

Boltzmann Equation for a Dissociating Gas

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The incorporation of three-body collisions for dissociation/recombination into the Boltzmann equation is discussed. Conditions are assumed such that collisions are completed in the sense of scattering theory, so the collision operator is determined by scattering and reaction cross sections. The resulting equation has an *H*-theorem, and the equilibrium solution requires the law of mass action in addition to the Maxwellian dependence on momentum. A brief discussion is given of the normal solution and the transport coefficients.

KEY WORDS: Boltzmann equation; three-body collisions; reactions; dissociation; recombination.

1. INTRODUCTION

The subject is the generalization of the Boltzmann equation to account for breakup and recombination in a gas of particles which form two-body bound states. The primary focus will be on the dissociation/recombination of diatomic molecules, but the method is applicable to other processes such as ionization.

The gas is treated as a reacting mixture, and the Boltzmann equation is a set of coupled equations, one for each component of the mixture. To avoid the introduction of a density matrix for internal motion, I assume the compound particles to have only a single internal state; each of the species is then described by a distribution function on the space of position and momentum. The three-body collision operator for reactive collisions is derived from the collision-rate formula of scattering theory. The resulting kinetic equations have an *H*-theorem, which in equilibrium yields the law of mass action in addition to the Maxwellian dependence on momentum.

This paper is dedicated to Prof. E. G. D. Cohen on the occasion of his 65th birthday.

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Application of the Chapman-Enskog procedure to construct a normal solution and to obtain formulas for the transport coefficients follows generally the same lines as for a nonreacting mixture.

The standard approach to the generalization of the Boltzmann equation is based on the BBGKY hierarchy and Bogoliubov's functional assumption (see, e.g., ref. 1). This approach, with a modification of the functional assumption, has been used to discuss the kinetic equations for a dissociating gas.⁽²⁾ The collision operators obtained in this general way include effects due to the spatial extent of a collision, and effects like those in the Waldmann-Snyder equation⁽³⁾ due to collision-induced coherence among elements of the density matrix for internal states. The result is rather complicated, primarily because the collision operator is not determined by cross sections for completed collisions. In the simpler description of reactions presented here, the spatial extent of a collision is neglected (as it is in the Boltzmann binary collision operator), and the Waldmann-Snyder coherence effects do not occur since there is only a single internal state. (Actually, the requirement of a single internal state is not essential to the argument, provided that off-diagonal elements of the internal density matrix are assumed to vanish, as in the theory of Wang Chang *et al.*⁽⁴⁾)

The collision operators obtained in the following may be compared with the Bogoliubov triple-collision operator.⁽¹⁾ In three-particle collisions there can occur disconnected collision sequences, for which one of the particles passes through without interaction. Such sequences must be omitted from the triple-collision operator, since they have already been counted in the binary-collision operator. The Bogoliubov triple-collision operator therefore depends on configurations during the course of the collision,⁽⁵⁾ as the presence of a disconnected sequence cannot be detected from the initial and final momenta alone. In the cases considered here, there are three free particles in either the initial or final state, but not both, so disconnected sequences cannot occur. The net effect of this, and the simplifications mentioned in the preceding paragraph, is that the collision operator is determined by scattering and reaction cross sections. There is a slight complication because of the bookkeeping necessary to keep track of three particles, but otherwise the reactive collision operator has many similarities to Boltzmann's binary-collision operator.

The Bogoliubov triple-collision operator yields density-dependent corrections to the transport coefficients, similar to those obtained from the Enskog equation. The processes considered here are also responsible for density-dependent corrections, but the dependence on density is quite different because of the strong temperature dependence contained in the law of mass action. For, say, hydrogen at standard conditions, it is a good approximation to neglect Enskog-like corrections, but a very poor

approximation indeed to use the low-density, or atomic, limit of the law of mass action.

The Boltzmann equation has been used extensively to treat bimolecular reactions in a gas (see refs. 6, and references cited therein). However discussions of three-body reactions have in the past been generally based on phenomenological rate equations, or on the introduction of "source" and "sink" terms in a Boltzmann equation.

2. THERMODYNAMICS

I first summarize the equilibrium thermodynamic properties of the system under consideration. Consider a gas of identical particles which can form a two-body bound state (or diatomic molecule). Suppose the gas to be in equilibrium, including chemical equilibrium under dissociation and recombination. Since my main concern is the handling of three-body collisions, I neglect excited molecular states and formation of ions.

Let N_A denote the number of atoms (unbound particles), and N_M the number of molecules (bound pairs), at a given temperature and total density. The total number of particles is

$$N_T = N_A + 2N_M \quad (1)$$

The densities of atoms and molecules are

$$n_A = N_A/V, \quad n_M = N_M/V$$

where V is the volume; also define

$$n = n_A + n_M, \quad n_T = n_A + 2n_M$$

and the mass density is $\rho = mn_T$, where m is the mass of an atom.

An equilibrium state is fixed by the values of the mass density ρ and Kelvin temperature T . (If the gas is in uniform motion, its velocity \mathbf{u} is an additional thermodynamic variable.) The individual densities n_A and n_M vary with ρ and T in accordance with the law of mass action,

$$n_M = Kn_A^2 \quad (2)$$

The equilibrium constant K is given by

$$K = \frac{h^3}{(\pi m \kappa T)^{3/2}} \exp\left(\frac{B}{\kappa T}\right)$$

where h is Planck's constant, κ is Boltzmann's constant, and $B > 0$ is the binding energy of the two-body bound state.

Let x denote the atomic mass fraction, $x = N_A/N_T$; then $n_A = xn_T$, $n_M = \frac{1}{2}n_T(1-x)$. Equations (1) and (2) yield the quadratic equation

$$2Kn_Tx^2 + x - 1 = 0$$

with solution

$$x = \frac{1}{4Kn_T} [(1 + 8n_TK)^{1/2} - 1]$$

This yields the useful relations

$$n_T \left(\frac{\partial x}{\partial n_T} \right)_T = -\frac{x(1-x)}{2-x}, \quad T \left(\frac{\partial x}{\partial T} \right)_{n_T} = \frac{x(1-x)}{2-x} \left(\frac{3}{2} + \frac{B}{\kappa T} \right) \quad (3)$$

The internal energy (per unit volume) and equation of state are

$$\varepsilon = \frac{3}{2} \eta \kappa T - n_M B, \quad p = n \kappa T \quad (4)$$

Using Eq. (3), we find for the isothermal compressibility

$$K_T = (1/n_T)(\partial n_T / \partial p)_T = (1/p)[1 + (n_A n_M / n_T^2)]$$

Let C_V and C_p denote the specific heats (per unit mass) at constant volume and pressure, respectively. For the former we get

$$\rho C_V = \left(\frac{\partial \varepsilon}{\partial T} \right)_\rho = \frac{3}{2} n \kappa \left[1 + \frac{2}{3} \frac{n_A n_M}{n_T^2 + n_A n_M} \left(\frac{B}{\kappa T} + \frac{3}{2} \right)^2 \right]$$

The specific heat at constant pressure can be obtained from

$$\rho(C_p - C_V) = TK_T \left[\left(\frac{\partial p}{\partial T} \right)_\rho \right]^2$$

Equation (3) yields

$$\left(\frac{\partial p}{\partial T} \right)_\rho = \frac{1}{TK_T} \left[1 + \frac{n_A n_M}{n_T^2} \left(\frac{5}{2} + \frac{B}{\kappa T} \right) \right]$$

from which follows

$$\rho C_p = \frac{5}{2} n \kappa \left[1 + \frac{2}{5} \frac{n_A n_M}{n_T^2} \left(\frac{5}{2} + \frac{B}{\kappa T} \right)^2 \right]$$

The specific heat has a strong peak as a function of temperature, the peak being more pronounced at low density and occurring at about the point where $x = 1/2$.

3. BOLTZMANN EQUATION

I now suppose the gas not to be in equilibrium, and construct a generalized Boltzmann equation to describe its behavior. I treat the atoms as identical particles, satisfying quantum statistics, but ignore any internal degrees of freedom such as spin; the density is assumed to be low enough that the gas is nondegenerate. Let f_s , $s = A, M$, denote the distribution functions for atoms and molecules, respectively; position and time will be written \mathbf{x} , t , while \mathbf{p} denotes momentum. With the normalization

$$N_s = \int d^3x d^3p f_s(\mathbf{x}, \mathbf{p}, t) \quad (5)$$

the local densities of atoms and molecules are given by

$$n_s(\mathbf{x}, t) = \int d^3p f_s(\mathbf{x}, \mathbf{p}, t) \quad (6)$$

The Boltzmann equations for f_s are

$$\frac{\partial f_s}{\partial t} + \mathbf{v} \cdot \nabla f_s = J_s \quad (7)$$

where $\mathbf{v} = \mathbf{p}/m_s$ and $m_A = m$, $m_M = 2m$. The collision operator J_s will be written as

$$J_s = J_s^S + J_s^X \quad (8)$$

corresponding, respectively, to elastic scattering and to reactive collisions. The former have the standard form; for example, the collision operator for scattering of atoms by atoms is

$$J_{AA}(\mathbf{p}_1) = \frac{1}{2} \int d^3p_2 \frac{q}{\mu_2} \int d\Omega(\mathbf{q}') \sigma_{AA}(\mathbf{q}' \rightarrow \mathbf{q}) \\ \times [f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) - f_A(\mathbf{p}_1) f_A(\mathbf{p}_2)] \quad (9)$$

Here \mathbf{p}'_1 , \mathbf{p}'_2 are initial momenta such that the momenta after the collision are \mathbf{p}_1 , \mathbf{p}_2 , and \mathbf{q} denotes the relative momentum of two atoms,

$$\mathbf{q} = \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2) \quad (10)$$

In addition, $d\Omega(\mathbf{q}')$ is the element of solid angle about \mathbf{q}' , $\mu_2 = m/2$ is the reduced mass, and σ_{AA} is the cross section for scattering of two atoms. The factor $1/2$ occurs to eliminate double counting of states for the two identi-

cal particles. An equivalent form, which explicitly shows conservation of energy and momentum, is⁽⁷⁾

$$\begin{aligned}
 J_{AA}(\mathbf{p}_1) = & \frac{1}{2}(2\pi h)^2 \int d^3p_2 d^3p'_1 d^3p'_2 \\
 & \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_{AA}(\mathbf{q} | \mathbf{q}')|^2 \\
 & \times [f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) - f_A(\mathbf{p}_1) f_A(\mathbf{p}_2)] \quad (11)
 \end{aligned}$$

Here T_{AA} is the T -matrix (with exchange term included) for the scattering of two atoms, related to the cross section by $\sigma_{AA} = |T_{AA}/(2\pi\mu_2 h)|^2$, and the total momentum and energy have been denoted by \mathbf{K} and E . The T -matrices occurring here and below are reduced by removal of the delta function for overall conservation of momentum; the scattering is described in the center-of-mass frame, so they depend on only the relative momenta.

4. REACTIVE COLLISION OPERATORS

The reactions considered are three-body collisions leading to the formation of a molecule and dissociation of a molecule induced by collision with an atom; for distinguishable particles (which are not considered here) rearrangement collisions must also be included. The reactive contribution to the collision operator can be obtained by counting the gain and loss rates, in a way similar to that frequently used to derive the Boltzmann equation for a monatomic gas. For this purpose we use the collision-rate formula of scattering theory.

Consider a general collision, in which m beams of particles of various kinds are incident on a scattering region, and n counters are set to observe emitted particles. Let $f_j(\mathbf{x}, \mathbf{p}, t) d^3p$ be the number of incident particles of the j th kind, per unit volume, with momentum in the range d^3p . Let $d\mathcal{R}$ denote the rate of collisions, per unit volume, leading to emitted particles with momenta in the ranges $d^3p'_1, \dots, d^3p'_n$. Then $d\mathcal{R}$ is given by⁽⁸⁾

$$\begin{aligned}
 d\mathcal{R} = & (2\pi)^2 h^{3m-4} \left[\prod_{j=1}^m f_j(\mathbf{p}_j) d^3p_j \right] \left[\prod_{k=1}^n d^3p'_k \right] \\
 & \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T(f|i)|^2 \quad (12)
 \end{aligned}$$

where $T(f|i)$ is the T -matrix for the transition between initial and final states.

Consider, for example, a dissociative collision in which atom number 3 collides with a bound pair of particles 1, 2. The collision rate for this process is

$$\begin{aligned} d\mathcal{R}_D &= (2\pi\hbar)^2 f_A(\mathbf{p}_3) d^3p_3 f_M(\mathbf{P}_{12}) d^3P_{12} \\ &\quad \times d^3p'_1 d^3p'_2 d^3p'_3 \delta(\mathbf{K} - \mathbf{K}') \\ &\quad \times \delta(E - E') |T_D(\mathbf{k}'_3, \mathbf{q}_{12} | \mathbf{k}_3)|^2 \end{aligned} \quad (13)$$

where T_D denotes the T -matrix for dissociation. As before, \mathbf{q} denotes the relative momentum of a pair, but subscripts have been attached to show the particles involved,

$$\mathbf{q}_{12} = \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2)$$

In addition, I use \mathbf{P} and \mathbf{k} to denote, respectively, the total momentum of a pair and the relative momentum of a third particle with respect to the pair:

$$\mathbf{P}_{12} = \mathbf{p}_1 + \mathbf{p}_2, \quad \mathbf{k}_3 = \frac{2}{3}\mathbf{p}_3 - \frac{1}{3}\mathbf{P}_{12}$$

The total momentum of the three-particle system is

$$\mathbf{K} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3$$

and the kinetic energy can be written in the forms

$$\frac{1}{2m}(p_1^2 + p_2^2 + p_3^2) = \frac{1}{2m}p_3^2 + \frac{1}{4m}P_{12}^2 + u_{12} = \frac{1}{6m}K^2 + w_3 + u_{12}$$

Here w , u are kinetic energies of relative motion,

$$w = k^2/2\mu_3, \quad u = q^2/2\mu_2$$

where $\mu_3 = 2m/3$ is the reduced mass of the atom-molecule system.

The δ -functions in Eq. (13) impose four restrictions on the nine components of the final momenta, so five scattering parameters are needed to specify the collision. Let us take these to be the directions of \mathbf{k}'_3 , \mathbf{q}'_{12} plus the energy w'_3 . The volume element for the final momenta can be written

$$\begin{aligned} d^3p'_1 d^3p'_2 d^3p'_3 &= d^3K' d^3k'_3 d^3q'_{12} \\ &= d^3K' \mu_3 k'_3 dw'_3 d\Omega(\mathbf{k}'_3) \mu_2 q'_{12} du'_{12} d\Omega(\mathbf{q}'_{12}) \end{aligned}$$

and when conservation of momentum is taken into account, the energy difference becomes

$$E - E' = w_3 - B - w'_3 - u'_{12}$$

The product of incident flux times target density is

$$(k_3/\mu_3) f_A(\mathbf{p}_3) d^3p_3 f_M(\mathbf{P}_{12}) d^3P_{12}$$

To identify the cross section, divide the collision rate (13) by this product and integrate over \mathbf{K}' , u'_{12} . This yields

$$\begin{aligned} \sigma_D(\mathbf{k}_3 \rightarrow \mathbf{k}'_3, \mathbf{q}'_{12}) &= \frac{d\sigma}{d\Omega(\mathbf{k}'_3) d\Omega(\mathbf{q}'_{12}) dw'_3} \\ &= (2\pi h)^2 \mu_2 \mu_3^2 \frac{k'_3 q'_{12}}{k_3} |T_D(\mathbf{k}'_3, \mathbf{q}'_{12} | \mathbf{k}_3)|^2 \end{aligned}$$

The final momenta are no longer independent variables, but are determined as functions of the initial momenta and the scattering parameters.

Recombination corresponds to a collision in which three atomic beams are incident and both atoms and diatomic molecules are emitted. If the emitted molecule is a bound pair of particles 1, 2, the collision rate is

$$\begin{aligned} d\mathcal{R}_R &= (2\pi)^2 h^5 f_A(\mathbf{p}_1) d^3p_1 f_A(\mathbf{p}_2) d^3p_2 f_A(\mathbf{p}_3) d^3p_3 \\ &\quad \times d^3p'_3 d^3P'_{12} \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_R(\mathbf{k}'_3 | \mathbf{k}_3, \mathbf{q}_{12})|^2 \end{aligned}$$

where T_R is the T -matrix for recombination. With three incident particles there are several options for the definitions of cross section; let us choose the product of incident flux times target density to be

$$(k_3/\mu_3)(q_{12}/\mu_2) f_A(\mathbf{p}_1) d^3p_1 f_A(\mathbf{p}_2) d^3p_2 f_A(\mathbf{p}_3) d^3p_3 \quad (14)$$

The volume element for the final momenta can be written

$$d^3p'_3 d^3P'_{12} = d^3K' d^3k'_3 = d^3K' \mu_3 k'_3 dw'_3 d\Omega(\mathbf{k}'_3)$$

Integrating the collision rate over \mathbf{K}' , w'_3 and dividing by the product (14), we obtain for the cross section

$$\begin{aligned} \sigma_R(\mathbf{k}_3, \mathbf{q}_{12} \rightarrow \mathbf{k}'_3) &= \frac{d\sigma}{d\Omega(\mathbf{k}'_3)} \\ &= (2\pi)^2 h^5 \mu_2 \mu_3^2 \frac{k'_3}{k_3 q_{12}} |T_R(\mathbf{k}'_3 | \mathbf{k}_3, \mathbf{q}_{12})|^2 \end{aligned}$$

It follows from microscopic reversibility and invariance to spatial inversions that

$$\bar{T}_D(\mathbf{k}'_3, \mathbf{q}'_{12} | \mathbf{k}_3) = T_R(\mathbf{k}_3 | \mathbf{k}'_3, \mathbf{q}'_{12}) \quad (15)$$

where the bar denotes the complex conjugate. Consequently, the cross sections satisfy the reciprocity relation

$$(k_3 q_{12})^2 \sigma_R(\mathbf{k}_3, \mathbf{q}_{12} \rightarrow \mathbf{k}'_3) = h^3 k_3'^2 \sigma_D(\mathbf{k}'_3 \rightarrow \mathbf{k}_3, \mathbf{q}_{12}) \tag{16}$$

The reactive collision operators have the Boltzmann gain-loss form with the gain and loss terms being obtained from the appropriate collision rates. Consider first the reactive collision operator J_M^X in the kinetic equation for molecules. Suppose a bound pair of particles with momentum \mathbf{P}_{12} collides dissociatively with an atom with momentum \mathbf{p}_3 . To derive the collision operator, it is necessary to calculate the net rates of loss and gain to molecules with momentum in the range d^3P_{12} . The rate of loss due to dissociation is obtained by integrating (13) over \mathbf{p}_3 and the three primed momenta. Let each of the latter range over the full space for momentum, but divide by 3! to eliminate multiple counting of states for identical particles. The result is

$$\begin{aligned} \text{rate of loss} = & \frac{1}{3!} \left\{ (2\pi h)^2 \int d^3p_3 f_A(\mathbf{p}_3) f_M(\mathbf{P}_{12}) \right. \\ & \times \int d^3p'_1 d^3p'_2 d^3p'_3 \delta(\mathbf{K} - \mathbf{K}') \\ & \left. \times \delta(E - E') |T_D(\mathbf{k}'_3, \mathbf{q}'_{12} | \mathbf{k}_3)|^2 \right\} d^3P_{12} \end{aligned}$$

The inverse collision corresponds to recombination, and contributes to the gain rate for molecules. To calculate the gain rate to molecules in d^3P_{12} , denoting the initial momenta by a prime, we find

$$\begin{aligned} \text{rate of gain} = & \frac{1}{3!} \left\{ (2\pi)^2 h^5 \int d^3p'_1 d^3p'_2 d^3p'_3 \right. \\ & \times f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) \int d^3p_3 \delta(\mathbf{K} - \mathbf{K}') \\ & \left. \times \delta(E - E') |T_R(\mathbf{k}_3 | \mathbf{k}'_3, \mathbf{q}'_{12})|^2 \right\} d^3P_{12} \end{aligned}$$

Taking the difference and using Eq. (15), we obtain the collision operator for molecular dissociation/recombination,

$$\begin{aligned} J_M^X(\mathbf{P}_{12}) = & \frac{1}{3!} (2\pi h)^2 \int d^3p_3 d^3p'_1 d^3p'_2 d^3p'_3 \\ & \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_D(\mathbf{k}'_3, \mathbf{q}'_{12} | \mathbf{k}_3)|^2 \\ & \times [h^3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) - f_A(\mathbf{p}_3) f_M(\mathbf{P}_{12})] \tag{17} \end{aligned}$$

In terms of the cross section, this takes the form

$$\begin{aligned}
 J_M^X(\mathbf{P}_{12}) &= \frac{1}{3!} \int d^3 p_3 \frac{k_3}{\mu_3} \int dw'_3 d\Omega(\mathbf{k}'_3) \\
 &\quad \times d\Omega(\mathbf{q}'_{12}) \sigma_D(\mathbf{k}_3 \rightarrow \mathbf{k}'_3, \mathbf{q}'_{12}) \\
 &\quad \times [h^3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) - f_A(\mathbf{p}_3) f_M(\mathbf{P}_{12})]
 \end{aligned}$$

The integration over \mathbf{p}_3 is limited by the threshold condition $w_3 = k_3^2/2\mu_3 \geq B$. Of course, the collision operator can be expressed in terms of σ_R rather than σ_D ; in some cases, as here, the form is slightly simpler if the cross section corresponds to the processes which contribute to the loss term.

The collision operator in the kinetic equation for atoms is derived in a similar way, but there are contributions to the loss and gain rates from both recombination and dissociation. The loss rate to atoms with momentum in the range $d^3 p_1$ due to recombination is

$$\begin{aligned}
 \text{rate of loss} &= \frac{1}{2} \left[(2\pi)^2 h^5 \int d^3 p_2 d^3 p_3 f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3) \right. \\
 &\quad \times \int d^3 p'_1 d^3 P'_{23} |T_R(\mathbf{k}'_1 | \mathbf{k}_1, \mathbf{q}_{23})|^2 \\
 &\quad \left. \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') \right] d^3 p_1
 \end{aligned}$$

where the factor 1/2 accounts for permutations of $\mathbf{p}_2, \mathbf{p}_3$. Denoting the initial momenta for the inverse (dissociative) collisions by a prime, we find for the rate of gain

$$\begin{aligned}
 \text{rate of gain} &= \frac{1}{2} \left[(2\pi h)^2 \int d^3 p'_1 d^3 P'_{23} f_A(\mathbf{p}'_1) f_M(\mathbf{P}'_{23}) \right. \\
 &\quad \times \int d^3 p_2 d^3 p_3 \delta(\mathbf{K} - \mathbf{K}') \\
 &\quad \left. \times \delta(E - E') |T_D(\mathbf{k}_1, \mathbf{q}_{23} | \mathbf{k}'_1)|^2 \right] d^3 p_1
 \end{aligned}$$

The associated collision operator is

$$\begin{aligned}
 J_A^R(\mathbf{p}_1) &= \frac{1}{2} (2\pi h)^2 \int d^3 p_2 d^3 p_3 d^3 p'_1 d^3 P'_{23} \\
 &\quad \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_R(\mathbf{k}'_1 | \mathbf{k}_1, \mathbf{q}_{23})|^2 \\
 &\quad \times [f_A(\mathbf{p}'_1) f_M(\mathbf{P}'_{23}) - h^3 f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3)]
 \end{aligned}$$

The rate of loss from d^3p_1 due to dissociative collisions is

rate of loss

$$= \frac{1}{3!} \left[(2\pi h)^2 \int d^3P_{23} f_A(\mathbf{p}_1) f_M(\mathbf{P}_{23}) \right. \\ \times \int d^3p'_1 d^3p'_2 d^3p'_3 \delta(\mathbf{K} - \mathbf{K}') \\ \left. \times \delta(E - E') |T_D(\mathbf{k}'_1, \mathbf{q}'_{23} | \mathbf{k}_1)|^2 \right] d^3p_1$$

and the gain rate due to the inverse collisions is

rate of gain

$$= \frac{1}{3!} \left[(2\pi)^2 h^5 \int d^3p'_1 d^3p'_2 d^3p'_3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) \right. \\ \left. \times \int d^3P_{23} \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_R(\mathbf{k}_1 | \mathbf{k}'_1, \mathbf{q}'_{23})|^2 \right] d^3p_1$$

This gives the collision operator for dissociation

$$J_A^D(\mathbf{p}_1) = \frac{1}{3!} (2\pi h)^2 \int d^3P_{23} d^3p'_1 d^3p'_2 d^3p'_3 \\ \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_D(\mathbf{k}'_1, \mathbf{q}'_{23} | \mathbf{k}_1)|^2 \\ \times [h^3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) - f_A(\mathbf{p}_1) f_M(\mathbf{P}_{23})] \quad (18)$$

The total reactive collision operator is $J_A^X = J_A^R + J_A^D$. In terms of cross sections it is

$$J_A^X(\mathbf{p}_1) = \frac{1}{2} \int d^3p_2 d^3p_3 \frac{k_1 q_{23}}{\mu_2 \mu_3} \int d\Omega(\mathbf{k}'_1) \sigma_R(\mathbf{k}_1, \mathbf{q}_{23} \rightarrow \mathbf{k}'_1) \\ \times [h^{-3} f_A(\mathbf{p}'_1) f_M(\mathbf{P}'_{23}) - f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3)] \\ + \frac{1}{3!} \int d^3P_{23} dw'_1 d\Omega(\mathbf{k}'_1) d\Omega(\mathbf{q}'_{23}) \frac{k_1}{\mu_3} \sigma_D(\mathbf{k}_1 \rightarrow \mathbf{k}'_1, \mathbf{q}'_{23}) \\ \times [h^3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_A(\mathbf{p}'_3) - f_A(\mathbf{p}_1) f_M(\mathbf{P}_{23})]$$

There are other situations of interest which can be described by straightforward modifications of the collision operator. For example, suppose the reacting species to be present at low concentration in an inert

buffer gas, with reactions being mediated only by the buffer atoms. In this case, the collision operator in the kinetic equation for molecules is

$$\begin{aligned}
 J_M^X(\mathbf{P}_{12}) = & \frac{1}{2} \int d^3 p_B (k_B / \mu_B) \int dw'_B d\Omega(\mathbf{k}'_B) \\
 & \times d\Omega(\mathbf{q}'_{12}) \sigma_D(\mathbf{k}_B \rightarrow \mathbf{k}'_B, \mathbf{q}'_{12}) \\
 & \times [h^3 f_A(\mathbf{p}'_1) f_A(\mathbf{p}'_2) f_B(\mathbf{p}'_B) - f_B(\mathbf{p}_B) f_M(\mathbf{P}_{12})]
 \end{aligned}$$

while for atoms

$$\begin{aligned}
 J_A^X(\mathbf{p}_1) = & \int d^3 p_2 d^3 p_B (k_B q_{12} / \mu_2 \mu_B) \\
 & \times \int d\Omega(\mathbf{k}'_B) \sigma_R(\mathbf{k}_B, \mathbf{q}_{12} \rightarrow \mathbf{k}'_B) \\
 & \times [h^{-3} f_B(\mathbf{p}'_B) f_M(\mathbf{P}'_{12}) - f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_B(\mathbf{p}_B)]
 \end{aligned}$$

Here the subscript B labels buffer atoms, and μ_B and \mathbf{k}_B are the reduced mass and relative momentum for a buffer atom with respect to a bound pair,

$$\frac{1}{\mu_B} = \frac{1}{m_B} + \frac{1}{2m_A}, \quad \frac{\mathbf{k}_B}{\mu_B} = \frac{\mathbf{p}_B}{m_B} - \frac{\mathbf{P}_{12}}{2m_A}$$

5. GENERAL PROPERTIES OF BOLTZMANN EQUATION

The conservation laws, H -theorem, and equilibrium solution are obtained from the Boltzmann equation in much the same way as for a monatomic gas.

The conservation laws follow from the existence of summational invariants $\psi = \{\psi_A, \psi_M\}$ with the property that

$$\sum_s \int d^3 p \psi_s J_s = 0$$

The summational invariant corresponding to conservation of mass is given by $\psi_s = m_s$, that for momentum is $\psi_s = \mathbf{p}$, and for the energy it is $\psi_s = (p^2/2m_s) - B_s$, where $B_A = 0$, $B_M = B$. It is readily checked that these satisfy the preceding equation, and the corresponding local conservation laws follow immediately. The only novel features concern the energy conservation law and the equations for the densities of the two species. The

energy density and flux, satisfying $\partial\varepsilon/\partial t + \nabla \cdot \mathbf{s} = 0$, now contain contributions from the internal energy

$$\varepsilon = \sum_s \int d^3p \left(\frac{p^2}{2m_s} - B_s \right) f_s(\mathbf{p}), \quad \mathbf{s} = \sum_s \int d^3p \left(\frac{p^2}{2m_s} - B_s \right) \frac{1}{m_s} \mathbf{p} f_s(\mathbf{p}) \quad (19)$$

The numbers of atoms and molecules are not independently conserved, but integration of (7) yields

$$\frac{\partial n_s}{\partial t} + \nabla \cdot \mathbf{j}_s = v_s \quad (20)$$

where n_s is determined by f_s according to Eq. (6) and the fluxes \mathbf{j}_s are given by

$$\mathbf{j}_s = \int d^3p \frac{1}{m_s} \mathbf{p} f_s \quad (21)$$

The source terms are

$$v_s = \int d^3p J_s$$

Nonvanishing contributions to v_s are obtained only from the collision operators for dissociation/recombination. For $v = v_M$ we have

$$v = \int d^3p J_M^X \quad (22)$$

It follows from conservation of momentum that $\sum_s m_s v_s = 0$, so $v_A = -2v$.

The H -theorem depends on the property of a collision operator that

$$\int d^3p \ln f J \leq 0 \quad (23)$$

The argument for the scattering collision operators is standard, so we need consider only reactive collisions. For the purpose at hand, the forms (17) and (18) for the collision operators are more convenient than those containing the cross sections. A relabeling of particles and interchange of primed and unprimed variables leads to

$$\begin{aligned} & \int d^3p \ln(h^3 f_A) J_A^X + \int d^3P \ln(h^3 f_M) J_M^X \\ &= \frac{1}{3!} (2\pi h)^2 \int d^3p_1 d^3p_2 d^3p_3 \int d^3p'_1 d^3P'_{23} \\ & \quad \times \delta(\mathbf{K} - \mathbf{K}') \delta(E - E') |T_D(\mathbf{k}_1, \mathbf{q}_{23} | \mathbf{k}'_1)|^2 \\ & \quad \times [f_A(\mathbf{p}'_1) f_M(\mathbf{P}'_{23}) - h^3 f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3)] \\ & \quad \times \ln[h^3 f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3) / f_A(\mathbf{p}'_1) f_M(\mathbf{P}'_{23})] \end{aligned} \quad (24)$$

which is nonpositive. Note that J_A, J_M do not individually satisfy (23), but only the combinations shown above.

Consider a spatially-homogeneous system and define the H -function by

$$H = \int d^3p \ln(h^3 f_A) f_A + \int d^3P \ln(h^3 f_M) f_M$$

Then

$$\frac{dH}{dt} = \int d^3p [1 + \ln(h^3 f_A)] J_A + \int d^3P [1 + \ln(h^3 f_M)] J_M$$

By what has just been shown,

$$\frac{dH}{dt} \leq \int d^3p J_A + \int d^3P J_M = -v$$

Consequently, the quantity $H' = H + n_A + n_M$ satisfies

$$dH'/dt \leq 0$$

That H' is bounded from below follows from that property of H , so H' approaches a limit for $t \rightarrow \infty$. In the limit $dH'/dt = 0$ and since it is a sum of nonpositive terms, each of these must vanish separately. The usual argument applied to the terms for scattering shows f_s to have the Maxwellian form,

$$f_s(\mathbf{p}) = n_s \phi_s(\mathbf{p} - m_s \mathbf{u}) \quad (25)$$

Here \mathbf{u} is the flow velocity and

$$\phi_s(\mathbf{p}) = (2\pi m_s \kappa T)^{-3/2} \exp(-\mathbf{p}^2/2m_s \kappa T)$$

For dissociation/recombination, conservation of energy and momentum in Eq. (24) are expressed by

$$\frac{1}{2m} p_1'^2 + \frac{1}{4m} P_{23}'^2 - B = \frac{1}{2m} (p_1^2 + p_2^2 + p_3^2), \quad \mathbf{p}_1' + \mathbf{P}_{23}' = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{p}_3$$

which in the case of Maxwellian distribution functions yields

$$\begin{aligned} h^3 f_A(\mathbf{p}_1) f_A(\mathbf{p}_2) f_A(\mathbf{p}_3) - f_A(\mathbf{p}_1') f_M(\mathbf{P}_{23}') \\ = [(Kn_A^2/n_M) - 1] f_A(\mathbf{p}_1') f_M(\mathbf{P}_{23}') \end{aligned} \quad (26)$$

Vanishing of the integral then requires the law of mass action to be satisfied, and the equilibrium solution to the Boltzmann equation is thereby determined.

The conserved densities obtained from the equilibrium distribution functions are

$$\rho = m(n_A + 2n_M), \quad \mathbf{g} = \rho \mathbf{u}, \quad \varepsilon = \frac{1}{2}\rho u^2 + \frac{3}{2}n\kappa T - n_M B \quad (27)$$

For a gas at rest, the energy is the same as given in Eq. (4). The equilibrium values of the pressure tensor $t_{ij} = \sum_s \int d^3p (p_i p_j / m_s) f_s$ and energy flux are

$$t_{ij} = n\kappa T \delta_{ij} + \rho u_i u_j, \quad \mathbf{s} = (\frac{1}{2}\rho u^2 + h) \mathbf{u} \quad (28)$$

where $h = \frac{5}{2}n\kappa T - n_M B$ is the enthalpy per unit volume. The first of these identifies the pressure as $p = n\kappa T$. Thus, the thermodynamic relations of Section 2, including the law of mass action, follow from the equilibrium solution to the Boltzmann equation.

6. NORMAL SOLUTION

Reactions are known to have a significant effect on the transport coefficients, particularly the thermal conductivity, of gases. In a dissociating gas the thermal conductivity exhibits a strong peak as a function of temperature, which is correlated with the peak in specific heat and reaches a maximum when the degree of dissociation passes through the region of rapid change. The magnitude of the increase depends on density, but increases greater than an order of magnitude are not unusual. An explanation by Hirschfelder⁽¹⁰⁾ is based on a modification of the equations for a nonreacting mixture to account for the internal energy of the molecules and for the effects of diffusion. The transport coefficients have been evaluated on the basis of Hirschfelder's theory for several dissociating gases.⁽¹¹⁾

The transport coefficients can be obtained by applying the Chapman-Enskog procedure⁽⁹⁾ to the equations obtained in the foregoing. The results are equivalent to Hirschfelder's except that the contribution of the reactive collision operators is included. I sketch the application of the Chapman-Enskog expansion.

Let the distribution functions be written in the form

$$f_s = f_{sL} [1 + \Phi_s] \quad (29)$$

where f_{sL} is the local-equilibrium distribution function and Φ_s is determined so that f_s satisfies the Boltzmann equation. The distribution functions for local equilibrium have the form (25),

$$f_{sL}(\mathbf{p}) = n_{sL} \phi_s(\mathbf{p} - m_s \mathbf{u}) \quad (30)$$

but n_{sL} , T , and \mathbf{u} are functions of position and time. These are determined, as functionals of the actual distribution functions f_s , by the requirement that they depend on the conserved densities ρ , \mathbf{g} , and ε in the same way as in (strict) equilibrium. In view of the form of f_{sL} , this is equivalent to saying that the conserved densities have the same values whether calculated from f_s or f_{sL} , which in turn is equivalent to

$$(\psi, \Phi) = 0 \tag{31}$$

where ψ is any summational invariant and the scalar product is defined by

$$n(\Psi, \Phi) = \sum_s n_{sL} \int d^3p \phi_s \bar{\Psi}_s \Phi_s \tag{32}$$

The densities n_{sL} associated with local equilibrium are definite functions of ρ and T , determined from the law of mass action as in Section 2, and are not necessarily the same as the n_s obtained from the exact distribution functions by Eq. (6). The latter have contributions from Φ which need not be related by mass action, but such contributions do not occur in the order treated here. The source terms v_s vanish when calculated at local equilibrium, but in higher order than we consider they have Φ -dependent contributions. Since to the order under consideration n_{sL} is the same as n_s , I henceforth drop the subscript L .

The local-equilibrium contributions to the energy and momentum fluxes have the same form as given in Eq. (28); the fluxes obtained from the actual distribution functions have additional, irreversible, contributions which will be labeled by a star:

$$t_{ij} = p \delta_{ij} + \rho u_i u_j + t_{ij}^*, \quad s_i = (h + \frac{1}{2} \rho u^2) u_i + t_{ij}^* u_j + s_i^* \tag{33}$$

The irreversible fluxes are given in terms of Φ by

$$\begin{aligned} t_{ij}^* &= \sum_s \int d^3p \frac{1}{m_s} p_i p_j f_{sL} \Phi_s \\ \mathbf{s}^* &= \sum_s \int d^3p \left(\frac{1}{2m_s} p^2 - B_s \right) \frac{1}{m_s} \mathbf{p} f_{sL} \Phi_s \end{aligned} \tag{34}$$

In the first Chapman-Enskog approximation, Φ is neglected on the left-hand side of the Boltzmann equation, and the time derivatives are calculated with the Euler equations (that is, the conservation laws with the fluxes replaced by their local-equilibrium values). One finds after some calculation

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) \ln f_{sL} = \frac{1}{\kappa T^2} \mathbf{S}_s \cdot \nabla T + \frac{1}{\kappa T} T_{sij} D_{ij} \tag{35}$$

where D_{ij} is the abbreviation

$$D_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right)$$

and I have introduced the “subtracted” fluxes:

$$S_s = \left(\frac{1}{2m_s} p^2 - B_s - \frac{hm_s}{\rho} \right) \frac{1}{m_s} \mathbf{p}, \quad T_{sij} = \frac{1}{m_s} \left(p_i p_j - \frac{1}{3} \delta_{ij} p^2 \right)$$

Equation (35) is written for $\mathbf{u} = 0$; the general case can be recovered by the replacement $\mathbf{p} \rightarrow \mathbf{p} - m_s \mathbf{u}$.

On the right-hand side of the Boltzmann equation, terms higher than first order in Φ are neglected in the first Chapman–Enskog approximation, so a linear operator on Φ is obtained. Let the linearized collision operator I be defined by

$$J_s = -n f_{sL} I_s \Phi \tag{36}$$

The contribution to I of elastic scattering has a standard form,⁽⁹⁾ while that from dissociation/recombination is conveniently expressed as the scalar product

$$\begin{aligned} n^2(\Psi, I^X \Phi) &= \frac{1}{3!} n_A n_M \int d^3 p_1 d^3 P_{23} \phi_A(\mathbf{p}_1) \phi_M(\mathbf{P}_{23}) \frac{k_1}{\mu_3} \\ &\times \int dw'_1 d\Omega(\mathbf{k}'_1) d\Omega(\mathbf{q}'_{23}) \\ &\times \sigma_D(\mathbf{k}_1 \rightarrow \mathbf{k}'_1, \mathbf{q}'_{23}) [\Psi]_X [\Phi]_X \end{aligned}$$

where the bracket symbol is defined by

$$[\Psi]_X = \Psi_A(\mathbf{p}_1) + \Psi_M(\mathbf{P}_{23}) - \Psi_A(\mathbf{p}'_1) - \Psi_A(\mathbf{p}'_2) - \Psi_A(\mathbf{p}'_3)$$

This shows I^X to be symmetric and nonnegative:

$$(\Psi, I^X \Phi) = (I^X \Psi, \Phi), \quad (\Phi, I^X \Phi) \geq 0$$

[The notation used here is related to that of Chapman and Cowling⁽⁹⁾ by $(\Psi, I^X \Phi) = (n_A n_M / n^2) \{ \Psi, \Phi \}$.] Then Eqs. (35) and (36) yield the integral equation for Φ

$$I\Phi = -\frac{1}{n\kappa T^2} \mathbf{S} \cdot \nabla T - \frac{1}{n\kappa T} T_{ij} D_{ij} \tag{37}$$

Solvability of Eq. (37) requires the right-hand side to be orthogonal to any summational invariant, and it is straightforward to confirm that $(\psi, \mathbf{S}) = (\psi, \mathbf{T}) = 0$. The solution for Φ can be expressed in the form

$$\Phi = -\frac{1}{\eta\kappa T^2} \mathcal{S} \cdot \nabla T - \frac{1}{\eta\kappa T} \mathcal{T}_{ij} D_{ij} \quad (38)$$

where \mathcal{S} and \mathcal{T} satisfy

$$I\mathcal{S} = \mathbf{S}, \quad I\mathcal{T} = \mathbf{T} \quad (39)$$

In view of (31), the solutions to these equations should satisfy $(\psi, \mathcal{S}) = (\psi, \mathcal{T}) = 0$.

By use of the conditions (31), the irreversible contribution to the pressure tensor can be written $t_{ij}^* = n(T_{ij}, \Phi)$. This shows that $t_{ii}^* = 0$, so the gas has no bulk viscosity. Substituting the expression (38) for Φ , we get

$$t_{ij}^* = -2\eta(D_{ij} - \frac{1}{3}\delta_{ij}\nabla \cdot \mathbf{u})$$

where the viscosity η is given by

$$\eta = \frac{1}{10\kappa T} (T_{ij}, \mathcal{T}_{ij})$$

Except for the reactive contributions to I , the viscosity is the same as for a nonreacting mixture.

The heat flux can be put in the form $\mathbf{s}^* = n(\mathbf{S}, \Phi)$, which then reduces to Fourier's law, $\mathbf{s}^* = -\lambda \nabla T$, where the thermal conductivity is given by

$$\lambda = \frac{1}{3\kappa T^2} (S_i, \mathcal{S}_i)$$

In the case of a nonreacting mixture, the right-hand side of Eq. (37) contains terms depending on the concentration gradients. These give rise to diffusion, and to a term in \mathbf{s}^* which depends on the velocity of diffusion. Reactions cause the concentration gradients to be fixed by the temperature gradient, so diffusion does not occur as an independent process. Nevertheless there is a contribution to the thermal conductivity, as calculated by Hirschfelder, which is due to energy transport associated with the relative velocity of the two species. Thus, the result just obtained for thermal conductivity differs from Hirschfelder's only by the reactive contribution to I . Generally, reactive collision rates are small in comparison to those for scattering, so the neglect of I^K should in most cases be a good approximation.

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