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Kinetic Equations for a Quantum Gas with Bound States

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The kinetic theory for dense gases is modified to take into account the existence of bound states. A molecular chaos condition is used which corresponds to the division of the two- and three-particle Hilbert spaces into scattering and bound-state subspaces. A kinetic stage results from a long-time limit which converges to yield time-independent functionals for the two- and three-particle density matrices, as functionals of the density matrices for atoms and molecules. Coupled kinetic equations are obtained which describe the gas as a reacting mixture of atoms and diatomic molecules. These include the effects of scattering and rearrangement collisions between the atom and the molecule, and of molecular formation and dissociation.

KEY WORDS: Kinetic theory; dense gases; bound states; polyatomic gases; reactions.

1. INTRODUCTION

The standard approach to the derivation of the kinetic equation for a dense monatomic gas contains two elements.[2] One is the BBGKY hierarchy for the reduced distribution functions F^s of order s, $s = 1, 2, 3 \ldots$. The second element is a functional assumption due to Bogoliubov, according to which the higher-order distribution functions are determined as time-independent functionals of F^1 (that is, they depend on time only through their dependence on F^1). When these functionals are substituted into the hierarchy, the result is a closed equation for F^1, which is the kinetic equation. The functional relations can be worked out explicitly only as series in powers of the density, and so the kinetic equation is also obtained as such a series. To lowest order in the density this equation is the Boltzmann equation, with a

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[2] For a recent review of the theory of dense gases see Ref. 1.

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modification due to the difference in position of the two colliding particles. Corrections to the (modified) Boltzmann equation are then obtained by continuing the procedure to higher order in the density.

Actually the straightforward density expansion must be modified because of a divergence which occurs in the third order; the time-independent functional for F^2 does not exist for functions F^1 of interest because of the large volume of phase space available to a four-body collision. For repulsive forces the nature of this divergence and methods to deal with it are by now well understood.⁽¹⁾ Here we will only consider the second order, and so our calculations are not affected by the divergence.

If the forces are attractive, particularly if the particles can form bound states, it is necessary to modify the procedure as outlined above. The necessary modifications will be discussed in this paper, with the purpose of developing a procedure applicable to polyatomic gases. The analysis will be quantum mechanical, so the F^s are actually density matrices rather than distribution functions.

In a polyatomic gas the density matrices for the atoms and molecules of various kinds should be independent, that is, it should be possible to assign initial values to them independently. Their time dependence would then be governed by a coupled set of kinetic equations. Thus the assumption that all density matrices are determined by F^1 is clearly too restrictive. Instead the higher-order F^s should depend on a basic set consisting of density matrices for the various chemical species which occur. This basic set itself should be constructed from the F^s which appear in the hierarchy.

For repulsive forces, the time-independent functionals are obtained by first imposing the molecular chaos condition that F^s be a product of F^1's at an initial time t_0. The solution to the hierarchy yields F^s at a later time t, which can be expressed in terms of F^1 at time t. The initial time t_0 is then moved back into the infinite past. When bound states are present, this procedure breaks down because the long-time limit does not exist. Here the molecular chaos condition is modified in such a way that the resulting long-time limit is convergent. For F^2, only its part acting in the subspace of free particles is written as a product of F^1's, and the remainder is the density matrix for bound pairs (including bound-to-free mixing). Similarly F^3 is projected onto subspaces corresponding to the channels in the three-body problem, and each part is written as a product of density matrices for the atoms and/or molecules present in the channel; a remaining part is due to channel mixing and three-body bound states. The long-time limit leading to the time-independent functionals for F^2 and F^3 is then convergent. Density matrices f^1 and f^2 for atoms and diatomic molecules are defined in terms of the F^s, and the time-independent functionals yield coupled kinetic equations for f^1 and f^2. These contain collision operators which include (in addition to the lowest-order binary collision part) contributions from the different three-body channels, namely, three-particle scattering, collision-induced dissociation and formation of a diatomic molecule, and scattering (including rearrangement collisions) between an atom and a diatomic molecule.

In other work on polyatomic gases, a modified Boltzmann equation which includes inelastic collisions was discussed by Wang-Chang, Uhlenbeck, and de Boer,(2) who assumed the distribution function to be a function of the internal molecular quantum numbers. Their theory was generalized by Waldmann(3) and Snider,(4) who took the distribution function to be a density matrix in the internal molecular states; the resulting kinetic equation is commonly called the Waldmann–Snider equation.[3] The Waldmann–Snider equation was derived by assuming the density matrix to be diagonal in the molecular energies, but this restriction has been removed by Snider and Sanctuary.(6) Reactions have been considered by Lowry and Snider(7) and by Olmsted and Curtiss.(8) In classical mechanics the effect of attractive forces has been discussed by several authors, including Kawasaki and Oppenheim,(9) Kim and Ross,(10) Davis, Rice, and Sengers,(11) Dufty and Gubbins,(12) and Marchetti and Dufty.(13) The classical Boltzmann equation for a polyatomic gas has been discussed by a number of authors; a recent paper by Curtiss(14) contains references to earlier work.

Previous discussions of polyatomic gases have all involved approximations of one kind or another. Usually the density expansion is not carried out consistently, but instead some terms occurring at a given order in the density are neglected while others are retained. Frequently special assumptions regarding the form of the molecular density matrix are introduced, such as the diagonality assumptions in the work leading to the Waldmann–Snider equation. The approach given below follows the standard treatment(1) of monatomic gases (including that of Resibois(15) for the quantum mechanical case) by developing the density expansion consistently. Furthermore no special assumptions regarding the form of the molecular density matrix are introduced.

The basic units which comprise the system will be called particles, and a particle which is not bound into a molecule will be called an atom.

2. HIERARCHY AND FUNCTIONAL ASSUMPTION

Consider a quantum mechanical system of N identical particles obeying Boltzmann statistics and interacting by two-body forces. The reduced

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[3] The Waldmann–Snider equation has been reviewed in Ref. 5.

density matrix F^s for a subset of s particles, say, particles numbered $1, \ldots, s$, is defined in terms of the N-particle density matrix F^N by

$$F^s(1, \ldots, s) = V^s \mathrm{Tr}(s+1, \ldots, N) F^N(1, \ldots, N) \tag{1}$$

Here V is the volume and Tr denotes the trace, with the particles traced over being denoted by the numbers in parentheses. The time dependence of F^N is determined by

$$\partial F^N/\partial t + \{F^N, H_N\} = 0 \tag{2}$$

where H_N is the Hamiltonian for the N-particle system. Here curly brackets are defined by

$$\{\ ,\ \} = (1/i\hbar)[\ ,\ ] \tag{3}$$

where square brackets denote the commutator, and $\hbar = h/2\pi$ where h is Planck's constant. For brevity in the following we will use units such that $\hbar = 1$.

Equation (2) implies the BBGKY hierarchy of equations for the time dependence of the F^s. In the thermodynamic limit ($V \to \infty$ with $n = N/V$ held fixed) the hierarchy is[4]

$$\begin{aligned} \partial F^1/\partial t + \{F^1, H_1\} &= n\mathrm{Tr}(2)\{v_{12}, F^2\} \\ \partial F^2/\partial t + \{F^2, H_2\} &= n\mathrm{Tr}(3)\{v^3, F^3\} \\ \partial F^3/\partial t + \{F^3, H_3\} &= n\mathrm{Tr}(4)\{v^4, F^4\}, \text{ etc.} \end{aligned} \tag{4}$$

Here H_s is the Hamiltonian for a set of s particles,

$$H_s = H_0 + \sum_\alpha v_\alpha \tag{5}$$

where H_0 denotes the Hamiltonian for free motion; the number of particles in H_0 will not be indicated explicitly as it can usually be determined from context. The potential energy for a pair α has been denoted by v_α, and the sum extends over all pairs which can be formed in the set of s particles. The particles to which F^s refer have not been indicated explicitly; F^1 refers to particle number 1, F^2 to particles 1 and 2, etc. In addition we have introduced the abbreviations

$$v^3 = v_{13} + v_{23}, \qquad v^4 = v_{14} + v_{24} + v_{34} \tag{6}$$

The initial-value problem for the hierarchy can be solved by an expansion in powers of the density n. To the order needed here, the

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[4] The hierarchy and functional assumption in quantum mechanics have been discussed recently by Boercker and Dufty (Ref. 16).

solution is$^{(17)}$

$$\begin{aligned}
F^1(1,t) &= S_1(1,t')F^1(1,t_0) \\
&\quad + n\,\mathrm{Tr}(2)\left[S_2(1,2,t') - S_0(1,2,t')\right]F^2(1,2,t_0) + \cdots \\
F^2(1,2,t) &= S_2(1,2,t')F^2(1,2,t_0) + n\,\mathrm{Tr}(3) \\
&\quad \times\left[S_3(1,2,3,t') - S_{(12)}(1,2,3,t')\right]F^3(1,2,3,t_0) + \cdots \\
F^3(1,2,3,t) &= S_3(1,2,3,t')F^3(1,2,3,t_0) + \cdots
\end{aligned} \tag{7}$$

Here $t' = t - t_0$ and S_s denotes a streaming operator defined by

$$S_s(t)F^s = U_s(t)F^sU_s^*(t), \qquad U_s(t) = e^{-iH_st} \tag{8}$$

where the asterisk denotes the adjoint (on the s-particle Hilbert space). In addition S_0 is the free streaming operator,

$$S_0(t)F^s = U_0(t)F^sU_0^*(t), \qquad U_0(t) = e^{-iH_0t} \tag{9}$$

while $S_{(\alpha)}$ is the streaming operator for a system of three particles in which only the pair α interacts,

$$S_{(\alpha)}(t)F^3 = U_{(\alpha)}(t)F^3U_{(\alpha)}^*(t), \qquad U_{(\alpha)}(t) = e^{-iH_{(\alpha)}t} \tag{10}$$

Here $H_{(\alpha)}$ is given by

$$H_{(\alpha)} = H_0 + v_\alpha \tag{11}$$

The usual derivation of the Boltzmann equation proceeds as follows. At an initial time t_0, suppose F^2 has the form corresponding to molecular chaos,

$$F^2(1,2,t_0) = F^1(1,t_0)F^1(2,t_0) \tag{12}$$

Then at a later time t, F^2 is, to lowest order in the density,

$$F^2(1,2,t) = U_2(1,2,t')F^1(1,t_0)F^1(2,t_0)U_2^*(1,2,t') \tag{13}$$

From the first of Eqs. (7) we obtain to lowest order in n

$$F^1(1,t_0)F^1(2,t_0) = U_0^*(1,2,t')F^1(1,t)F^1(2,t)U_0(1,2,t') \tag{14}$$

so

$$F^2(1,2,t) = U_2(1,2,t')U_0^*(1,2,t')F^1(1,t)F^1(2,t)U_0(1,2,t')U_2^*(1,2,t') \tag{15}$$

If the limit for $t' \to \infty$ exists, it yields F^2 as a time-independent functional of F^1,

$$F^2(1,2) = \lim_{t'\to\infty} U_2(1,2,t')U_0^*(1,2,t')F^1(1)F^1(2)U_0(1,2,t')U_2^*(1,2,t') \tag{16}$$

For a wide class of potentials, it is known that the limit

$$\omega = \lim_{t\to\infty} U_2(t)U_0^*(t) \tag{17}$$

exists as a strong limit; ω is known as the wave operator.[5] (Actually there are two wave operators; the one of interest here is the one usually denoted by a subscript +.) It follows from the unitarity of U_2 and U_0 that ω is isometric:

$$\omega^*\omega = 1 \tag{18}$$

If the potential does not support bound states, then

$$\omega^* = \lim_{t\to\infty} U_0(t)U_2^*(t) \tag{19}$$

where the limit on the right also exists as a strong limit, and we have

$$\omega\omega^* = 1 \tag{20}$$

In this case Eq. (16) can be written as

$$F^2(1,2) = \omega_{12}F^1(1)F^1(2)\omega_{12}^* \tag{21}$$

where the subscripts on ω_{12} denote the particles on which it acts. (Here we have used the fact that for strong limits, the limit of a product equals the product of the limits provided the latter exist.) Substitution of this expression into the first equation of the hierarchy yields

$$\partial F^1/\partial t + \{F^1,H_1\} = nJ_0[F^1] \tag{22}$$

where

$$J_0[F^1] = \mathrm{Tr}(2)\{v_{12},\omega_{12}F^1(1)F^1(2)\omega_{12}^*\} \tag{23}$$

For the spatially homogeneous case, J_0 can be reduced to the Boltzmann collision operator. If F^1 is not spatially homogeneous, then J_0 is a modified Boltzmann collision operator which takes into account the difference in position of the two colliding particles.

The manipulations leading to Eq. (22) can be extended to higher order in a straightforward manner. The time-independent functional (21) becomes a series in powers of n, and the first hierarchy equation yields

$$\partial F^1/\partial t + \{F^1,H_1\} = nJ[F^1] \tag{24}$$

where

$$J = J_0 + nJ_1 + \cdots \tag{25}$$

However, at the third order it is found that the time-independent functional

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[5] For a derivation of the basic properties of wave operators see Ref. 18.

actually does not exist (for F^1 of interest) because of the large extent in space and time of four-body collisions. Hence, as mentioned in the Introduction, the straightforward density expansion must be modified. Here we will be concerned only with the order corresponding to J_1, and so the divergence has no effect on our discussion.

Now suppose there are two-body bound states. Then Eq. (20) is replaced by

$$\omega\omega^* = 1 - P \tag{26}$$

where P is the projection onto the subspace of bound states. (For simplicity we will assume there to be only one bound state, so P is a one-dimensional projection.) It follows from Eqs. (18) and (26) that

$$\omega^* P = P\omega = 0 \tag{27}$$

The limit in Eq. (19) does not exist except on the range of ω, where

$$\lim_{t\to\infty} U_0(t)U_2^*(t)\omega = 1 \tag{28}$$

However, F^2 is not restricted to the subspace orthogonal to P, and so we cannot take the limit in Eq. (16) to obtain Eq. (21).

One symptom of nonexistence of the long-time limit is the failure of the result (21) in equilibrium. In equilibrium F^1 is, to lowest order in the density,

$$F^1 = V_0 e^{-\beta H_1} \tag{29}$$

Here $\beta = 1/kT$, where k is Boltzmann's constant and T the Kelvin temperature, while V_0 is the de Boer parameter,

$$V_0 = h^3[2\pi mkT]^{-3/2} \tag{30}$$

where m is the mass of a particle. The intertwining relation for ω is

$$\omega H_0 = H_2\omega \tag{31}$$

Equation (21) then yields for F^2 (to lowest order)

$$F^2 = V_0^2 e^{-\beta H_2}(1 - P) \tag{32}$$

whereas the correct equilibrium formula for F^2 (to lowest order) is

$$F^2 = V_0^2 e^{-\beta H_2} \tag{33}$$

Thus the result (21) projects out the bound-state part of F^2.

Curiously the usual Bogoliubov functional assumption [that is, Eq. (21) extended to higher order in the density, together with similar formulas for the higher-order F^s] still yields a formal solution to the hierarchy even when bound states exist. This can be verified by substituting it into the hierarchy and using the intertwining relations for the wave operators.

However, this solution is likely to be unstable since it does not arise as a long-time limit.

3. FUNCTIONAL ASSUMPTION WITH BOUND STATES

It is readily shown that $\omega\omega^*$ is a projection,

$$(\omega\omega^*)^2 = \omega\omega^* \tag{34}$$

indeed it is the projection onto scattering states (i.e., states which are orthogonal to the bound states). Hence we may decompose any F^2 into a part which acts entirely in the subspace of scattering states plus a remainder by

$$F^2 = \omega\omega^* F^2 \omega\omega^* + D \tag{35}$$

Then D can be obtained from F^2 by

$$D = \tilde{P} F^2 \tag{36}$$

where $\tilde{P}$ is a projection on two-particle density matrices defined by

$$\tilde{P} F^2 = F^2 - \omega\omega^* F^2 \omega\omega^* = F^2 - (1 - P) F^2 (1 - P) \tag{37}$$

Clearly D is to be interpreted as the density matrix for diatomic molecules (or actually the lowest-order approximation to the latter). Note, however, that it need not act entirely in the subspace of bound states, that is, it is not necessarily the case that $D = PDP$. However,

$$(1 - P) D (1 - P) = 0 \tag{38}$$

We now impose the molecular chaos condition (12) only to the projection of F^2 on the scattering subspace. Thus we assume at time t_0

$$F^2(1,2,t_0) = \omega_{12}\omega^*_{12} F^1(1,t_0) F^1(2,t_0) \omega_{12}\omega^*_{12} + D(1,2,t_0) \tag{39}$$

To lowest order in the density, F^2 satisfies

$$\partial F^2/\partial t + \{F^2, H_2\} = 0 \tag{40}$$

It follows from Eq. (36) that D satisfies the same equation,

$$\partial D/\partial t + \{D, H_2\} = 0 \tag{41}$$

Hence

$$D(t) = U_2(t') D(t_0) U^*_2(t') \tag{42}$$

where again $t' = t - t_0$. Equation (15) is therefore replaced by

$$\begin{aligned} F^2(1,2,t) = {} & \omega_{12}\omega^*_{12} U_2(t') U^*_0(t') F^1(1,t) F^1(2,t) U_0(t') U^*_2(t') \omega_{12}\omega^*_{12} \\ & + D(1,2,t) \end{aligned} \tag{43}$$

To obtain this form we have used the fact that H_2 commutes with $\omega\omega^*$. We can now take the limit $t' \to \infty$, and the result is

$$F^2(1,2) = \omega_{12}F^1(1)F^1(2)\omega_{12}^* + D(1,2) \tag{44}$$

Substitution of Eq. (44) into the first equation of the hierarchy yields

$$\partial F^1/\partial t + \{F^1, H_1\} = n\,\mathrm{Tr}(2)\{v_{12}, \omega_{12}F^1(1)F^1(2)\omega_{12}^* + D\} \tag{45}$$

Equation (41) enables us to rewrite this in a more convenient form,

$$\partial f^1/\partial t + \{f^1, H_1\} = nJ_0[f^1] \tag{46}$$

where

$$f^1(1) = F^1(1) - n\,\mathrm{Tr}(2)D(1,2) \tag{47}$$

On the right-hand side of Eq. (46) the difference between F^1 and f^1 has been neglected since it is higher order in the density.

Clearly f^1 is to be interpreted as the density matrix for atoms; the second term in Eq. (47) subtracts from F^1 the contribution of particles which are bound into molecules. Equation (46) is then the (modified) Boltzmann equation for atoms, while D satisfies the collisionless Eq. (41).

The introduction of D provides the freedom needed to satisfy the equilibrium relation between F^1 and F^2; in equilibrium we have

$$D = V_0^2 e^{-\beta H_2} P \tag{48}$$

In general f^1 and D are to be treated as independent quantities.

4. THREE-PARTICLE TERMS

The existence of two-body bound states splits the three-body problem into channels.[6] There are three channels corresponding to the scattering (and reactions) of a two-body bound pair (i.e., a diatomic molecule) with the third particle, and a fourth channel in which the three particles are initially unbound. The corresponding wave operators are defined by

$$\begin{aligned} \Omega_\alpha &= \lim U_3(t)\,U_{(\alpha)}^*(t)P_\alpha \\ \Omega_0 &= \lim U_3(t)\,U_0^*(t) \end{aligned} \tag{49}$$

Here P_α is the projection onto the bound state for pair α, but considered now as an operator on the three-particle Hilbert space.

The wave operators satisfy

$$\Omega_\alpha^*\Omega_\beta = \delta_{\alpha\beta}P_\alpha, \qquad \Omega_0^*\Omega_\alpha = 0, \qquad \Omega_0^*\Omega_0 = 1 \tag{50}$$

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[6] See Ref. 19 for some useful references to the three-body problem. See also the book by Reed and Simon cited in Ref. 18.

It follows that $\Omega_0\Omega_0^*$ and $\Omega_\alpha\Omega_\alpha^*$ are orthogonal projections; they project onto the channel subspaces. In addition they satisfy

$$\Omega_0\Omega_0^* + \sum_\alpha \Omega_\alpha\Omega_\alpha^* = 1 - Q \tag{51}$$

where Q is the projection onto three-body bound states. It follows from the above equations that

$$\Omega_0^* Q = Q\Omega_0 = \Omega_\alpha^* Q = Q\Omega_\alpha = 0 \tag{52}$$

The intertwining relations are

$$H_3\Omega_\alpha = \Omega_\alpha H_{(\alpha)}, \qquad H_3\Omega_0 = \Omega_0 H_0 \tag{53}$$

As a consequence of the intertwining relations, H_3 commutes with $\Omega_0\Omega_0^*$ and $\Omega_\alpha\Omega_\alpha^*$.

If the adjoint of the product of operators in Eq. (49) is taken, the limits do not exist on the full Hilbert space. However, they do exist on the ranges of the corresponding wave operators, that is,

$$\begin{gathered} \lim P_\alpha U_{(\alpha)}(t)\, U_3^*(t)\Omega_\alpha = P_\alpha \\ \lim U_0(t)\, U_3^*(t)\Omega_0 = 1 \end{gathered} \tag{54}$$

exist as strong limits.

In analogy to Eq. (35) we may write any F^3 as a sum of parts which act in the channel subspaces plus a remainder,

$$F^3 = \Omega_0\Omega_0^* F^3 \Omega_0\Omega_0^* + \sum_\alpha \Omega_\alpha\Omega_\alpha^* F^3 \Omega_\alpha\Omega_\alpha^* + T \tag{55}$$

As the molecular chaos condition we require that at time t_0 the part of F^3 acting in a channel subspace be a product of the density matrices for the atoms and molecules in the channel,

$$\begin{aligned} F^3(1,2,3,t_0) = {} & \Omega_0\Omega_0^* G(1,2,3,t_0)\Omega_0\Omega_0^* \\ & + \sum_\alpha \Omega_\alpha\Omega_\alpha^* F^1(\alpha,t_0) D(\alpha,t_0)\Omega_\alpha\Omega_\alpha^* + T(1,2,3,t_0) \end{aligned} \tag{56}$$

Here for brevity α has been used to denote both a particle and a pair so for example $\alpha = 1,2$ (or $\alpha = 3$) means pair $1,2$ as well as particle number 3. In addition G is the abbreviation

$$G(1,2,3) = F^1(1)F^1(2)F^1(3) \tag{57}$$

It follows from Eq. (55) that T satisfies

$$\Omega_0^* T\Omega_0 = \Omega_\alpha^* T\Omega_\alpha = 0 \tag{58}$$

We will interpret T as the density matrix for triatomic molecules. However, it is possible that T contains terms which mix channels, since it does not follow from Eq. (55) that, e.g., $\Omega_0^* T \Omega_\alpha$ must vanish. Thus it may be necessary to retain T even in the absence of three-body bound states.

To lowest order in the density F^3 satisfies

$$\partial F^3/\partial t + \{F^3, H_3\} = 0 \tag{59}$$

and it follows that T satisfies the same equation,

$$\partial T/\partial t + \{T, H_3\} = 0 \tag{60}$$

Hence

$$F^3(t) = U_3(t')F^3(t_0)U_3^*(t'), \qquad T(t) = U_3(t')T(t_0)U_3^*(t') \tag{61}$$

In addition we have

$$\begin{aligned} G(t_0) &= U_0^*(t')G(t)U_0(t') \\ F^1(\alpha, t_0)D(\alpha, t_0) &= U_{(\alpha)}^*(t')F^1(\alpha, t)D(\alpha, t)\,U_{(\alpha)}(t') \end{aligned} \tag{62}$$

The molecular chaos condition (56) yields

$$\begin{aligned} F^3(1,2,3,t) = {} & \Omega_0\Omega_0^*\, U_3(t')U_0^*(t')G(1,2,3,t)U_0(t')U_3^*(t')\Omega_0\Omega_0^* \\ & + \sum_\alpha \Omega_\alpha\Omega_\alpha^*\, U_3(t')\,U_{(\alpha)}^*(t')F^1(\alpha,t)D(\alpha,t) \\ & \times U_{(\alpha)}(t')U_3^*(t')\Omega_\alpha\Omega_\alpha^* + T(1,2,3,t) \end{aligned} \tag{63}$$

Taking the limit $t' \to \infty$, we obtain the time-independent functional for F^3,

$$F^3(1,2,3) = \Omega_0 G(1,2,3)\Omega_0^* + \sum_\alpha \Omega_\alpha F^1(\alpha)D(\alpha)\Omega_\alpha^* + T(1,2,3) \tag{64}$$

To confirm the validity of Eq. (64) in equilibrium, we insert Eqs. (29) and (48). Using Eq. (51), we get

$$F^3 = V_0^3 e^{-\beta H_3}(1 - Q) + T \tag{65}$$

The equilibrium formula for F^3 (to lowest order in the density) is

$$F^3 = V_0^3 e^{-\beta H_3} \tag{66}$$

so in equilibrium T has the expected form

$$T = V_0^3 e^{-\beta H_3} Q \tag{67}$$

The kinetic equation for D is obtained by substituting Eq. (64) into the second equation of the hierarchy and using Eq. (36) for D. The result is

$$\partial D/\partial t + \{D, H_2\} = n\,\mathrm{Tr}(3)\tilde{P}\left\{v^3, \Omega_0 G\Omega_0^* + \sum_\alpha \Omega_\alpha F^1(\alpha)D(\alpha)\Omega_\alpha^* + T\right\} \tag{68}$$

Using Eq. (60) we rewrite this as

$$\partial f^2/\partial t + \{f^2, H_2\} = nR[f^1] + nS[f^1, f^2] \tag{69}$$

where

$$f^2 = D - n\,\mathrm{Tr}(3)\tilde{P}T \tag{70}$$

and R, S are collision operators defined by

$$\begin{aligned} R[f^1] &= \mathrm{Tr}(3)\tilde{P}\{v^3, \Omega_0 G \Omega_0^*\} \\ S[f^1, f^2] &= \mathrm{Tr}(3)\tilde{P}\Big\{v^3, \sum_\alpha \Omega_\alpha f^1(\alpha) f^2(\alpha) \Omega_\alpha^*\Big\} \end{aligned} \tag{71}$$

Here G can be written with f^1 instead of F^1,

$$G(1,2,3) = f^1(1) f^1(2) f^1(3) \tag{72}$$

since the difference is higher order in the density. In the above expression for S the difference between f^2 and D, and between f^1 and F^1, has been neglected for the same reason. The collision operator R gives the rate of change of the density matrix for diatomic molecules due to formation and breakup, while S describes scattering (including rearrangement collisions) between an atom and a diatomic molecule. Clearly f^2 is the density matrix for diatomic molecules, and differs from D by a correction for pairs which are bound into triatomic molecules.

To include atom–molecule collisions in the kinetic equation for f^1 it is necessary to extend the functional assumption (44) for F^2 to the next order in the density. We use the same molecular chaos condition (39) but include density-dependent corrections in the equations for the time dependence of F^1 and F^2. A calculation which is summarized in the Appendix then yields the time-independent functional for F^2,

$$\begin{aligned} F^2(1,2) = {} & \omega_{12} f^1(1) f^1(2) \omega_{12}^* + f^2(1,2) + n\,\mathrm{Tr}(3) T(1,2,3) + n\,\mathrm{Tr}(3)(1 - \tilde{P}_{12}) \\ & \times \Big\{\Omega_0 G(1,2,3)\Omega_0^* \\ & \quad - \omega_{12}\big[\omega_{13} G(1,2,3)\omega_{13}^* + \omega_{23} G(1,2,3)\omega_{23}^* - G(1,2,3)\big]\omega_{12}^* \\ & \quad + \sum_\alpha \Omega_\alpha F^1(\alpha) D(\alpha) \Omega_\alpha^*\Big\} \end{aligned} \tag{73}$$

This is to be inserted into the first equation of the hierarchy, and we get

$$\begin{aligned} \partial F^1/\partial t + \{F^1, H_1\} = {} & nJ_0[f^1] + n^2 J_1[f^1] \\ & + n^2\,\mathrm{Tr}(2,3)\Big\{v_{12}, (1 - \tilde{P}_{12}) \sum_\alpha \Omega_\alpha F^1(\alpha) D(\alpha) \Omega_\alpha^*\Big\} \\ & + n\,\mathrm{Tr}(2)\{v_{12}, D + n(1 - \tilde{P}_{12})\mathrm{Tr}(3) T\} \end{aligned} \tag{74}$$

Here J_1 is defined by

$$J_1[f^1] = \mathrm{Tr}(2,3)\{v_{12}, \omega_{12}[\omega_{12}^* \Omega_0 G \Omega_0^* \omega_{12} - \omega_{13} G \omega_{13}^* - \omega_{23} G \omega_{23}^* + G]\omega_{12}^*\} \tag{75}$$

In the last term of Eq. (74) we use Eq. (70); then Eqs. (60) and (69) yield

$$\begin{aligned}
&\mathrm{Tr}(2)\{v_{12}, D + n(1 - \tilde{P}_{12})\mathrm{Tr}(3)T\} \\
&\quad = \mathrm{Tr}(2)\{v_{12}, f^2 + n\,\mathrm{Tr}(3)T\} \\
&\quad = \frac{\partial}{\partial t}\left[\mathrm{Tr}(2)f^2 + \tfrac{1}{2}n\,\mathrm{Tr}(2,3)T\right] + \left\{\mathrm{Tr}(2)f^2 + \tfrac{1}{2}n\,\mathrm{Tr}(2,3)T, H_1\right\} \\
&\quad\quad - n^2\mathrm{Tr}(2)\{R[f^1] + S[f^1, f^2]\}
\end{aligned} \tag{76}$$

We extend the definition (47) of f^1 to

$$\begin{aligned}
f^1 &= F^1 - n\,\mathrm{Tr}(2)D - \tfrac{1}{2}n^2\,\mathrm{Tr}(2,3)T \\
&= F^1 - n\,\mathrm{Tr}(2)f^2 + \tfrac{1}{2}n^2\,\mathrm{Tr}(2,3)T
\end{aligned} \tag{77}$$

Then Eq. (74) becomes the desired kinetic equation for f^1,

$$\partial f^1/\partial t + \{f^1, H_1\} = nJ_0[f^1] + n^2 J_1[f^1] + n^2 B[f^1] + n^2 C[f^1, f^2] \tag{78}$$

Here B and C are defined by

$$\begin{aligned}
B[f^1] &= -\mathrm{Tr}(2)R[f^1] \\
C[f^1, f^2] &= \mathrm{Tr}(2,3)\left\{v_{12}, (1 - \tilde{P}_{12})\sum_\alpha \Omega_\alpha f^1(\alpha) f^2(\alpha)\Omega_\alpha^*\right\} \\
&\quad - \mathrm{Tr}(2)S[f^1, f^2]
\end{aligned} \tag{79}$$

The coupled kinetic equations (69) and (78) describe the gas as a reacting mixture of atoms and diatomic molecules. In the absence of bound states, $\omega\omega^* = 1$ and J_1 reduces to the usual triple-collision operator of dense-gas theory. The explicit dependence of the collision operators on the various scattering and reaction amplitudes will not be worked out here; this has been done elsewhere(20) for the related operator which occurs in the density expansion of a Green–Kubo formula. However, it may be noted that

$$U_{3\alpha} = v^3 \Omega_\alpha \tag{80}$$

is equivalent to the Lovelace(21) expression for the transition operator between channels 1,2 and α. Hence in Eq. (71) for S the term with $\alpha = 1,2$ corresponds to scattering while the terms with $\alpha = 1,3$ and $\alpha = 2,3$ describe rearrangement collisions. Other terms in the various collision operators can be characterized in a similar way.

5. DISCUSSION

The procedure described above follows the lines of the density expansion for monatomic gases, with a modification of the molecular chaos condition to accomodate the existence of bound states. The projection of F^2 on the subspace for free particles is expressed in the usual product form, while the projections of F^3 on the three-body channel subspaces are written as products of the density matrices for the atoms and/or molecules in the channel. The long-time limiting process then converges to yield F^2 and F^3 as time-independent functionals of the density matrices for atoms and molecules. This results in coupled kinetic equations which describe the gas as a reacting mixture.

The third order, which has not been worked out here, would provide a description of the molecular processes which can occur in a system of four particles, including collisions between two diatomic molecules, and between an atom and a triatomic molecule. The divergence mentioned in the Introduction occurs in this order, and it is not clear to what extent the bound-state contributions are affected. Undoubtedly scattering, say, of two diatomic molecules, will give finite contributions since the available phase space is essentially that for two particles. However, a collision with four particles in the initial or final state (such as breakup of two diatomic molecules) may result in a divergence.

This derivation of kinetic equations from the density expansion has several advantages over previous work on polyatomic gases. All terms occurring at a given order in the density are retained in a consistent way. In addition, the various scattering channels are explicitly taken into account, so that all scattering and reaction processes which occur are treated together in a unified manner. Furthermore, it has not been necessary to impose any special restrictions on the form of the molecular density matrix. Diagonality assumptions in particular have been avoided; this is desirable since the fluxes of energy and momentum (and, in a mixture, of particle number) are in fact not diagonal (indeed they even have elements which mix free and bound states), and it follows that a nonequilibrium process will induce nondiagonal elements in the density matrix.

APPENDIX

The molecular chaos assumption (39) for F^2 is to be substituted into Eq. (7) for $F^1(t)$ and the resulting equation solved for $F^1(t_0)$. This yields

$$\begin{aligned} F^1(t_0) = {} & S_1^*(1)F^1(t) - n\,\mathrm{Tr}(2) \\ & \times \left\{ S_0^*(1,2)\left[S_2(1,2) - S_0(1,2)\right](1 - \tilde{P}_{12})S_0^*(1,2)F^1(1,t)F^1(2,t) \right. \\ & \left. + \left[S_0^*(1,2) - S_2^*(1,2)\right]D(1,2,t)\right\} + \cdots \qquad (81) \end{aligned}$$

(Here the S's are evaluated at time t'.) This and Eq. (56) is to be inserted into Eq. (7) for $F^2(t)$. The result is a long expression in which the leading terms are those given by Eq. (44). For some of the terms in this expression the limit $t \to \infty$ can be taken with the aid of the formulas already given for the wave operators. Other terms depend on operators defined by

$$\Omega'_\alpha = \lim U_3(t) U^*_{(\alpha)}(t) \tag{82}$$

for which existence of the (strong) limit has been proven by Hack.$^{(22)}$ For the adjoint of the above product, the limit exists only on the range of Ω'_α, and

$$\lim U_{(\alpha)}(t) U^*_3(t) \Omega'_\alpha = 1 \tag{83}$$

These operators satisfy

$$\begin{aligned} \Omega'_\alpha P_\alpha &= \Omega_\alpha \\ \Omega'_\alpha &= \Omega_\alpha + \Omega_0 \omega^*_\alpha \\ \Omega'^*_\alpha \Omega'_\alpha &= \delta_{\alpha p} P_\alpha + \omega_\alpha \omega^*_\beta \end{aligned} \tag{84}$$

It is straightforward to reduce the limiting form for F^2 to the expression given in the text, plus a term X which is given by

$$\begin{aligned} X = \lim\Big[& n \operatorname{Tr}(3)(1 - \tilde{P}_{12}) \\ & \times \Big\{ -\omega_{12} G \omega^*_{12} + U_{(12)} \\ & \quad \times \Big[-\Omega_0 \Omega^*_0 U^*_0 G U_0 \Omega_0 \Omega^*_0 + \omega_{13}\omega^*_{13} U^*_0 G U_0 \omega_{13}\omega^*_{13} \\ & \quad + \omega_{23}\omega^*_{23} U^*_0 G U_0 \omega_{23}\omega^*_{23} - \sum_\alpha \Omega_\alpha \Omega^*_\alpha U^*_{(\alpha)} F^1(\alpha) D(\alpha) U_{(\alpha)} \Omega_\alpha \Omega^*_\alpha \\ & \quad + U^*_{(13)} F^1(2) D(1,3) U_{(13)} \\ & \quad + U^*_{(23)} F^1(1) D(2,3) U_{(23)} - U^*_3 T U_3 \Big] U^*_{(12)} \Big\} \Big] \end{aligned} \tag{85}$$

The remaining task is to show that X vanishes. First we have

$$\begin{aligned} \lim U_{(12)} \Omega_0 \Omega^*_0 U^*_0 &= \lim U_{(12)} U^*_0 U_0 U^*_3 \Omega_0 \Omega^*_0 U_3 U^*_0 = \omega_{12} \\ \lim U_{(12)} \omega_{13}\omega^*_{13} U^*_0 &= \lim U_{(12)} U^*_0 U_0 U^*_{(13)} \omega_{13}\omega^*_{13} U_{(13)} U^*_0 = \omega_{12} \end{aligned} \tag{86}$$

Using these and related formulas, one can show that the terms in X which depend on G cancel. Next we have

$$\begin{aligned} \lim U_{(\alpha)} \Omega_\alpha \Omega^*_\alpha U^*_{(\beta)} &= \lim U_{(\alpha)} U^*_3 \Omega_\alpha \Omega^*_\alpha U_3 U^*_{(\beta)} \\ &= \Omega'^*_\alpha \Omega_\alpha \Omega^*_\alpha \Omega'_\beta = \delta_{\alpha p} P_\alpha \end{aligned} \tag{87}$$

Consequently in the sum over α, the terms with $\alpha \neq 1, 2$ drop out, while the term with $\alpha = 1, 2$ is canceled by the operator $1 - \tilde{P}_{12}$. We are left with

$$X = \lim n \operatorname{Tr}(3)(1 - \tilde{P}_{12}) U_{(12)} \big[U^*_{(13)} F^1(2) D(1,3) U_{(13)} + U^*_{(23)} F^1(1) D(2,3) U_{(23)} - U_3^* T U_3 \big] U^*_{(12)} \tag{88}$$

Now

$$\lim U_{(13)} U^*_{(12)} \omega_{12} = \lim U_{13} U_0^* U_0 U^*_{(12)} \omega_{12} = \omega_{13} \tag{89}$$

The product $U^*_{(12)} U_{(13)}$ does not have a strong limit. However, if a weak limit is taken, it yields a factor in the first term above of $\omega^*_{13} D(1,3) \omega_{13}$, and this vanishes because of Eq. (36). It can be seen in a similar way that the other terms have a weak limit which vanishes. If D and T in the molecular chaos assumptions (39) and (56) are replaced by PDP and QTQ, then the limits exist in the strong topology, and the same kinetic equations for f^1 and f^2 are obtained. However, the formulas relating f^1 and f^2 to F^1 and F^2 appear not to be as convenient.

NOTE ADDED IN PROOF

After submission of the manuscript a paper by Y. L. Klimontovich and D. Kremp, *Physica* (Utrecht) **109A**:517 (1981), appeared in which the same problem is treated. Their approach is similar to the one used here, but they consider only the spatially homogeneous case.

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