. In this section, however, we regard  $(\mathbf{U}_\alpha - \mathbf{U}_\beta)$  and  $(T_\alpha - T_\beta)$  as being small,<sup>7</sup> say  $O(\delta)$ , although not necessarily in a way that is related to  $\epsilon$ . Further we only carry out the analysis to  $O(\delta)$ . [This requires that  $\delta \ll O(\epsilon^{\frac{1}{2}})$ .] Otherwise the expressions become too cumbersome to be of use. This might for example be seen by introducing Eq. (48) into the curly bracket term of Eq. (46) and eliminating time derivatives in the usual way in order to find the higher-order diffusion equation. In situations requiring higher orders, the two-fluid theory of the previous section should be used directly. For even though the two-fluid equations carry some higher orders, there is no restriction placed on the size of  $(\mathbf{U}_\alpha - \mathbf{U}_\beta)$  and  $(T_\alpha - T_\beta)$  in their derivation. This issue becomes important in a number of applications, e.g., in the shock structure of mixtures.

<sup>7</sup> In saying that for example  $(\mathbf{U}_\alpha - \mathbf{U}_\beta)$  is small, we naturally mean that it is small when suitably normalized. The proper normalization in most instances is the composite speed of sound  $(\gamma p/\rho)^{\frac{1}{2}}$ .

We have still to examine the behavior of  $(T_\alpha - T_\beta)$ . The equation governing the "temperature diffusion" is gotten by taking appropriate differences of the individual energy equations (26).

$$\begin{aligned}
 & -\lambda_T(T_\alpha - T_\beta) - \left[ \frac{2}{3} \lambda_U \frac{m_{\alpha\beta}}{k} \frac{(\rho_\alpha - \rho_\beta)}{\rho} (\mathbf{U}_\alpha - \mathbf{U}_\beta)^2 \right] \\
 & = \frac{\partial}{\partial t} (T_\alpha - T_\beta) + (\mathbf{U}_\alpha - \mathbf{U}_\beta) \cdot \nabla T + \mathbf{U} \cdot \nabla (T_\alpha - T_\beta) + \frac{2}{3} T \nabla \cdot (\mathbf{U}_\alpha - \mathbf{U}_\beta) \\
 & + \frac{2}{3} (T_\alpha - T_\beta) \nabla \cdot \mathbf{U} - \frac{2}{3n_\alpha k} \nabla \cdot (\bar{\kappa}_\alpha \nabla T) + \frac{2}{3n_\beta k} \nabla \cdot (\bar{\kappa}_\beta \nabla T) - \left( \frac{2\bar{\mu}_\alpha}{3n_\alpha k} - \frac{2\bar{\mu}_\beta}{3n_\beta k} \right) \{U_{i,i}\}^2 \\
 & + \left[ (\mathbf{U}_\alpha - \mathbf{U}) \cdot \nabla (T_\alpha - T) - (\mathbf{U}_\beta - \mathbf{U}) \cdot \nabla (T_\beta - T) + \frac{2}{3} (T_\alpha - T) \nabla \cdot (\mathbf{U}_\alpha - \mathbf{U}) \right. \\
 & - (T_\beta - T) \nabla \cdot (\mathbf{U}_\beta - \mathbf{U}) + \frac{2}{3n_\alpha k} \nabla \cdot (Q_\alpha + \bar{\kappa}_\alpha \nabla T) - \frac{2}{3n_\beta k} \nabla \cdot (Q_\beta + \bar{\kappa}_\beta \nabla T) \\
 & \left. + \frac{2}{3n_\alpha k} (\{P_\alpha^{ij}\} U_{\alpha i,i} + \bar{\mu}_\alpha \{U_{i,i}\}^2) - \frac{2}{3n_\beta k} (\{P_\beta^{ij}\} U_{\beta i,i} + \bar{\mu}_\beta \{U_{i,i}\}^2) \right], \tag{50}
 \end{aligned}$$

with

$$\begin{aligned}
 \bar{\mu}_\alpha &= \bar{\mu}_{\alpha\alpha} + \bar{\mu}_{\alpha\beta}, & \bar{\kappa}_\alpha &= \bar{\kappa}_{\alpha\alpha} + \bar{\kappa}_{\alpha\beta}, \tag{51} \\
 m_{\alpha\beta} &= m_\alpha m_\beta / (m_\alpha + m_\beta)
 \end{aligned}$$

and

$$\lambda_T = (2m_{\alpha\beta} n / \rho) \lambda_U. \tag{52}$$

It is clear by inspection that all terms contained in the square brackets of Eq. (50) are of a negligible order. It now remains to consider  $\lambda_T/\lambda_s$ . After some algebra we may in fact show that

$$\lambda_T/\lambda_s < 1.$$

Hence temperature relaxation is in general the slowest relaxation process.

### A. Two-Temperature Theory

With the exception of the case when  $\lambda_T/\lambda_s \approx 1$ , Eq. (50) cannot be simplified further than by dropping the terms in the square brackets. The "temperature diffusion" equation is

$$\begin{aligned}
 & \frac{\partial}{\partial t} (T_\alpha - T_\beta) + (\mathbf{U}_\alpha - \mathbf{U}_\beta) \cdot \nabla T + \mathbf{U} \cdot \nabla (T_\alpha - T_\beta) \\
 & + \frac{2}{3} T \nabla \cdot (\mathbf{U}_\alpha - \mathbf{U}_\beta) + \frac{2}{3} (T_\alpha - T_\beta) \nabla \cdot \mathbf{U} \\
 & - \frac{2}{3n_\alpha k} \nabla \cdot (\bar{\kappa}_\alpha \nabla T) + \frac{2}{3n_\beta k} \nabla \cdot (\bar{\kappa}_\beta \nabla T) \\
 & - \frac{2}{3k} \left( \frac{\bar{\mu}_\alpha}{n_\alpha} - \frac{\bar{\mu}_\beta}{n_\beta} \right) \{U_{i,i}\}^2 = -\lambda_T (T_\alpha - T_\beta). \tag{53}
 \end{aligned}$$

For obvious reasons this will be referred to as the two-temperature theory. The remaining equations governing this regime are: two continuity equations

(13), (27); the momentum equation (28); the diffusion equation (48); the energy equation (29); the "temperature diffusion equation" (53). In view of the perturbation procedure the constitutive equations (42) and (43) are also considerably reduced. We now have

$$P_{ii} = p \delta_{ii} - 2\mu \{U_{i,i}\}, \tag{54}$$

$$\mu = \bar{\mu}_\alpha + \bar{\mu}_\beta,$$

$$Q = -\kappa \nabla T + \frac{5}{2} k T \frac{n_\alpha n_\beta (m_\beta - m_\alpha)}{\rho} (\mathbf{U}_\alpha - \mathbf{U}_\beta), \tag{55}$$

$$\kappa = \bar{\kappa}_\alpha + \bar{\kappa}_\beta.$$

We note that  $\mu$  and  $\kappa$  are exactly the expressions for viscosity and heat conductivity of a binary mixture given by Eqs. (12.5<sub>1</sub>) and (13.5<sub>1</sub>) in the work of Chapman and Cowling.<sup>2</sup>

For purposes of application, we list the reduced forms in two limiting cases of the two-temperature regime (see the close of this section)

Case (a):

$$m_\alpha/m_\beta \ll 1, \quad n_\alpha/n_\beta \approx O(1),$$

$$\bar{\mu}_\alpha = \mu_\alpha [1 + (B/B_{\alpha\alpha})(\rho_\beta/\rho_\alpha)]^{-1},$$

$$\bar{\kappa}_{\alpha\alpha} = \kappa_\alpha [1 + (A/2B_{\alpha\alpha})(\rho_\beta/\rho_\alpha)]^{-1},$$

$$\bar{\mu}_\beta = \mu_\beta, \quad \bar{\kappa}_{\beta\beta} = \kappa_\beta, \quad \bar{\kappa}_{\alpha\beta} = \bar{\kappa}_{\beta\alpha} = 0.$$

Case (b):

$$m_\alpha/m_\beta \ll 1, \quad n_\alpha/n_\beta \ll 1,$$

$$\bar{\mu}_\alpha = (B_{\alpha\alpha}/B)(\rho_\alpha/\rho_\beta)\mu_\alpha,$$

$$\bar{\kappa}_{\alpha\alpha} = 2(B_{\alpha\alpha}/A)(\rho_\alpha/\rho_\beta)\kappa_\alpha,$$

$$\bar{\mu}_\beta = \mu_\beta, \quad \bar{\kappa}_{\beta\beta} = \kappa_\beta, \quad \bar{\kappa}_{\alpha\beta} = \bar{\kappa}_{\beta\alpha} = 0.$$



We refer to the theory just obtained as the two-temperature theory. In contrast to the classical Chapman-Enskog theory of mixtures where only the composite temperature occurs, the temperatures of each species now appear.

**B. Classical Chapman-Enskog Theory**

In the special case

$$\lambda_T/\lambda_s \approx 1 \tag{56}$$

a further reduction occurs. It is now clear from Eq. (50) that  $(T_\alpha - T_\beta)$  is  $O(\epsilon^2, \epsilon\delta)$ . The diffusion equation is immediately reduced to

$$(\mathbf{U}_\alpha - \mathbf{U}_\beta) = -\frac{n^2}{n_\alpha n_\beta} D_{\alpha\beta} \cdot \left[ \nabla \left( \frac{n_\alpha}{n} \right) + \frac{n_\alpha n_\beta}{\rho n} (m_\beta - m_\alpha) \nabla \ln p \right], \tag{57}$$

which is the classical diffusion equation<sup>2</sup> (again without thermo-diffusion). The temperature diffusion is also considerably reduced,

$$T_\alpha - T_\beta = -\frac{1}{\lambda_T} \left[ (\mathbf{U}_\alpha - \mathbf{U}_\beta) \cdot \nabla T + \frac{2}{3} T \nabla \cdot (\mathbf{U}_\alpha - \mathbf{U}_\beta) - \frac{2}{3k} \left( \frac{1}{n_\alpha} \nabla \cdot (\bar{\kappa}_\alpha \nabla T) - \frac{1}{n_\beta} \nabla \cdot (\bar{\kappa}_\beta \nabla T) \right) - \left( \frac{\bar{\mu}_\alpha}{n_\alpha} - \frac{\bar{\mu}_\beta}{n_\beta} \right) \{U_{\alpha i}\}^2 \right]. \tag{58}$$

In this regime the governing equations are: two continuity equations (13) and (27); the momentum equation (28); the diffusion equation (57); the energy equation (29); and the temperature diffusion equation (58). The latter decouples from the remaining equations. That is, one can solve for  $(\mathbf{U}_\alpha, \mathbf{U}_\beta, T, n_\alpha, n_\beta)$  without a knowledge of  $(T_\alpha - T_\beta)$ . In fact it is just the classical Chapman-Enskog equations which govern  $(\mathbf{U}_\alpha, \mathbf{U}_\beta, T, n_\alpha, n_\beta)$ . Therefore, only in the limiting situation (56) can we expect the classical Chapman-Enskog theory to hold. It is important to note that the temperature difference between gas species is obtained directly by a substitution of the Chapman-Enskog solution into the right-hand side of Eq. (58).

For use in application we give the reduced forms of the transport coefficients in some of the unusual limiting situations in which the Chapman-Enskog theory holds (we justify these limits shortly).

Case (a):

$$m_\alpha/m_\beta \approx O(1), \quad n_\alpha/n_\beta \ll 1, \\ \bar{\mu}_\alpha = \mu_\alpha \left\{ \left[ \frac{2}{3} m_{\alpha 0} (A/B_{\alpha\alpha}) + m_{\beta 0} (B/B_{\alpha\alpha}) \right] \rho_\beta / \rho_\alpha \right\}^{-1},$$

$$\bar{\mu}_\beta = \mu_\beta,$$

$$\bar{\kappa}_\alpha = \kappa_\alpha \left\{ \left[ \left( \frac{2}{3} m_{\alpha 0}^2 + \frac{1}{2} m_{\beta 0}^2 \right) \cdot (A/B_{\alpha\alpha}) + 2m_{\alpha 0} m_{\beta 0} (B/B_{\alpha\alpha}) \right] \rho_\beta / \rho_\alpha \right\}^{-1},$$

$$\bar{\kappa}_\beta = \kappa_\beta.$$

Case (b):

$$n_\alpha/n_\beta \gg m_\alpha n_\alpha / m_\beta n_\beta \geq O(1),$$

$$\bar{\mu}_\alpha = \mu_\alpha, \quad \bar{\kappa}_\alpha = \kappa_\alpha,$$

$$\bar{\mu}_\beta = \mu_\beta \left\{ \left[ \frac{2}{3} (A/B_{\alpha\alpha}) + m_{\beta 0} (B/B_{\alpha\alpha}) \right] \rho_\alpha / \rho_\beta \right\}^{-1},$$

$$\bar{\kappa}_\beta = \kappa_\beta \left\{ \left[ \frac{2}{3} (A/B_{\beta\beta}) + \frac{1}{2} m_{\alpha 0} (B/B_{\beta\beta}) \right] \rho_\alpha / \rho_\beta \right\}^{-1}.$$

**C. Delimitation of the Classical Chapman-Enskog and Two-Temperature Theories**

The criteria for the Chapman-Enskog regime to hold is that the ratio  $\lambda_T/\lambda_s$  be near unity. For a number of reasons this is not a convenient parameter to use. This is mainly due to the presence of the Maxwellization scale,  $\lambda_s$ . This quantity is not readily obtainable from experimental measurements. Also,  $\lambda_s$  does not explicitly occur in either the two-fluid or Chapman-Enskog equations, but is in fact buried in the composite viscosity,  $\mu$ . In order to find a substitute for  $\lambda_s$ , we define a mean free path for the mixture based on the simple gas result,

$$l = \mu / (p\rho)^{1/2}. \tag{59}$$

From this we obtain a relaxation frequency

$$\lambda_\mu = p/\mu.$$

Using the inequalities displayed at the beginning of this section, we may show

$$\lambda_\mu \approx \frac{\lambda_s^\alpha \lambda_s^\beta}{(n_\alpha/n) \lambda_s^\beta + (n_\beta/n) \lambda_s^\alpha}.$$

Although  $\lambda_\mu$  is not a conservative estimate of  $\lambda_s$ , it is a good approximation to it (e.g., if  $\lambda_s^\alpha = \lambda_s^\beta$ ,  $\lambda_\mu = \lambda_s$ ). Using  $\lambda_\mu$  instead of  $\lambda_s$ , we define

$$C = \frac{\lambda_T}{\lambda_\mu} = \frac{2\mu}{(m_\alpha + m_\beta) n D_{\alpha\beta}}. \tag{60}$$

This parameter is used to indicate the importance of two-temperature effects.  $C$  is related to the Schmidt number  $[= \mu / (\rho D_{\alpha\beta})]$  and we refer to it as the modified Schmidt number.

In Fig. 1 we have plotted curves of constant  $C$ , for Maxwell molecules. For simplicity the force constants in the intermolecular force law have been taken equal. In Fig. 2 we have the similar plot for rigid sphere molecules. In this all molecular diameters have been taken equal.

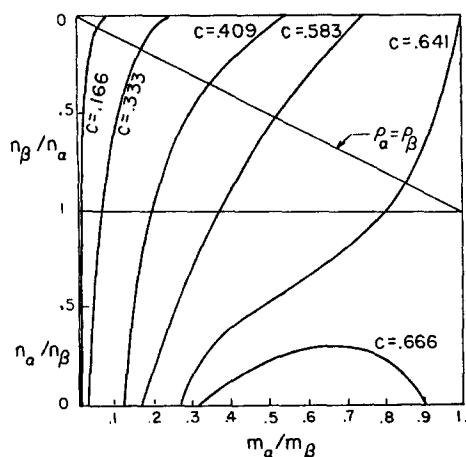


FIG. 1. Modified Schmidt number for Maxwell molecules.

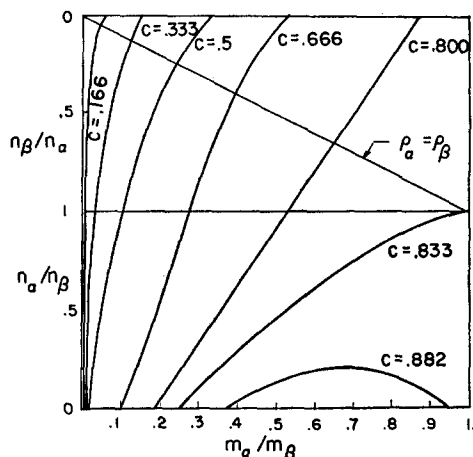


FIG. 2. Modified Schmidt number for rigid sphere molecules.

Table I contains a list of values for the modified Schmidt number, Eq. (60), as computed from experimental data.<sup>8,9,10</sup> Diffusion data were not available for all the mixtures listed and an approximate computation was then performed. Using the simple gas rigid sphere viscosity formula,<sup>2</sup> molecular diameters were calculated for individual gas components. The interaction diameter was then simply taken as the arithmetic mean of the molecular diameters. This method of calculating the diffusion coefficient,  $D_{a\beta}$ , is discussed in Chapman and Cowling,<sup>2</sup> and they point out that it leads to values which are within 10% of experimentally correct values. This approximate calculation is referred to in the table as the semi-experimental determination.

On comparing the noble gas mixtures listed in Table I with the comparable values given in Figs. 1 and 2, we observe that the experimental values of  $C$  fall below the theoretical values. The plots 1 and 2 may therefore be regarded as conservative. On the other hand, the other mixtures can have values of  $C$  which are relatively large. This however only reflects the effect of the internal structure of individual gas components.

We can now give a simple interpretation to the results of this section. For simple gas theory the Chapman-Enskog equations are generally regarded as applicable when typical scale variations are large compared to the mean free path  $l$ . For gas mixtures, this must be altered to say that Chapman-Enskog

theory is applicable when scale variations are large compared to  $l/C$ . The two-temperature theory on the other hand restores the statement to the simple gas stipulation, i.e., it may be regarded as applicable for scale variations large compared to the mean free path, Eq. (59). Since  $C$  can be quite small this can be of considerable importance. In addition we recall the earlier remark concerning the diffusion. If the last is not small [i.e.  $\ll O(\epsilon^{\frac{1}{2}})$ ], neither the Chapman-Enskog nor the two-temperature theories furnish a self consistent set of equations.

## V. ONE-DIMENSIONAL HEAT FLOW

As an example of the equations which have been discussed we consider one-dimensional heat flow

TABLE I. Experimentally based values for the modified Schmidt number  $C$ . All values of the table are for NTP and equal number densities.

Mixture	Mass ratio	Modified Schmidt number $C$
Xenon-Helium <sup>a</sup>	0.03	0.170
Krypton-Helium <sup>b</sup>	0.047	0.216
Argon-Helium <sup>c</sup>	0.1	0.325
Helium-Nitrogen <sup>b</sup>	0.143	0.391
Xenon-Nitrogen <sup>a</sup>	0.215	0.500
Krypton-Neon <sup>d</sup>	0.24	0.566
Xenon-Argon <sup>a</sup>	0.30	0.600
CO <sub>2</sub> -Neon <sup>e</sup>	0.459	1.150
Krypton-Argon <sup>a</sup>	0.476	0.666
CO <sub>2</sub> -Nitrogen <sup>b</sup>	0.637	1.300
Argon-Nitrogen <sup>d</sup>	0.70	0.816
Oxygen-Nitrogen <sup>c</sup>	0.87	0.796
CO <sub>2</sub> -Argon <sup>b</sup>	0.908	0.666

<sup>a</sup> Values obtained from the formula of Hirschfelder, Curtiss, and Bird (Ref. 8).

<sup>b</sup> Experimental values in Ref. 10.

<sup>c</sup> Experimental values found in Ref. 2.

<sup>d</sup> The semi-experimental determination.

<sup>e</sup> Experimental values in Ref. 9.

<sup>8</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 257.

<sup>9</sup> J. D. Breetveld, R. DiPippo, and J. Kestin, *J. Chem. Phys.* **45**, 124 (1966).

<sup>10</sup> J. Kestin, Y. Kobayashi, and R. Wood, *Physica* **32**, 1065 (1966).

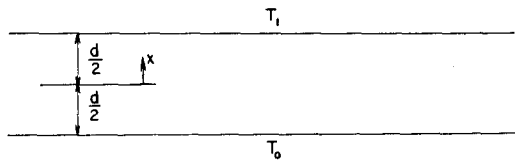


FIG. 3. Heat flow between parallel plates.

in the absence of convection. The two-temperature energy and temperature equations are

$$\frac{d}{dx} \left[ (\bar{\kappa}_\alpha + \bar{\kappa}_\beta) \frac{dT}{dx} \right] = 0, \tag{61}$$

$$\frac{2}{3n_\alpha k} \frac{d}{dy} \left( \bar{\kappa}_\alpha \frac{dT}{dy} \right) - \frac{2}{3n_\beta k} \frac{d}{dy} \left( \bar{\kappa}_\beta \frac{dT}{dy} \right) = \lambda_T (T_\alpha - T_\beta). \tag{62}$$

From the momentum and diffusion equations one obtains

$$p_\alpha = n_\alpha k T_\alpha = \text{const} = p_\alpha^0, \tag{63}$$

$$p_\beta = n_\beta k T_\beta = \text{const} = p_\beta^0.$$

[For Chapman-Enskog regimes the diffusion equation (57) should be used. This leads instead to  $n_\alpha k T$  and  $n_\beta k T$  being constant. Within the framework of the Chapman-Enskog derivation this is compatible with Eq. (63).] Introducing Eqs. (61) and (63) into Eq. (62) we obtain

$$(T_\alpha - T_\beta) = \frac{2}{3\lambda_T} \left( \frac{T_\alpha}{p_\alpha^0} + \frac{T_\beta}{p_\beta^0} \right) \frac{d}{dy} \left( \bar{\kappa}_\alpha \frac{dT}{dy} \right). \tag{64}$$

From the definition of composite temperature we obtain

$$\frac{p_\alpha^0}{p_\beta^0} \left( 1 - \frac{T_\alpha}{T} \right) = \left( \frac{T_\beta}{T_\alpha} - 1 \right),$$

which with Eq. (64) determines  $T_\alpha$  and  $T_\beta$ . It is clear that  $(T_\alpha - T_\beta)$  vanishes if  $\bar{\kappa}_\alpha$  and  $\bar{\kappa}_\beta$  have the same functional dependence on  $T$ . Since the heat conductivity of simple gases can exhibit widely different functional dependences on temperature (this is even true among the noble gases<sup>2</sup>) two temperature effects can be expected in most gas mixtures. Since the calculation of  $(T_\alpha - T_\beta)$  can easily be accomplished in particular examples, we do not pursue this further.

A possible second source of two temperature effects is the wall. However, in deriving the two-temperature equations we have, because of a singular perturbation, eliminated one temperature boundary condition at the wall. Only  $T$  (or an equivalent) may be prescribed at the wall. To investigate this further we reconsider the one-dimensional heat flow problem with the two-fluid equations.

Assuming no convection, the two-fluid equations (see Sec. III) become,

$$\frac{d}{dx} p_\alpha = 0, \tag{65}$$

$$\frac{d}{dx} \left[ \bar{\kappa}_{\alpha\alpha} \frac{dT_\alpha}{dx} + \bar{\kappa}_{\alpha\beta} \frac{dT_\beta}{dx} \right] = A \rho_\alpha \rho_\beta \frac{3k(T_\alpha - T_\beta)}{m_\alpha + m_\beta}.$$

The remaining equations are obtained by setting  $\alpha \rightleftharpoons \beta$  in the above. For simplicity we restrict attention to small mass ratio,  $m_\beta \gg m_\alpha$ , in which case  $\bar{\kappa}_{\alpha\beta}$  and  $\bar{\kappa}_{\beta\alpha}$  are negligible.

First we consider the boundary conditions on  $T_\alpha$  and  $T_\beta$ . It is clear from our perturbation procedure that the form of the distribution function within the two-fluid approximation is

$$f_\alpha \sim n_\alpha \left( \frac{m_\alpha}{2\pi k T_\alpha} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \tilde{c}^2_\alpha}$$

$$\cdot \left[ 1 - \frac{1}{5} \left( \frac{m_\alpha}{k T_\alpha} \right)^{\frac{1}{2}} \frac{\bar{\kappa}_{\alpha\alpha}}{p_\alpha} (\tilde{C}_\alpha^2 - 5) \tilde{C}_{\alpha 1} \frac{dT_\alpha}{dx} \right], \tag{66}$$

where

$$\tilde{C}_\alpha = \xi (m_\alpha / k T_\alpha)^{\frac{1}{2}}.$$

In the above, we have introduced the conditions of the heat flow problem and associated the  $\xi_1$  direction with the  $x$  direction. We first consider the lower wall and denote all quantities evaluated there by a zero subscript (Fig. 3). Denoting the wall temperature by  $T_0$  and assuming diffuse reflection, we have

$$f_{\alpha 0}(\xi_1 > 0) = n_\alpha^\alpha \left( \frac{m_\alpha}{2\pi k T_0} \right)^{\frac{3}{2}} e^{-\frac{1}{2} \tilde{c}^2_{\alpha 0}}, \tag{67}$$

where  $n_\alpha^\alpha$  denotes emitted particles and,

$$\tilde{C}_{\alpha 0} = \left( \frac{m_\alpha}{k T_0} \right)^{\frac{1}{2}} \xi.$$

The zero flux condition yields

$$n_\alpha^\alpha (T_0)^{\frac{1}{2}} = n_{\alpha 0} (T_{\alpha 0})^{\frac{1}{2}}.$$

The temperature slip is computed according to Maxwell's method, i.e., we take,

$$Q_\alpha = \iiint_{-\infty}^{\infty} \frac{m_\alpha \xi_1 \xi^2}{2} f_{\alpha 0} d\xi,$$

where  $f_{\alpha 0}(\xi_1 < 0)$  is given by Eq. (66) and  $f_{\alpha 0}(\xi_1 > 0)$  by (67).<sup>11</sup> This yields

<sup>11</sup> For a simple gas this method is known to give results which are within 20% of the exact value of  $l_{\alpha 0}$ .

$$T_{\alpha 0} - T_0 = l_{\alpha 0} \frac{dT_{\alpha}}{dx}, \tag{68}$$

$$l_{\alpha 0} = \frac{\bar{\kappa}_{\alpha\alpha}}{3n_{\alpha 0}k} \left( \frac{2\pi m_{\alpha}}{kT_{\alpha 0}} \right)^{\frac{1}{2}} \frac{dT_{\alpha}}{dx}$$

with similar expressions for slip and  $l_{\alpha 1}$  at the wall with temperature  $T_1$ . Instead of also considering temperature slip for the  $\beta$  gas, we restrict attention to those cases within the two-temperature theory for which

$$l_{\beta} \ll l_{\alpha} \ll d,$$

where  $l_{\alpha}$  and  $l_{\beta}$  are, roughly speaking, the mean free paths of the  $\alpha$  and  $\beta$  gases and  $d$  is the plate separation. [An example of such a case is  $m_{\alpha}/m_{\beta} < O(1)$ ,  $n_{\alpha}/n_{\beta} < O(1)$ .] If we choose  $l_{\alpha}$  as a length scale, we "spoil" the  $l_{\beta}$  layer. The boundary conditions on  $T_{\beta}$  are therefore

$$T_{\beta}(-\frac{1}{2}d) = T_0, \quad T_{\beta}(\frac{1}{2}d) = T_1. \tag{69}$$

We next introduce the normalization

$$x' = x/l_{\alpha}, \quad t_{\alpha} = T_{\alpha}/T_r, \quad t_{\beta} = T_{\beta}/T_r, \tag{70}$$

$$T_r = \frac{1}{2}(T_1 + T_0),$$

where  $T_r$  is the reference temperature. Substituting for the densities in Eq. (65) the equation for the  $\alpha$  and  $\beta$  gases becomes (recall that we are considering cases for which  $\bar{\kappa}_{\alpha\beta}, \bar{\kappa}_{\beta\alpha} \sim 0$ )

$$\frac{d}{dx'} \bar{\kappa}_{\alpha} \frac{d}{dx'} t_{\alpha} = \frac{t_{\alpha} - t_{\beta}}{t_{\alpha} t_{\beta}}, \tag{71}$$

$$\frac{d}{dx'} \bar{\kappa}_{\beta} \frac{d}{dx'} t_{\beta} = -\frac{t_{\alpha} - t_{\beta}}{t_{\alpha} t_{\beta}},$$

where

$$\bar{\kappa}_{\alpha} = \frac{l_{\alpha}^2 k^2 T_r}{A p_{\alpha} p_{\beta} m_{\alpha} m_{\beta}} \bar{\kappa}_{\alpha\alpha}, \tag{72}$$

$$\bar{\kappa}_{\beta} = \bar{\kappa}_{\alpha} \frac{\bar{\kappa}_{\beta\beta}}{\bar{\kappa}_{\alpha\alpha}}.$$

Taking  $(T_0 - T_1)/T_r$  to be small, we expand about  $T_r$ ,

$$t_{\alpha,\beta} = 1 + t_{\alpha,\beta}^{(1)} + t_{\alpha,\beta}^{(2)} + \dots$$

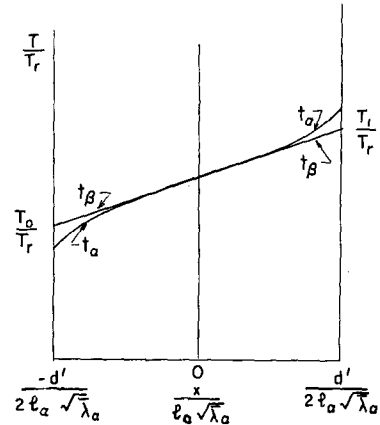


FIG. 4. Temperature distribution in a binary gas between parallel plates.

and Eqs. (71) become

$$\frac{d^2}{dx'^2} t_{\alpha}^{(1)} = \frac{t_{\alpha}^{(1)} - t_{\beta}^{(1)}}{\bar{\kappa}_{\alpha r}}, \tag{73}$$

$$\frac{d^2}{dx'^2} t_{\beta}^{(1)} = -\frac{\bar{\kappa}_{\alpha r} (t_{\alpha}^{(1)} - t_{\beta}^{(1)})}{\bar{\kappa}_{\beta r} \bar{\kappa}_{\alpha r}}. \tag{74}$$

$\bar{\kappa}_{\alpha r}$  is  $\bar{\kappa}_{\alpha}$  with  $\bar{\kappa}_{\alpha\alpha}$  evaluated at the reference temperature. Under the condition that  $l_{\beta} \ll l_{\alpha}$ , it can be shown from the previous analysis that

$$\bar{\kappa}_{\beta r} \gg \bar{\kappa}_{\alpha r}.$$

Since the right-hand side of Eq. (74) is small compared to that of Eq. (73), Eq. (74) is now taken to be

$$(d^2/dx'^2) t_{\beta}^{(1)} = 0. \tag{75}$$

The solution of Eqs. (73) and (75), subject to conditions (67) and (69), is

$$t_{\beta}^{(1)} = \frac{T_1 - T_0}{T_r} \frac{x}{d} + 1, \tag{76}$$

$$t_{\alpha}^{(1)} = \frac{(T_1 - T_0)}{T_r} \frac{x}{d} + 1 + C_1 \exp[-(x/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})] + C_2 \exp(x/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}}), \tag{77}$$

where

$$C_1 = \frac{[l_{\alpha 0} \exp[-(d/2l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})] - l_{\alpha 1} \exp(d/2l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})](T_1 - T_0)/T_r d}{2[1 + (l_{\alpha 0}/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})]^2 [1 - (l_{\alpha 1}/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})] \sinh(d/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})},$$

$$C_2 = \frac{[l_{\alpha 1} \exp(d/2l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}}) - l_{\alpha 0} \exp[-(d/2l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})]](T_1 - T_0)/T_r d}{2[1 + (l_{\alpha 0}/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})][1 - (l_{\alpha 1}/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})] \sinh(d/l_{\alpha}\bar{\kappa}_{\alpha}^{\frac{1}{2}})}.$$

These solutions are shown qualitatively in Fig. 4. This problem illustrates the interesting fact that the thermal slip of individual gas components can occur on vastly different scales. A similar statement

may be made for velocity slip, however this situation requires further discussion. The slip velocity of a composite gas is found by taking the mass-density average of the individual component slip

velocities. Both the Chapman-Enskog and two-temperature theories replace a momentum equation by a diffusion equation (48), (57). Therefore we expect that only one (vector) velocity boundary condition may be imposed, viz., the composite gas slip velocity. Hence for both the Chapman-Enskog and two-temperature theories, individual component velocity slip cannot be specified. Moreover the diffusion equations (48), (57), themselves, furnish relative slip velocities at boundaries. (These cannot in general be expected to be correct.) This situation was to be expected inasmuch as a number of scales were "spoiled" in order to obtain the Chapman-Enskog and two-temperature theories.

On the other hand, the two-fluid equations (13), (25), (26), (42), and (43) do allow specification of individual component slip velocities. Furthermore, they relax to the two-temperature and Chapman-Enskog equations. We can therefore expect the two-fluid equations to give a description of the relative velocity slip layers.

APPENDIX

In Sec. IV,  $\lambda$ , was taken to be a measure of the Maxwellization scale of both gases in a binary mixture. We now discuss this in more detail and show that the stress relaxation can indeed be used to estimate this event. Several partial discussions of the relaxation theory in mixtures are to be found in the literature<sup>12-14</sup> as well as a complete discussion for mixtures of Maxwell molecules.<sup>15</sup> These are largely based on the eigentheory available for Maxwell molecules.<sup>12,13,15-17</sup> The discussion given below follows that given in Ref. 15.

We consider the linearized, spatially homogeneous Boltzmann equations for mixtures of Maxwell molecules,

$$\frac{\partial \phi_\alpha}{\partial t} = \Sigma_\beta \int_{-\infty}^{\infty} f_{0\alpha} f_{0\beta} [\phi'_\alpha + \phi'_\beta - \phi_\alpha - \phi_\beta] \cdot B^{\alpha\beta}(\theta) d\epsilon d\theta d\xi_\beta, \tag{A1}$$

where standard notation has been used.  $f_{0\alpha}\phi_\alpha$  denotes the perturbed distribution function away from the absolute Maxwellian  $f_{0\alpha}$ . The polynomials

$$\psi_{rjm}^\alpha = S_{l+\frac{1}{2}}^r \left( \frac{\xi^2 m_\alpha}{2kT} \right) \left| \xi \left( \frac{m_\alpha}{2kT} \right)^{\frac{1}{2}} \right|^l P_l^m(\cos \theta) e^{imz}, \tag{A2}$$

(where  $S_l^r$  and  $P_l^m$  are Sonine and Legendre polynomials, respectively) have been shown to be characteristic for the linearized collision integral.<sup>15</sup> From this property we have for a binary gas,

$$0 = \left\{ \frac{\partial}{\partial t} - \begin{bmatrix} n_\alpha \lambda_{rj}^\alpha + n_\beta \mu_{rj}^\alpha & n_\beta \nu_{rj} \\ n_\alpha \nu_{rj} & n_\beta \lambda_{rj}^\beta + n_\alpha \mu_{rj}^\beta \end{bmatrix} \right\} \begin{bmatrix} a_{rjm}^\alpha \\ a_{rjm}^\beta \end{bmatrix}, \tag{A3}$$

where

$$a_{rjm}^\alpha = \frac{\int \psi_{rjm}^\alpha \phi_\alpha f_{0\alpha} d\xi}{\int \psi_{rjm}^\alpha \psi_{rjm}^\alpha f_{0\alpha} d\xi}. \tag{A4}$$

Explicit expressions for the eigenvalues  $\lambda$ ,  $\mu$ ,  $\nu$  can be given, but for our purposes only the following properties are needed<sup>16</sup>:

$$\nu_{00} = 0, \quad \nu_{r0} > \nu_{m0} > 0 \quad \text{for } m > r > 0, \\ \nu_{r0} > \nu_{rl}, \quad \nu_{rl} \rightarrow 0 \quad \text{as } |r+l| \rightarrow \infty, \tag{A5}$$

$$\mu_{00} = 0, \quad \mu_{rl} < 0 \quad \text{for } r \text{ or } l \neq 0, \\ \mu_{r0} > \mu_{m0} \quad \text{for } m > r > 0, \quad \mu_{r0} > \mu_{rl}, \tag{A6}$$

$$\lambda_{00} = \lambda_{01} = \lambda_{10} = 0 \quad \text{otherwise } \lambda_{rl} < 0, \\ \lambda_{r0} > \lambda_{rl}, \quad \lambda_{r0} > \lambda_{m0} \quad \text{for } m > r > 0. \tag{A7}$$

Regarding the matrix of (A3) we see from (A5)-(A7) that the diagonal elements are nonincreasing and that the off-diagonal elements go to zero. It is therefore clear that the relaxation frequency of a low-order moment is representative of the time in which the distribution functions become Maxwellian. The stress [for which  $(r, l) = (0, 2)$ ] relaxation time can therefore be taken as a measure of the time of Maxwellization.

<sup>12</sup> L. Sirovich, Phys. Fluids 5, 908 (1962).  
<sup>13</sup> C. F. Curtiss, University of Wisconsin, Department of Chemical Engineering, Report NSF-7 (1957).  
<sup>14</sup> T. F. Morse, Phys. Fluids 6, 14 (1963).  
<sup>15</sup> L. Sirovich, Phys. Fluids 9, 2323 (1966).  
<sup>16</sup> J. Naze, Compt. Rend. 215, 854 (1960).  
<sup>17</sup> C. S. Wang Chang and G. E. Uhlenbeck, University of Michigan, Department of Engineering, Report (1954).