The reactive quantum Boltzmann equations: A derivation from an arrangement channel space representation and BBGKY hierarchy

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Abstract
A rigorous derivation of the reactive quantum Boltzmann equations is presented for systems where breakup and recombination are excluded. The use of an arrangement channel space representation allows an exact decomposition of the $N$ particle density matrix into components for different chemical compositions and an exact definition of reduced species density matrices (as opposed, e.g., to standard projection operator techniques). This necessitates the use of the combinatorially complex arrangement channel BBGKY hierarchy which, however, avoids the need for the usual heuristic specification of collision terms. Another advantage is that scattering equations generated for the reactive and nonreactive many body $T$ matrices appearing in the Boltzmann equations have “well-behaved” kernels (unlike the corresponding Lippmann–Schwinger equations). From the derived equations we readily obtain, e.g., reaction-diffusion equations and nonequilibrium expressions for the chemical reaction rates.

Keywords
Boltzmann equations, Matrix equations, Chemical reactions, Chemical composition, Many body scattering

Disciplines
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Comments
The reactive quantum Boltzmann equations: A derivation from an arrangement channel space representation and BBGKY hierarchy

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A rigorous derivation of the reactive quantum Boltzmann equations is presented for systems where breakup and recombination are excluded. The use of an arrangement channel space representation allows an exact decomposition of the $N$ particle density matrix into components for different chemical compositions and an exact definition of reduced species density matrices (as opposed, e.g., to standard projection operator techniques). This necessitates the use of the combinatorially complex arrangement channel BBGKY hierarchy which, however, avoids the need for the usual heuristic specification of collision terms. Another advantage is that scattering equations generated for the reactive and nonreactive many body $T$ matrices appearing in the Boltzmann equations have "well-behaved" kernels (unlike the corresponding Lippmann–Schwinger equations). From the derived equations we readily obtain, e.g., reaction-diffusion equations and nonequilibrium expressions for the chemical reaction rates.

I. INTRODUCTION

The classical form of the reactive Boltzmann equations naturally incorporates collision terms involving cross sections for both nonreactive elastic and inelastic as well as reactive collisions. A primary application of these equations is in obtaining expressions for the chemical rate coefficients and specifically examining the deviation from equilibrium (0th order) form. Most treatments have used the Chapman–Enskog (CE) method of solution, where the chemical and kinetic time scales are assumed well separated and a Sonine polynomial expansion is implemented. Early alternative methods of solution include Lorentz gas, variational, and neutron transport techniques. Gas phase bimolecular reactions of the form $A + A \rightarrow$ products (single component) or $A + B \rightarrow C + D$ (multicomponent) are analyzed often neglecting the effect of products or making other simplifying assumptions. Kapral et al. have extended the CE procedure to describe the short time dependence of the rate deviation from equilibrium form. Simons has compared the results of this method, the CE and a multiple time scales technique with the exact solution of a solvable (single relaxation time) model. In a recent detailed series of papers Shizgal and Karplus verify previously questioned convergence behavior of the Sonine polynomial expansion for bimolecular reactions involving structureless particles. Their analysis suggests the experimentally observed rate deviation is primarily the result of internal rather than translational disequilibrium. Shizgal has assessed the validity of the assumptions associated with the CE method by comparing the above results with those of a time dependent moment method of solutions. The moment method allows treatment of nonreactive and reactive collisions on an equal footing and has been further extended by Eu and Li and Xytris and Dahler.

We remark that these nonequilibrium effects have also been analyzed heuristically from a master equation approach typically for systems with discrete (quantum) internal states.

The derivation of the above classical reactive Boltzmann equations and/or rates and their quantum analogs necessitates an explicit definition of reduced species distribution functions or density matrices thus introducing a considerable complication over the nonreactive case. Classically a geometric or phase space definition seems appropriate, however in the quantum case one might more naturally try, e.g., using bound state projection operators (with inherent problems of nonorthogonality for different channels) or Fock space techniques. A rigorous development of the latter has been given by Giradeau and Brittin and Sakakura though applications usually assume ideal commutation relations for species creation and annihilation operators (cf. the above mentioned nonorthogonality) and model Hamiltonians.

A few approaches circumventing the Boltzmann equations have been used to derive, from first principles, expressions for the quantum rate coefficients. These are reviewed for comparison. General statistical mechanical linear response theory was used by Yamamoto with various simplifying assumptions to obtain expressions for rate coefficients involving time derivatives of appropriate species number operators or channel projection operators. These are evaluated in terms of cross sections using a geometric characteriza-

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tion of molecular species. Hudson31 modified this treatment using bound state projection operators. The density–density retarded Green function expression for a progress variable obtained from linear response theory was analyzed by Berrondo.32 A different approach has been developed by Paul and others33,34 using the equation-of-motion method for real time Green functions of many-body theory. The first hierarchy equation for the single particle Green function is truncated and a suitable choice of vertex function gives rate coefficient expressions involving cross sections. Various non-Markovian modifications are considered and interpreted as density corrections to the rate coefficients. Kutz et al.35 using a creation/annihilation operator formalism demonstrated that Yamamoto's results are strictly only valid in the weak coupling limit. They also used the Green function approach which has the advantage that explicit representation of the above operators are not required. To extend this approach to dense fluids avoiding, e.g., Green function factorization approximations, Der et al.36,37 developed modified field theoretic techniques predicated on an ansatz for a certain "representative ensemble."

The first derivation of reactive quantum Boltzmann equations by Olmstead and Curtiss38 starts with the Wigner transformed version of the standard BBGKY hierarchy for a system of stable atomic and diatomic constituents. Modified cluster type molecular chaos assumptions are introduced for \( f^{(2)} \) and \( f^{(3)} \) incorporating \( f^{(1)} \) \([ f^{(n)} \] is the n-particle reduced distribution function) and a diatomic distribution function \( f_2 \). Substituting into the first and second hierarchy equations provides a closed coupled set of equations for \( f^{(1)} \) and \( f_2 \) (diatom–diatom collisions are thus ignored). In a similar treatment with the density matrix form of the standard BBGKY hierarchy, McLennan39 introduces for each of the n-particle reduced density matrices \( \rho^{(2)}, \rho^{(3)}, \ldots \), a suitable molecular chaos factorization ansatz. Free atomic, diatomic, triatomic \( \ldots \) density matrices \( \rho_1, \rho_2, \rho_3, \ldots \), respectively, are extracted from the \( \rho^{(n)} \) (should the corresponding bound states exist with projection operator \( P_2 \)) and satisfy \( (1 + P_2)\rho_n(1 - P_2) = 0 \). A similar treatment is envisioned for the corresponding classical theory.

Lowry and Snider40,41 consider a gaseous mixture of atoms and diatoms and motivate a decomposition of the standard reduced density matrices into those for monatoms and diatoms by considering the ideal gas case. The assumption of "strong orthogonality" of composition (or channel) projection operators is used to justify more general use of this decomposition. These relations are anticipated to be "almost exact" for suitably dilute systems if interpreted in the (physically important) trace operator topology with respect to these dilute states. Here the diatomic density matrix \( \rho_2 \) satisfies \( \rho_2 = P_2 \rho^{(2)} P_2 \). Appropriate kinetic equations are obtained from the von Neumann equation by a heuristically motivated partial tracing procedure and interpretation of collision terms followed by application of a molecular chaos factorization ansatz. For example with \( \rho_2 \), we retain three-body collision terms corresponding to monatom/diatom collisions and monatom recombination collisions as well as four-body terms for diatom/diatom collisions. A gaseous system with a simple bimolecular reaction has been considered by Er40 using a heuristic approach involving time dependent tracing to define species density matrices and obtaining kinetic equations by a procedure similar to that described above. In both these analyses, after applying an energy diagonality assumption to the species density matrices, a T-matrix form of the Boltzmann collision terms is obtained analogous to that of the nonreactive Waldmann–Snider equations.42,43 Corresponding expressions for rate coefficients are also obtained.

Ivanov44 defines density matrices for different chemical compositions by applying bound state projection operators to the full N-particle density matrix. A Prigogine type analysis45 together with various simplifying assumptions then yields Boltzmann-like equations for these (N-particle) quantities. They incorporate Enskog-like corrections in the form of reactive correlations associated in part with the nonorthogonality of different chemical compositions. In later work on chemical kinetics, the question of rigorous definition of chemical observables, species density matrices, etc., and problems with nonorthogonality are addressed using Boolean algebra techniques.42 In both cases there appear to be problems with the reduction from the N particle to the reduced description.48

It is clearly important to implement a precise and operational definition of the "arrangement channel" components of the full and reduced density matrices to avoid uncontrollable approximations being built into the reactive theory, from the beginning. The difficulties inherent in Fock space techniques (ideal commutation relations are assumed or can approximate Hamiltonian used) or bound state projection operator approaches (similar "nonorthogonality" difficulties) have been mentioned previously. Consequently, we adopt a different approach utilizing a representation of quantum mechanics in which the wave functions and operators have an additional vector or matrix structure associated with the various arrangement channels. A componentwise interpretation property, described later, is crucial here. The derivation of the corresponding arrangement channel BBGKY hierarchy from the (arrangement) channel space von Neumann equations has been given by Hoffman et al.49 It resembles (and incorporates) the derivation of the nonreactive hierarchy but is necessarily more complicated due to the additional channel space structure. Another prerequisite for the representation used here is that it provides an operational basis for calculations of few body reactive scattering theory. The choice used allows us to utilize recent advances in this field associated with the avoidance of nonuniqueness and disconnected kernel problems in the corresponding T-matrix equations.50,51

In Sec. II, we develop the idea of arrangement channel space representations. Various concepts and quantities associated with the corresponding BBGKY hierarchy and its derivation are then presented in generalized form. To provide a relatively simple illustration of the theory, we confine our attention to a reactive gaseous
system where breakup and recombination have negligible affect on the kinetics. The reactive quantum Boltzmann equations are derived from the hierarchy in Sec. III for a corresponding model system. The appropriate reactive Boltzmann ansatz is used and the techniques of arrangement channel space scattering theory are implemented. In Sec. IV, we introduce both an \( S \)-matrix form and a Wigner transformed version of these equations which are used, e.g., to derive reaction-diffusion equations. An example and some concluding remarks are given in Sec. V.

II. ARRANGEMENT CHANNEL REPRESENTATIONS AND CORRESPONDING BBGKY HIERARCHIES

A generalized concept of arrangement channel space representations for the quantum mechanics of \( N \) distinguishable particles is first introduced. Here the wave function is represented as a vector with Hilbert space components for each clustering, stable (i.e., supporting at least one bound state) or otherwise, of the \( N \) particles. The basic physical requirements for such a representation are described and the structure elucidated. Also we emphasize the interpretational features required of the wave function components essential for our purposes.

Next, in this general context, we review and in several cases extend various concepts and results developed previously by Hoffman et al. The terminology of this reference is used here. First, we introduce a natural partial summation/trace definition of the reduced (channel space) density matrices for each atomic content. Some remarks are next made on the normalization of the diagonal components of these density matrices and their connection with species number densities. This connection follows from the componentwise interpretational property of the representation used (and the details of the partial summation/trace procedure). The concept of reduced channel space operators corresponding to general observables on the full channel space is introduced. For any choice of reduced operators, there exists a decomposition of these into residual parts from which a natural expression for expectation values results.

The arrangement channel BBGKY hierarchy is then presented (which has precisely the form derived by Hoffman et al. in a more restricted context). The structure of the collision terms relevant for the derivation of the reactive Boltzmann equations is then elucidated.

If the physics is such that certain channels are dynamically disconnected, then this feature may be naturally incorporated into the choice of reduced channel space Hamiltonians. For example, in the absence of external forces, any bound cluster is dynamically disconnected from the finer clusters for that group of particles. Another example is afforded by a cluster of particles. Another example is afforded by a cluster of particles for which there is no chemical affinity. Such features may be manifested as an uncoupling or block diagonality in the corresponding channels. Some examples relevant to the problem under consideration are given. The ramifications for the structure of the reduced density matrices are also discussed.

A. The arrangement channel space representations

We consider a spatially confined system of \( N \) distinguishable particles (atoms) and denote them by \( J_N \). The atomic content \( |J_N \rangle \) in general includes more than one type of atomic species. The system is characterized by a Hilbert space Hamiltonian \( H(|J_N \rangle) = H_N \). The arrangement channel space representation is determined by a choice of channel space Hamiltonian \( H(|\psi_m \rangle) = H_m \) and a precise specification of the space on which it acts. The components of this matrix are Hilbert space operators labeled by the various partitions or clusterings (arrangement channels) of the \( N \) particles. All clusterings are included; some correspond to identifiable molecular compositions but most do not. If these are denoted \( \alpha, \beta, \ldots \), then the components of \( H_N \) are denoted \( (H_N)_{\alpha \beta} \). In the present work we shall ignore the possibility of isomers so that each stable atomic clustering corresponds uniquely to a molecule in the system.

To provide a representation of the desired form, \( H_N \) must satisfy the following conditions:

(A) The eigenvectors \( |\psi_m \rangle \) of \( H_N \) must be in one to one correspondence with a subset of (physical) eigenvectors \( |\phi_m \rangle \) of \( H_N \) with the same real eigenvalues.

(B) Condition A is also satisfied by the dual eigenvectors. The dual eigenvectors \( \langle \xi_m | \) of \( H_N \) are trivially related to the \( |\phi_m \rangle \) if \( H_N \) is normal (e.g., self-adjoint) but in general this is not the case.

These channel space eigenvectors and their duals will ordinarily be chosen biorthogonal. Channel space injection and projection operators onto the physical solutions are then given by

\[
J = \sum_m |\psi_m \rangle \langle \psi_m | , \quad P = \sum_m |\xi_m \rangle \langle \xi_m | .
\]

Other eigenvectors of \( H_N \) may be chosen so that \( P \) and \( J \) are projections on the physical solutions then give

\[
0 = \sum_m |\phi_m \rangle \langle \phi_m | .
\]

(C) We suppose that \( J \) and \( P \) are bounded (a useful technical requirement).

We may now define a trace class channel space density matrix \( \rho \) from a Hilbert space density matrix \( \rho \) by

\[
\rho = \mathcal{J} \rho \mathcal{J}^\dagger .
\]

In particular, if \( \rho = \rho_0(i) \) satisfies the Hilbert space von Neumann equation then \( \rho = \rho_0(i) \) satisfies

\[
\frac{\partial}{\partial t} \rho_0 = [H_N, \rho_0] ,
\]

noting that \( \mathcal{J} H_N \mathcal{J}^\dagger = H_N \) and \( H_N \mathcal{J} = \mathcal{J} H_N \).

(D) There is a correspondence between Hilbert and channel space observables \( A_N \rightarrow A_m \) so that we have agreement of expectation values

\[
\langle A_N \rangle = \text{Tr}(\rho_N A_N) = \text{tr}(\rho_m A_m) .
\]

Here \( \text{Tr} \) and \( \text{tr} \) are, respectively, the Hilbert and channel space traces (\( \text{tr} \) is the sum of the \( \text{Tr} \) over diagonal channel components). We have chosen \( \text{Tr} \rho = \text{tr} \rho = 1 \).

(E) An essential property of the choice of \( H_N \), for our purposes, is that the components of the \( |\psi_m \rangle \) (or alter-
natively the \( \langle \xi_n \rangle \), or both) have the appropriate physical clustering interpretation.

An analysis in asymptotic regions for each clustering then shows that the diagonal components of \( H_p \) must include the corresponding channel Hamiltonian. This in turn indicates that the components of \( \langle \xi_n \rangle \) (or alternatively the \( |\Phi_n\rangle \), or both) contain at least the part of the full Hilbert space wave function corresponding to that clustering (see the examples at the end of this section). In any case, the diagonal components of \( \rho_p \) can always be associated with the corresponding molecular composition.

To achieve the property \( E \), it may be convenient to sacrifice the self-adjointness of \( H_p \) (and of \( P \) and \( \rho_p \)). This introduces no difficulties in the required scattering theory manipulations. In fact, the avoidance of non-uniqueness and disconnected kernel problems in such calculations first motivated the introduction of these Hamiltonians. 52,53

It is important to realize that connectivity of the scattering equations of a wave function theory is not equivalent to the componentwise interpretation property of the wave functions. The latter is crucial for a well-defined statistical theory. For example, although three-particle, four-channel Faddeev, and BKLT equations are connected, breakup is spread between all four wave function components. 52,53,49 On the other hand, for the three-particle problem, where breakup is strictly excluded and there exist only two stable molecular compositions, the corresponding disconnected two channel Faddeev-like equations do provide the appropriate componentwise interpretation. 53

It is clear that all representations which have property \( E \) are "equivalent asymptotically." This has important ramifications for the form of the Boltzmann equations.

Finally we remark that, in the context of above mentioned difficulties with many-body scattering theory, it may also be convenient to choose \( H_p \) so that its components are not symmetric on interchange of labels for particles of the same atomic species (unlike \( H_f \)). 53

B. The reduced channel space density matrices

It is impossible to deal with Eq. (2.2) directly for the systems of interest, i.e., of \(-10^{23}\) particles. In any case \( \rho_p \) contains more information than is needed to calculate the quantities of interest. For this reason one deals with the few lowest order reduced channel space density matrices, which we shall now consider.

It is necessary first to review some appropriate combinatorial concepts. 49 Let \( J \) be a subset of the \( J_p \) particles. Labeled subchannels are then denoted by \( A_j \), \( B_j \), etc., whereas \( A, B \), etc., are unlabeled ordered subchannels. For example,

\[
J = a_{21}, a_{34}, b_{53}^1, \quad A_j = (a_{24}b_{53})a_{31}
\]

where \( a, b, \ldots \) denote atomic species, superscripts denote specific atoms, and the parentheses indicate clusters.

Also

\[
|J| = ||A|| = \text{two atoms of } a \text{ and one of } b \quad (2.5)
\]

denotes the atomic content. Finally if \( J \subseteq K \), then \( A_j \in B_K \) indicate the \( A_j \) is contained in the larger subchannel \( B_K \).

For each atomic content \( ||A|| \), we define a corresponding reduced channel space operator \( \rho(\langle A \rangle) \) with operator valued components \( \rho(\langle A \rangle)_{BC} \) indexed by various unlabeled ordered subchannels \( B, C \) for which \( ||B|| = ||C|| = ||A|| \). The operators \( \rho(\langle A \rangle) \) are obtained from \( \rho_p \) by a natural summation/trace procedure. Specifically \( \rho(\langle A \rangle)_{BC} \) includes contributions from those "compatible" components \( \rho_p \alpha \) of \( \rho_p \) for which there exists a set of labels \( K \) such that

\[
B_K \in \alpha, \quad C_K \in \beta, \quad \text{and } \alpha - B_K = \beta - C_K. \quad (2.6)
\]

The natural representation for evaluating the trace as shown in detail in Ref. 49 is the coordinate representation. The operator \( \rho(\langle A \rangle) \) is well defined (nonvanishing and locally trace class) in the thermodynamic limit. It is important to note that these \( \rho(\langle A \rangle) \) are completely determined by \( \rho_p \) and thus by the choice of \( H_p \) (and the initial conditions).

We now turn to the question of normalization of the diagonal components of the \( \rho(\langle A \rangle) \). Let \( A \) be a single cluster subchannel corresponding to a stable molecule (meaning, here, that at least one bound state exists) and consider

\[
\text{Tr}(\rho(\langle A \rangle)) = \sum_{\alpha} \sum_{\kappa} \text{Tr}[\delta((\langle A \rangle)_{\kappa} \subset \alpha) \rho_p_{\alpha \kappa}], \quad (2.7)
\]

where Eq. (2.6) has been used. Consider first a system in which the molecular composition is well defined for "almost all" times. From property \( E \), in any region corresponding to some separated clustering of particles, \( \rho_p_{\alpha \kappa} \) is nonzero only if \( \alpha \) corresponds to that clustering and is a stable chemical composition for the system. Furthermore, most of the weight of Eq. (2.7) and of \( \text{tr} \rho_p \) is contained in those \( \alpha \) where

\[
N(\langle A \rangle, \alpha) = \sum_{\kappa} \delta((\langle A \rangle)_{\kappa} \subset \alpha) - \overline{N(\langle A \rangle)}
\]

the mean number of molecules of \( A \) in the gas. In fact, the fluctuations in \( N(\langle A \rangle, \alpha) / \overline{N(\langle A \rangle)} \) (calculated via an ensemble average) vanish in the thermodynamic limit. Thus from Eq. (2.7),

\[
\text{Tr}(\rho(\langle A \rangle)) = \overline{N(\langle A \rangle)} \text{tr} \rho_p = \overline{N(\langle A \rangle)}, \quad (2.8)
\]

or

\[
\text{Tr}(\rho(\langle A \rangle)) / V = n(\langle A \rangle) \quad (2.9)
\]

in the thermodynamic limit, where \( V \) is the volume of the system and \( n(\langle A \rangle) \) is the mean number density of molecules of type (A). If the trace over the whole system is replaced by that over a macroscopic volume element, then a local form of Eq. (2.9) is obtained. In asymptotic configurations, only stable molecular species occur, hence in the low density limit, nonstable molecular species are of decreasing importance (i.e., \( n(\langle A \rangle) \to 0 \) if \( A \) is unstable more rapidly than for a stable species). If the molecular composition is not well defined for
"almost all" times, then the $n(A)$ are representation
dependent (corresponding to arbitrariness in assignment of
molecular composition) and may be significant for un-
stable $(A)$. The generalization of Eq. (2.9) for two clusters $(A)$,
$(B)$ which may or may not be stable species becomes
\[
\text{Tr} \left( \frac{(g(IIAII))_{AA}(IIAII)}{V} \right) - \frac{1}{S_2(IIAII || II BII)} \text{Tr} \left( \frac{(g(IIAII))_{AA}(IIAII)}{V} \right)
\]
\[
\times \text{Tr} \left( \frac{h(IIAII || II BII)}{S_2(IIAII || II BII)} \right) \frac{n(A)}{n(B)}
\]
in the thermodynamic limit. Here $S_2(IIAII || II BII)$ is the
number of distinct labelings of atoms in ordered clusters
with atomic contents $IIAII$ and $II BII$. Note that
$S_2(IIAII || II BII) = m_k m_l \cdots$, where $m_k$ is the number of
distinct labelings of atoms of type $a$ in the two ordered
clusters. This factor arises from the implicit or-
dering associated with the sampling Eq. (2.6). For
example, consider
\[
\text{Tr} \rho(2a, b)_{(a_1^a_1^a_2^b_1^a_2^b_2)} = \sum_{\alpha} \sum_{\beta} \sum_{\alpha} \sum_{\beta} \text{Tr} \left[ \delta((a_\alpha)(a_\beta)) \in \alpha \right] \left( \rho_{\alpha \beta} \right)_{aa}.
\]
For the dominant contributing $\alpha$, there are on the average
$\frac{1}{2} N(a) N(ab)$ choices of $i, j, k$ so $S_2(ab) = 2$ as stated. Similarly
\[
\text{Tr} \rho(4a)_{(a_1^a_1^a_2^a_2^a_3^a_4^a_4)} = \sum_{i<j<k<l} \text{Tr} \left[ \delta((a_\alpha)(a_\beta)) \in \alpha \right] \left( \rho_{\alpha \beta} \right)_{aa} \sim \left( \frac{1}{2} \right) N(aa)^2.
\]
The extension to the multicluster case should be clear
but is not needed here.

C. General reduced and residual channel space
operators
For an additive observable $G_x$ on the $N$ particle
channel space, we suppose there is a natural definition of
corresponding residual operators $G((IIAII)$ for each atomic
content $IIAII$ with components $G((IIAII))_{BC}$ where $II BII$
$= II CII = II AII$. The most important example is where
$G_x = H_x$. As one might expect, $H((IIAII)$ will describe the
streaming of $\rho((IIAII)$ in the hierarchy equations. An
interesting feature here is the substantial nontrivial flexi-
bility in the choice of $H((IIAII)$ due to the channel struc-
ture for a fixed $H_x$ and thus $p_x$ and $\rho((IIAII)$. Formally
any choice is possible for a strictly finite system. How-
ever to avoid divergences in the hierarchy on taking the
thermodynamic limit, there must be some constraints on
the $H((IIAII)$. Basically we require that the $H((IIAII)$
provide a representation for the quantum mechanics of
$IIAII$ distinguishable particles with Hilbert space Hamilton-
ian $H((IIAII)$ in the same sense as described for $H_x$ in the
$N$-particle case. We also demand that $i\hbar \frac{\partial}{\partial t} \rho((IIAII)$ $= \text{CT}((IIAII))$.
\[
\text{CT}((IIAII)) = \text{CT}1((IIAII)) + \text{CT}2((IIAII)) ,
\]
where $\text{CT}1((IIAII))_{BC}$ couples particles $II BII$ of $II CII$ to all possible $[H((IIAII)), \rho((IIAII))]_{BC}$, where both $B\subset E$ and $C\subset F$. This is a generalization of the usual nonreactive
collision term. However $\text{CT}2((IIAII))_{BC}$ couples to
$\rho((IIAII))_{BC}$, where either $B\subset E$ and $C\subset F$ but $C\subset F \neq \phi$, or $C\subset F$ and $B\subset E$ but $B\subset \phi$ and the form of the
coupling is not "commutator like" as in $\text{CT}1$. There is
no nonreactive analog of this term.

In the low density regime, we shall consider only the
Boltzmann evolution equation for the single species dens-
ity matrix. Let the single cluster $(A)$ correspond to a
stable molecular species. For our purposes it will
suffice to consider only the matrix elements
$\langle \text{CT}((IIAII))_{(A)}(A) \rangle_{(A)} = 0$ and it is possible to show that
(CT([|A|]))_{A(A)} = (CT1([|A|]))_{A(A)}

\begin{equation}
\sum_{\lambda, \rho} \text{Tr} (\text{h}(|D|), \rho(|D|))_{BD},
\end{equation}

which is reminiscent of the form of the collision term in the nonreactive BBGKY hierarchy. Here \( \sum \) represents a sum over appropriate subsets of ordering labels for \( D \).

E. Dynamic disconnectivity and block diagonality of \( H(|A|), \rho(|A|) \)

These ideas are first illustrated with the important example of the dynamic disconnectivity of isolated totally bound clusters. It follows that for a finite system with periodic boundary conditions or for a system in the thermodynamic limit where all walls have gone to infinity, it is natural to choose \( H(|A|) \) of the form

\begin{equation}
H(|A|) = \begin{pmatrix}
H^*(|A|) & 0 \\
0 & H(|A|)
\end{pmatrix},
\end{equation}

where \( (A) \) is the single cluster channel. Also \( H(|A|) \) could be replaced by \( P(|A|)H(|A|) \), where \( P(|A|) \) is the projection operator for totally bound \(|A|\) particles states. In the presence of an external potential such as a wall, the totally bound cluster may not be "dynamically disconnected" in which case the choice \( H(|A|) \) will not be appropriate.

In general the \( \rho(|A|) \) will not exhibit a corresponding block diagonal structure because the single cluster channel will be coupled to the remaining channels through the collision term, e.g., a particle from the rest of the fluid could induce breakup of \( (A) \). An exception to this rule is \( \rho_{\nu} \) for a system with periodic boundary conditions.

There are other examples where dynamic disconnectivity may be used to simplify the structure of \( H(|A|) \) and still allow retention of the important interpretational requirement of the representation. These include situations where certain clusters do not exist as stable species. Such channels may be disconnected from the rest. Another example is a model system where breakup and recombination collisions are strictly excluded so that the number of molecules is conserved. Here \( H(|A|) \) may be chosen block diagonal where the blocks correspond to channels with a fixed number of clusters.

It is appropriate to establish a criterion determining when uncoupling or block diagonality in the \( H(|A|) \) leads to the corresponding uncoupling in the \( \rho(|A|) \). From Eq. (2.6), one expects this to be true if

\[ A, B \text{ uncoupled in } H(|A|) \text{ and for any } K \text{ such that } \]

\[ A_K \in A, B_K \in B, A - A_K = B - B_K \]

implies

\[ \alpha, \beta \text{ are uncoupled in } H_{\nu}. \]

Using Eq. (2.8) for \( h(|A|) \), the consistency of Eq. (2.19) with the hierarchy equations can be demonstrated from a detailed analysis of the collision terms. This result is applicable in the two cases described above.

If there is any uncoupling, it is natural to introduce a block index "\( b \)" and denote the corresponding blocks of \( H(|A|) \) by \( H^b(|A|) \). Clearly \( b \) must be compatible with the arrangement channel matrix labeling.

F. Examples of some classes of representations

(i) Consider the class of representations which satisfy a "summation condition" of the form

\begin{equation}
\sum_{A} (H^b(|A|))_{AB} = H^b(|A|) \text{ for all } B \text{ (in block } b \).
\end{equation}

The components of the physical eigenvectors of \( H^b \) must carry the interpretational property and sum to the corresponding eigenvector of \( H^b \). Those of the physical duals are naturally chosen all equal to the full \( H^b \) dual eigenvector. Where there is a single block for each \( |A| \) (including \( J_0 \), the fact that \( \rho_{\nu}|_A \) is independent of \( \beta \) implies \( \rho(|A|)_{BC} \) is independent of \( C \). More generally, if the block diagonality of the \( H(|A|) \)'s leads to a corresponding block diagonality in the \( \rho(|A|) \)'s, we have

\[ \rho^b(|A|)_{BC} = \rho^b(B) \text{ for all } C \text{ (in block } b \).
\]

If the system has well defined chemical composition, then contributions to \( \text{Tr } \rho^b(B) \) come from the B clustering region.

Representations of the form of Eq. (2.20) with \( H^b \) as a differential operator have been termed "arrangement channel quantum mechanics" (acqm) by Kouri et al. and originated in the work of Ref. 53. A rigorous mathematical foundation for these theories has been recently developed by Evans et al. The standard versions cannot, however, suitably handle breakup from the interpretational point of view.

(ii) Consider classes of representations where the \( H^b(|A|) \) are self-adjoint. Here the eigenvectors and duals are trivially related and consequently both must satisfy the interpretational property. If the chemical composition of the system is well defined, then the \( \rho(|A|) \) are "almost diagonal."

(iii) For any representation associated with a set \{\( H(|A|) \)\}, we can define a corresponding adjoint representation associated with a choice of Hamiltonians \{\( H(|A|)^* \)\}, where \( * \) represents the adjoint operation on the \(|A|\)-particle channel space. In representations adjoint to those of type (i), the physical dual eigenvectors now carry the interpretational property and the eigenvectors have the equal component property. Representations of type (ii) are of course identical to their adjoints.

A more detailed development of general channel space representations and BBGKY hierarchies will be given in a future paper.

III. THE HIERARCHY AND CORRESPONDING BOLTZMANN EQUATIONS IN THE ABSENCE BREAKUP AND RECOMBINATION

We first describe a chemical system where breakup and recombination have negligible effect on the kinetics.
and a corresponding mathematical model where these are strictly excluded. The latter allows a corresponding block diagonal choice of $H^{\text{\tiny IIAI}}$'s still leaving considerable freedom of choice within the blocks. Next we investigate the ramifications of this choice for the residual Hamiltonians $H^{\text{\tiny IIAI}}$. Of particular interest is the resulting structure of those collision terms in the lowest order hierarchy equations (i.e., for single species reduced density matrices) which lead to the Boltzmann collision operators. The convergence of these terms is discussed and we note that the pair (i.e., two cluster) density matrices appearing there are evaluated in the "interaction region."

These reduced channel space density matrices may be expressed in terms of their "asymptotic precollisional forms" using channel space scattering theory. Upon application of a suitable reactive Boltzmann ansatz, these forms are factorized in terms of single species density matrices, thus closing the hierarchy to obtain the desired reactive Boltzmann equations. Simplified forms and the representation invariance of these equations are then discussed.

A. The chemical and model systems

Henceforth we shall consider a dilute gaseous system with several stable molecular species which may be monatomic, diatomic, or polyatomic. We suppose that breakup and recombination collisions are unlikely and thus do not appreciably affect the kinetics. This is predicated on energetic assumptions excluding simple breakup and the formation of activated (quasibound) complexes existing on the order of a mean free time (which could act as sources for recombination), and on the low density of the system. The collisions in such a gas predominantly preserve molecular number resulting in an approximate conservation law, i.e., the total number of molecules in the system is approximately constant. The above assumptions do not preclude the possibility that a significant proportion of collisions involve rearrangement, i.e., are reactive.

Our approach here is to consider a model system corresponding to that described above in which breakup and recombination collisions are strictly excluded. This may be achieved, at the $N$-particle level, by the inclusion of a suitable $N$-body potential. Such a potential should be chosen not to significantly interfere with the few body nonreactive and rearrangement collision dynamics of the physical system for the range of thermal energies of interest. For this model, the number of molecules is strictly conserved.

In the previous section, we noted that a choice of the $H^{\text{\tiny IIAI}}$ block diagonal in channels with a fixed number $b$ of clusters, is appropriate for this model (here $b$ is also the block label). Some implications of the model on the characteristics of the blocks $H^{\text{\tiny IIAI}}$ are discussed in Appendix A. We also have the option of uncoupling those channels with clusters corresponding to unstable molecules. Although such uncoupling may seem most natural, we leave this option open. If acqm type representations are used, retention of these "unphysical" channels leads to improved (connected) scattering equations for the $T$ matrices that appear later and still allows the required interpretational property.

If there exists a stable molecular species not accessible for the range of energies statistically available at a given gas temperature, then we might further adjust the model so these are strictly inaccessible and then uncouple the corresponding channels.

B. The $H^{\text{\tiny IIAI}}$ and hierarchy equation structure

A decomposition of the $H^b(\text{\tiny IIAI})$ is first introduced here which provides a natural interaction picture. Let $(H^b(\text{\tiny IIAI}))_{AB} = \delta_{AB} H^b(\text{\tiny A})$, where $H^b(\text{\tiny A})$ is the $A$-channel Hamiltonian and write

$$H^b(\text{\tiny IIAI}) = H^b(\text{\tiny IIAI}) + V^b(\text{\tiny IIAI}) \quad \text{ (3.1)}$$

Note that $V^b$ need not be off-diagonal. The block diagonal choice of the $H^{\text{\tiny IIAI}}$ described above produces a corresponding block diagonality in the $H^{\text{\tiny IIAI}}$ and $\rho^{\text{\tiny IIAI}}$. A $b$ superscript will again denote the $b$-cluster block. From the definition in Eq. (2.13) of the $h^{\text{\tiny IIAI}}$, we obtain the crucial result:

$$h^b(\text{\tiny IIAI}) = V^b(\text{\tiny IIAI}) \quad \text{ (3.2)}$$

determining the structure of the Boltzmann collision operator. Also $h^b(\text{\tiny IIAI}) = h^b(\text{\tiny IIAI})$ and if $n_b$ is the number of particles in $\text{\tiny IIAI}$, then $h^b(\text{\tiny IIAI}) = h^\text{\tiny A}_b(\text{\tiny IIAI})$, the true $n_b$-body potential in $H^\text{\tiny A}_b(\text{\tiny IIAI})$.

Now we return to the consideration of the hierarchy Eqs. (2.15) and (2.17) for the single species density matrices

$$\rho^{\text{\tiny IIAI}}(\text{\tiny A}_1, \text{\tiny A}_2) = \rho^b(\text{\tiny IIAI}) \quad \text{ (3.3)}$$

for each stable cluster $(\text{\tiny A}_j)$. We also write $H^b(\text{\tiny IIAI}) = H^b(\text{\tiny IIAI})$. In the Boltzmann regime the nonideal part of the evolution of the system is dominated by binary collisions effects. Consequently, at this level, we need to retain only terms in Eq. (2.17), where $D = (\hat{\text{\tiny A}}_1)(\hat{\text{\tiny A}}_2)$, where $\hat{\text{\tiny A}}_b = \text{\tiny IIAI}_b$. These terms correspond to collisions involving stable clusters $(\text{\tiny A}_1)$ and $(\text{\tiny A}_2)$ as either reactants, products, or both. Thus we obtain

$$i\hbar \sum_{\hat{\text{\tiny A}}_1} \frac{\partial}{\partial t} \rho^b(\text{\tiny A}_1, \text{\tiny A}_2) = \{ H^b(\text{\tiny IIAI}), \rho^b(\text{\tiny IIAI}) \}$$

$$= \sum_{\text{\tiny stable cluster}} \sum_{\text{\tiny order of labels}} \text{Tr}[V^b(\text{\tiny IIAI})],$$

$$\rho^b(\text{\tiny IIAI}) = \rho^b(\text{\tiny IIAI}) + V^b(\text{\tiny IIAI}) \rho^b(\text{\tiny IIAI}) + \rho^b(\text{\tiny IIAI}) V^b(\text{\tiny IIAI}), \quad \text{ (3.4)}$$

where $\hat{\text{\tiny A}}_1 - \text{\tiny A}_1$ indicates the assignment of $\hat{\text{\tiny A}}_1$ to $\text{\tiny A}_1$ variables after evaluating the trace in each term and the sum over labelings has $S_b(\text{\tiny IIAI}_b || \text{\tiny IIAI}_b)$ terms. The hierarchy has now been reduced to a form analogous to the nonreactive case.

Let us now consider the convergence of the terms on the right-hand side of Eq. (3.4). Specifically, the quantity traced over is

$$\sum_{\text{\tiny order of labels}} V^b_{\hat{\text{\tiny A}}_1, \text{\tiny C}_1} \rho^b_{\hat{\text{\tiny A}}_2, \text{\tiny C}_2} = \sum_{\text{\tiny order of labels}} \rho^b_{\hat{\text{\tiny A}}_1, \text{\tiny C}_1} V^b_{\hat{\text{\tiny A}}_1, \text{\tiny C}_1} \rho^b_{\hat{\text{\tiny A}}_2, \text{\tin C}} \quad \text{ (3.5)}$$
setting $\hat{A} = (\hat{A}_1)(\hat{A}_2)$. The basic feature to be observed here is that the product of the $V^2_{A_1}$ and $\rho^2_A$ restricts the effective support to the intersection of the $\hat{A}$ and some other tube, a bounded region of space, thus guaranteeing convergence. This is readily checked using the interpretational property for the different classes of representations listed at the end of Sec. III.

In summary, in Eq. (3.4), $\rho^2((A_1, A_2))$ is only sampled in the spatially confined interaction region where all particles are together.

C. Reduction to the reactive Boltzmann equation

The procedure used here parallels that for the derivation of the nonreactive classical Boltzmann equation, the Waldmann–Snyder classical and other generalized Boltzmann equations from their respective hierarchies. We first express the operator $\rho^2((A_1, A_2))$ in Eq. (3.4) in terms of its asymptotic precollisional form. One must describe its time evolution from the midst of the collision to a time sufficiently prior to the collision so that chemical composition of the reactants is resolved. This "collision time interval" is the one associated with the convergence of the corresponding Hilbert space Möller operators. From the low density assumption and the lack of long-lived activated complexes, we conclude that this time interval is much shorter than the mean free time between collisions in the gas. Consequently, the CT terms in the $\rho^2$ hierarchy associated with complicated recollision sequences is (as well as true three-body collisions) will not significantly affect its evolution over this period. We therefore use

$$i\hbar \frac{\partial}{\partial t}\rho^2 = [H^2, \rho^2]$$

(3.6)

as the equation describing this evolution.

Integrating this equation we utilize channel space scattering theory for the two-cluster Hamiltonian $H^2_A$. The details are presented in Ref. 55. Despite many formal similarities with the usual Hilbert space scattering theory, there are some significant differences. In general, one must consider scattering for both the eigenvectors and their duals since the Hamiltonian's may not be self-adjoint. A crucial feature is that the interaction picture unifies the various representations described by always providing an asymptotic precollisional form for $\rho^2$ diagonal in the channel labels (we have invoked the assumption of resolution of the chemical composition here).

The interaction picture useful for describing the two cluster scattering process is defined by

$$A^2(t') = \exp[iH^2_A(t' - t)]A^2(t)\exp[-iH^2_A(t' - t)]$$

(3.7)

with time $t$ being in the midst of the collision. Remember that $H^2_A$ is composed of two-cluster channel Hamiltonians and thus can describe the asymptotics. From Eq. (3.6) we may write

$$\rho^2(t) = \rho^2(0) = \Omega(t' - t)\rho^2_A(t')\Omega(t' - t)^{-1},$$

(3.8)

where

$$\Omega(s) = \exp(\pm i/\hbar H^2_A s)\exp(-i/\hbar H^2_{A_2} s).$$

(3.9)

The right-hand side of Eq. (3.8) is independent of $t'$ so the limit as $t' - t \to -\infty$ exists. However, $\lim_{t' \to -\infty} \Omega(s)$ does not exist if $H^2_A$ has complex eigenvalue spurious solutions. This problem can be remedied by replacing $H^2_A$ in Eq. (3.9) with $P^2 H^2_A$, where $P^2$ projects onto the physical solutions of $H^2_A$ [cf. Eq. (2.1)]. We define

$$\Omega^* = \lim_{s \to \infty} \exp[+i/\hbar P^2_H^2] \exp(-i/\hbar H^2_A s),$$

(3.10)

where the $P^2$ is inserted explicitly if required. Similarly define

$$\Omega^* = \lim_{s \to \infty} \exp[+i/\hbar H^2_A s] \exp(-i/\hbar P^2 H^2_A s),$$

(3.11)

on the subspace of physical solutions. Note that $\Omega^* \Omega^* = 1$.

The precollisional form of $\rho^2_A(t')$ may be deduced from the following observation. Let $|\phi^A_{t'}\rangle$, $(\phi^A_{t'})^\dagger$ be wave pulses corresponding to $|\phi^B_{t'}\rangle$ with precollisional $B$-channel bound state clustering $|\phi_B\rangle$, where $B = (B_1)(B_2)$ with $B_i$ stable clusters. One can show that

$$|\phi^A_{t'}\rangle - \delta_{A,B} - (\phi^A_{t'}\rangle - \delta_{A,B} (\phi_B\rangle$$

(3.12)

as $t' \to t = -\infty$. The convergence is "strong," where the components satisfy an interpretational property and "weak" otherwise. As a consequence we conclude that the asymptotic precollisional form of $\rho^2_A(t')$ is diagonal in the channel labels provided the precollisional chemical composition is well defined.

We can now employ the REACTIVE BOLTZMANN ANSATZ which, in physical terms, states that the molecules are independent prior to collision. It is essential that the precollisional chemical composition be well defined (leading to the above diagonality) and that the gas be sufficiently dilute (thus avoiding dynamic correlations from, e.g., ring collision sequences)). This ansatz leads to the following density matrix factorization:

$$\rho^2_A(t')_{\lambda,\omega} = -\delta_{\lambda,\omega} \frac{1}{S_0(|B_1||B_2}) \rho^A_B(t', t') \rho^B_B(t, t')$$

(3.13)

for $t'$ prior to the collision, where

$$\rho^A_B(t, t') = \exp[+i/\hbar H^2_A(t' - t)] \exp(-i/\hbar H^2_B(t' - t)].$$

(3.14)

The factor $S_0(|B_1||B_2)$ provides the correct normalization [cf. Eq. (2.10)].

Next, in Eq. (3.13), we approximate the evolution of $\rho^A_B(t, t')$ from $s = t$ to $t'$ by free molecule streaming (the resulting error can be consistently neglected at the Boltzmann level on the time and length scales considered here). Thus one obtains

$$\rho^2_A((t'))_{\lambda,\omega} = -\delta_{\lambda,\omega} \frac{1}{S_0(|B_1||B_2}) \times \rho^A_B(t, t') \rho^B_B(t', t) = (|\phi^A_{t'}\rangle_{\lambda,\omega}$$

(3.15)

for $t'$ prior to the collision.

Using these results we obtain the reactive Boltzmann equations by making the following replacement in the right-hand side of the hierarchy Eq. (3.4):

$$\gamma^2 = \gamma^2 \Delta^2 A^2(t) \Omega^* - \Omega^* \gamma^2(t') \Delta^2 \gamma^2.$$  

(3.16)
Instead of adopting the time dependent representations as input for the Möller operators here, we use\(^{55}\)

\[
\Omega^* | \phi_B) = \Omega^* (E_B) | \phi_B) \quad \text{and} \quad \langle \xi_k, \tilde{\Omega}^* = \langle \xi_k, \tilde{\Omega}^* (E_A) , \quad (3.17)
\]

where \(| \phi_B)\) and \(\langle \xi_k, \) are B and A cluster \(H_z\) eigenvectors and duals with energy eigenvalues \(E_B\) and \(E_A\) respectively. Also \(\Omega^*(E) = \lim_{\varepsilon \rightarrow 0^+} (E \mp \varepsilon) \times \tilde{\Omega}(E \mp \varepsilon)\), where if \(G_0(x) = (x - H)_0\) then,

\[
\Omega(x) = 1 + G_0(x) V \Omega(x), \quad \tilde{\Omega}(x) = 1 + \tilde{\Omega}(x) V G_0(x) . \quad (3.18)
\]

It is convenient to have an expression for the Boltzmann collision terms involving channel space \(T\) matrices

\[
T^* = \Omega^* \tilde{T}^* \quad \text{and} \quad \tilde{T}^* = \Omega^* \tilde{T}^* . \quad (3.19)
\]

The corresponding energy dependent operators are obtained from Eqs. (3.17) and (3.18). With a suitable choice of \(H\), the integral equations for these \(T\)'s will have "well behaved" kernels, unlike the standard Lippmann–Schwinger equations, and thus have practical calculational value.\(^{50–53}\) Furthermore, one may show that \(T^*\) and \(\tilde{T}^*\) coincide on the \(H_z\) energy shell. Using also corresponding expressions for the \(\Omega\)'s in terms of the \(T\)'s, one obtains

\[
[V^2, \rho^2(t)] = T \rho_{\text{elas}}^2(t) - T \rho_{\text{elas}}^2(t) \tilde{T}^* \quad \text{(LOSS)}
\]

\[
+ T \rho_{\text{elas}}^2(t) \tilde{T} G_0^2(E_1) - G_0^2(E_2) T \rho_{\text{elas}}^2(t) \tilde{T} \quad \text{(GAIN)} , \quad (3.20)
\]

where \(E_1/E_2\) are the energies associated with the bras/kets of \(\rho_{\text{elas}}^2(t)\). The association with gain and loss terms should be anticipated by comparison with the nonreactive case and will be elucidated in the following analysis.

Note finally that the right-hand side of Eqs. (3.16) and (3.20) may be regarded as \(\mathcal{S} \rho_{\text{elas}}(t)\), where \(\mathcal{S}\) is the collision superoperator.\(^{55}\)

Our derivation of the Boltzmann equation has been rather intuitive. It is clear that in a more rigorous setting the equalities of Eqs. (3.16) and (3.20) (and their nonreactive analogs) must be interpreted in an appropriate trace operator topology.\(^{57,60}\)

D. \(\rho([A_i], t)\) energy diagonality and the simplified representation invariant form of the reactive Boltzmann equations

If we substitute

\[
G_0^2(E) = \Phi([E - H_0^2]^{-1}) \times \Phi([E - H_2^2]) , \quad (3.21)
\]

where \(\Phi(\cdot)\) is the Cauchy principal value integral, into Eq. (3.20), then we obtain the following form of the reactive Boltzmann equations:

\[
\rho^2([A_i], t) - \rho([A_i], t) - [H([A_i], p([A_i], t)]
\]

\[
= \sum \sum \mathrm{stable clusters} \quad \text{ordered labellings} \quad \chi_2 \quad \text{of} \quad \{A_i, A_i'\}
\]

\[
+ \sum \sum \mathrm{stable clusters} \quad \text{ordered labellings} \quad \chi_1 \quad \text{of} \quad \{A_i, A_i'\}
\]

\[
\int_{\tau_1 \times A_1} \Phi([E - H_0^2([A_i], A_i')]) \times [E - H_2^2([A_i], A_i')] \chi_1 \chi_2 , \quad (3.22)
\]

where again \(E_0/E_2\) are the energies of the \(\rho_{\text{elas}}^2\) bras/kets and \(d \tau / d t\) is the total time derivative.

At this stage we restrict our consideration to the case of approximately energy diagonal single species density matrices as is often appropriate, e.g., in the study of transport processes. Any significantly off–energy diagonal component would be associated with a highly oscillatory time dependence and thus would be negligible since the \(\rho([A_i], t)\) incorporates a distribution of phases. Consistently applying this approximation to Eq. (3.22), we see that both \(E_0\) and \(E_2\) correspond to the unique energy \(E\) of \(\rho_{\text{elas}}^2\) and all the \(H_0^2\) act on states of the same energy (the sum of the energies of the \(A_1\) and \(A_2\) states). Consequently, the Cauchy principal value terms cancel and we obtain:

\[
\rho^2([A_i], t) - \rho([A_i], t) - [H([A_i], p([A_i], t)]
\]

\[
= \sum \sum \mathrm{stable clusters} \quad \text{ordered labellings} \quad \chi_2 \quad \text{of} \quad \{A_i, A_i'\}
\]

\[
+ 2 \pi \int \Phi([E - H_0^2([A_i], A_i')]) \times [E - H_2^2([A_i], A_i')] \chi_1 \chi_2 , \quad (3.23)
\]

At this level of approximation the matrix elements of all operators appearing on the right-hand side of Eq. (3.23) are evaluated on shell. Since the on-shell components of \(\langle T \rangle_{A_1}^A\), \(\langle T \rangle_{A_1}^A\) agree with the Hilbert space operators \(T_{A_1}^A\), \(\bar{T}_{A_1}^A = T_{A_1}^A\), respectively, for all choices of channel space representation,\(^{55}\) we have demonstrated the desired representation invariance of the reactive Boltzmann equations.

It is convenient to introduce an explicit matrix representation for Eq. (3.23) here. For some stable cluster \((A_i)\), let \(d(A_i), e(A_i), \ldots\), label the corresponding molecular eigenfunctions of \(H([A_i],\) and set \(\rho_{\text{elas}}([A_i], e(A_i)) = \rho([A_i], e(A_i)) \). The label for the direct product of states \(d(A_i)\) and \(d(A_i')\) is denoted \(d(A)\) and \(d(A)\) is the sum of the corresponding energies. Since the Hilbert space \(T\)-matrix elements, together with the single species density matrices are symmetric on interchange of labels of particles of the same atomic type, in Eq. (3.23), we may replace

\[
\sum \sum \mathrm{stable clusters} \quad \text{ordered labellings} \quad \chi_1 \quad \text{of} \quad \{A_i, A_i'\}
\]

\[
\int \Phi([E - H_0^2([A_i], A_i')]) \times [E - H_2^2([A_i], A_i')] \chi_1 \chi_2 , \quad (3.24)
\]

with \( \delta_{\text{cluster}} \) for any single labeling choice of \((A_2)\) and \((A_2')\) to obtain

\[
\frac{\partial}{\partial t} \rho_{\text{cluster}}(A_2;A_2') - [H(\|A_2\|), \rho([A_2], t)]_{\text{cluster}} = \\
\sum_{\text{cluster term}} \sum_{\text{stable}} \delta_{\text{cluster}}(A_2;A_2') \left( T^*_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') - \rho_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') T_{\text{cluster}}(A_2;A_2') \right) \\
+ 2\pi i \sum_{\text{cluster term}} \sum_{\text{stable}} \frac{S_{\|B_1\| \|B_1\|}}{S_{\|B_2\| \|B_2\|}} \delta_{\text{cluster}}(A_2;A_2') \delta(E_t - E_f) T^*_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(B_1;B_2) \rho_{\text{cluster}}(B_1;B_2) T_{\text{cluster}}(B_1;B_2). 
\]

(3.25)

As in the nonreactive case, \( \delta_{\text{cluster}} \) the streaming term \([H(\|A_2\|), \ldots] \) vanishes if the density matrix is strictly energy diagonal but is typically retained to describe change on a hydrodynamic scale. Also the existence of well-defined macroscopically local quantities implies that the \( \rho([A_2], t) \) are approximately diagonal in the linear momentum (as well as the total energy). Thus any off-diagonality in \( \rho_{\text{cluster}}(A_2;A_2') \) occurs with respect to the energy degenerate internal states.

To elucidate the physical interpretation of the terms on the right-hand side of Eqs. (3.22), (3.23), and (3.25), we introduce a set of time dependent states \( d(A_2), \delta(A_2), \ldots \) with respect to which \( \rho([A_2], t) \) is diagonal, i.e.,

\[
\rho_{\text{cluster}}(A_2;A_2') = \delta_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2'). 
\]

(3.26)

In the energy and momentum diagonal approximation, these are just (time dependent) mixtures of internal degenerate states.

The first term on the right-hand side of Eq. (3.25) now involves the difference of diagonal components of the Hilbert space \( T \) matrix and its adjoint (or the corresponding channel space difference). Using an appropriate reactive optical theorem, e.g., in the channel space setting\(^5\)

\[
T^*(E) - T^*(E) = -2\pi i T^*(E) \delta(E - \mathcal{H}) T^*(E), \quad (3.27)
\]

one may express this difference as a product of \( T \)-matrix elements. Further, it is convenient to remove the explicit diagonality in the center-of-mass momenta \( p_c \) for \( e() \), etc., of the \( T \) matrices by defining

\[
T_{e^*}^* = T^*_{e^*} \delta(p_e - p_p) \quad \text{and} \quad T_{e^*} = T_{e^*} \delta(p_e - p_p). \quad (3.28)
\]

The following quasiclassical form for the collision terms Eq. (3.25) is then obtained:

\[
\frac{d}{dt} \rho_{\text{cluster}}(A_2) = 2\pi i \sum_{\text{stable}} \sum_{\text{cluster}} \delta_{\text{cluster}}(A_2;A_2') \left( T^*_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') - \rho_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') T_{\text{cluster}}(A_2;A_2') \right) \\
\times \left( -\left| T_{\text{cluster}}(A_2;A_2') \right|^2 \rho_{\text{cluster}}(A_2;A_2') \rho_{\text{cluster}}(A_2;A_2') + \left| T_{\text{cluster}}(B_1;B_2) \right|^2 \rho_{\text{cluster}}(B_1;B_2) \rho_{\text{cluster}}(B_1;B_2) \right). \quad (3.29)
\]

From Eq. (3.29), the interpretation of the first term of the right-hand side as "loss" and the second as "gain" in more general forms of the Boltzmann equation becomes apparent. The appearance of the factor \( S_{\|B_1\| \|B_1\|}/S_{\|B_2\| \|B_2\|} \) is necessary in order that the gain in the number of molecules of types \((A_2)\) and \((A_2')\) and the loss of molecules of types \((B_1)\) and \((B_2)\) from collisions of the type \( \text{balance} \) (see Sec. IV).

IV. STRUCTURE AND PROPERTIES OF THE REACTIVE BOLTZMANN EQUATIONS

Various structural features and properties of the equations derived in the last section are examined here. Sometimes in applications of the nonreactive quantum Boltzmann equation, the collision superoperator is expressed in terms of \( S \) rather than \( T \) matrices.\(^4\) The reactive analog is presented here and used in several formal manipulations. The Wigner transformed version of the reactive Boltzmann equations is also introduced and used to derive coupled reaction diffusion equations for the local species number densities. Microscopic expressions for the local reaction rates then follow and various relationships, including detailed balance, are derived. Conservation of molecular number is also demonstrated consistent with our original assumption.

A. An S-matrix representation of the Boltzmann collision operator

We first introduce the channel space \( S \) matrices corresponding to the \( T \) matrices defined earlier:

\[
S^* = \tilde{S}^* \tilde{S}^* = I + 2\pi i \delta(E - E') T^* \quad (4.1)
\]

and \( T^* \) here may be replaced by \( \tilde{T}^* \). It follows that \(^5\)

\[
S^* S^* = S^* S^* = S^* S^* = S^* S^* = I. \quad (4.2)
\]

It is necessary to introduce some notation for energy diagonal operators \( A^2 \) (i.e., operators commuting with \( \mathcal{H} \)). Since the matrix elements between \( H \) eigenvectors with eigenvalues \( E, E' \) incorporate an energy delta function \( \delta(E - E') \), we may write

\[
A^2 = \delta(E - E') A^2. \quad (4.3)
\]
Thus, e.g.,
\[ T^* = i/2\pi (\mathbf{S}^* - \mathbf{I}), \quad T = -i/2\pi (\mathbf{S}^* - \mathbf{I}) , \] (4.4)
which also defines \( \mathbf{S}^* - \mathbf{I} \) and \( \mathbf{S} - \mathbf{I} \) off shell and from Eqs. (3.19), (3.19), and (3.21) we have
\[ \Omega^*(E) = i/2\pi \sigma((E - H_0^*)^{-1})(\mathbf{S}^* - \mathbf{I}) + \frac{i}{2}\mathbf{S}^* + \mathbf{I}, \] (4.5)
\[ \Omega^*(E) = i/2\pi \sigma((E - H_0^*)^{-1}) + \frac{i}{2}\mathbf{S}^* + \mathbf{I} \].

To obtain the desired form of the Boltzmann equations, we may substitute Eqs. (4.4) and (4.5) into Eq. (3.16) and then Eq. (3.4) canceling Cauchy principal value terms (in an energy diagonal approximation) as done with Eq. (3.23). Alternatively, we may directly substitute Eq. (4.4) into Eq. (3.23) to obtain
\[ i\hbar \frac{\partial}{\partial t} \rho(\mathbf{A}_t) = -[H(\mathbf{A}_t), \rho(\mathbf{A}_t)] \]
\[ + \sum_{\text{stable clusters}} \sum_{\lambda_1, \lambda_2} \text{Tr}(\mathcal{S}_t^*(\mathbf{A}_t)) \rho(\mathbf{A}_t) \mathcal{S}_t(\mathbf{A}_t) , \]
with \( \mathcal{S}_t = \mathbf{S}^* \otimes \mathbf{S}^* \otimes \mathbf{I} \). In the energy diagonal approximation of the right-hand side, the position of the "-" in \( \mathcal{S}_t^* \) can be changed to the operators appearing first. Thus \( \rho(\mathbf{A}_t) \) and \( \rho(\mathbf{A}_t)^* \) satisfy the same equations (and initial conditions) proving that they are identical.

B. The Wigner-transformed version of the reactive Boltzmann equations

For comparison with classical kinetic equations and derivation of various hydrodynamic equations, it is most convenient to start with equations for the species Wigner distribution functions described below. Choose \( d(\mathbf{A}_t) = d(\mathbf{A}_t), p \) where \( p \) is the center-of-mass momentum for cluster \( \mathbf{A}_t \) and \( d(\mathbf{A}_t) \) is a suitable set of labels for the internal states. Define the Wigner distribution function \( f(\mathbf{A}_t)/r, p, t) \) for species \( \mathbf{A}_t \) by
\[ f(\mathbf{A}_t)/r, p, t) = \frac{1}{h^3} \int dq \exp(iq \cdot r/\hbar)p(\mathbf{A}_t)(r, \mathbf{p} + q, t) \rho(\mathbf{A}_t) \]
(4.9)
for which one has the inverse transformation
\[ \rho(\mathbf{A}_t) = \int d\mathbf{p} \exp(-i\mathbf{p} \cdot \mathbf{r}/\hbar)f(\mathbf{A}_t)/\mathbf{r}, \mathbf{p} + q, t) . \] (4.10)
Thus \( f(\mathbf{A}_t)/r, p, t) \) is a function with respect to the center-of-mass-position \( \mathbf{r} \) and momentum \( \mathbf{p} \) and a density matrix with respect to the internal variables.

Applying the transform (4.9) to (3.23), using Eq. (4.10) to introduce \( f^* \)s into the right-hand side, and then evaluating all \( f^* \)s at the same \( \mathbf{r} \), we obtain
\[ \frac{d}{dt} f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t) = \frac{\partial}{\partial t} f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t) + \frac{\partial}{\partial t} f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t) - (\mathbf{r})^T [H_{\mathbf{A}_1}(\mathbf{A}_1), f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t)] \]
\[ - \frac{2\pi h^3}{K} \sum_{\text{stable clusters}} \sum_{\mathbf{A}_1, \mathbf{A}_2} \int d\mathbf{p}_1 d\mathbf{p}_2 d(\mathbf{A}_1) d(\mathbf{A}_2) \rho(\mathbf{A}_1, \mathbf{A}_2, \mathbf{p}_1 + \mathbf{p}_2, t) \left( \frac{\partial}{\partial t} f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t) + f(\mathbf{A}_1)/\mathbf{r}, \mathbf{p}_1, t) - f(\mathbf{A}_2)/\mathbf{r}, \mathbf{p}_2, t) - f(\mathbf{A}_2)/\mathbf{r}, \mathbf{p}_2, t) \right) \]
\[ = \frac{2\pi h^3}{K} \sum_{\text{stable clusters}} \sum_{\mathbf{A}_1, \mathbf{A}_2} \int d\mathbf{p}_1 d\mathbf{p}_2 d(\mathbf{A}_1) d(\mathbf{A}_2) \rho(\mathbf{A}_1, \mathbf{A}_2, \mathbf{p}_1 + \mathbf{p}_2, t) \]
(4.11)
where $M(A_1)$ is the total mass of cluster $(A_1)$, $H_{\text{int}}(\|A_1\|)$ is obtained from $H(\|A_1\|)$ by removing the center-of-mass kinetic energy and $p_{12} = [M(A_1)p_1 - M(A_2)p_2]/[M(A_1) + M(A_2)]$ is the relative momentum of clusters $(A_1)$ and $(A_2)$.

The Wigner transformed version of Eq. (4.6) may also be readily obtained and is used in the next section.

C. Reaction-diffusion equations, chemical rate coefficients, and conservation of molecular number

The number density $n^A(r,t)$ for species $(A)$ at a point $r$ is obtained from

$$n^A(r,t) = Tr [f^A(r,p,t)/M(A)] ,$$

(4.12)

where $Tr(A) = \int dp Tr A$ and the trace is over internal variables. The corresponding species flux density is given by

$$j^A(r,t) = Tr [p f^A(r,p,t)/M(A)] .$$

(4.13)

Applying this operation to the Wigner transformed version of Eq. (4.6), one obtains

$$\frac{\partial}{\partial t} n^A(r,t) + \frac{\partial}{\partial r} \cdot j^A(r,t) = \sum_{\text{stable clusters}} \sum_{A_1 \neq A_2} Tr \left\{ \delta^2(||A_1 A_2||) f^A||A_1 A_2|| - f^A||B_1 B_2|| \right\} ,$$

(4.14)

where $[\text{cf. Eq. (4.11)}]$

$$f^A||B_1 B_2|| = \delta_{||B_1||} \delta_{||B_2||} \delta_{||A_1||} \delta_{||A_2||} f^A||B_1 B_2|| (r,p_1,t) f^A||B_1 B_2|| (r,p_2,t) .$$

(4.15)

After some addition and subtraction of terms, we obtain

$$\frac{\partial}{\partial t} n^A(r,t) + \frac{\partial}{\partial r} \cdot j^A(r,t) = \sum_{\text{stable clusters}} \sum_{A_1 \neq A_2} Tr \left\{ \delta^2(||A_1 A_2||) f^A||A_1 A_2|| - f^A||B_1 B_2|| \right\} ,$$

(4.16)

The $\text{tr}$ in the first term of the right-hand side is the channel space analog of $Tr$ and consequently this term vanishes. In the second sum where $||B_1|| = ||A_1||$ but $||B_2|| = ||A_2||$ we may write $f^A||B_1 B_2|| = \delta_{||A_1||} \delta_{||A_2||} f^A||B_1 B_2||$, where $\delta$ is a permutation operator on atomic labels. This term cancels with the choice $f^A||B_1 B_2|| = \delta_{||A_1||} \delta_{||A_2||}$ in third sum as we have agreement of $S$-matrix elements for these cases. This cancellation occurs since no net change in the number of molecules of type $(A_1)$ results from collisions with such $(A_1)(A_2)$ as products and $(B_1)(B_2)$ as reactants or vice versa.

From this discussion, we conclude that the reaction-diffusion equations have the form

$$\frac{\partial}{\partial t} n^A(r,t) + \frac{\partial}{\partial r} \cdot j^A(r,t) = \sum_{\text{stable clusters}} \sum_{A_1 \neq A_2} S_{A_1 \text{int} A_2} n^A(r,t) ,$$

(4.17)

where the symmetry number $S_{A_1 \text{int} A_2} = 2$, if $||A_1|| = ||A_2||$, and $= 1$ otherwise. The sum $\sum_{\text{int}}^A (B_1)(B_2)$ indicates that we have picked one $(B_1)(B_2)$ labeling from $n^A_{||A_1||} (||A_2||)$ "equivalent" ones for each dynamically equivalent class $j$ of rearrangement collisions (see Appendix B). This decomposition of the source and sink terms in Eq. (4.17) is finer than the usual one which separates only distinct $||B_1|| 
eq ||A_2||$. The forward and reverse local chemical rates $k_f(\cdot)$ and $k_r(\cdot)$ are most conveniently expressed in terms of the normalized local species Wigner distributions

$$j^C||A(A_2) = f^C||A(A_2) n^C||A(A_2) ,$$

(4.18)

as

$$S_{A_1 \text{int} A_2} k_f(B_1)(B_2) - (A_1)(A_2) = n^A_{||B_1||} (||B_2||) f^A||B_1 B_2|| (r,p_1,t) n^A_{||A_1||} (||A_2||) ,$$

(4.19)

where $(B_1)(B_2), (A_1)(A_2)$ is in the $j$th equivalence class and

$$k_f[(B_1)(B_2) - (A_1)(A_2)] = k_f[(B_1)(B_2) - (A_1)(A_2)]$$

(4.20)

using Eq. (B2). This formula does not assume diagonality in the energy degenerate internal states. Further $f^A||A(A_2)$
need not have the equilibrium form.

Of course, it is possible to derive Eq. (4.16) starting with the T-matrix form of the reactive Boltzmann equations, e.g., Eq. (4.11) and using the reactive optical theorem to rewrite the "loss" term. The corresponding expression for \( k_i(\tau) \) from this approach or by rewriting Eq. (4.19) is

\[
S_{A_1A_2} k_i[(B_1)(B_2)] \rightarrow (A_1)(A_2)] = (2\pi \hbar)^2 \delta(E \rightarrow E) \left< \frac{\hat{\delta}(B)}{P_1} \right> \left< \frac{\hat{\delta}(A)}{P_2} \right> \left< \frac{\hat{\delta}(A_1)}{P_1} \right> \left< \frac{\hat{\delta}(A_2)}{P_2} \right> \left< \frac{\hat{\delta}(B_1)}{P_1} \right> \left< \frac{\hat{\delta}(B_2)}{P_2} \right> \ .
\]

(4.21)

The total molecular number density and the corresponding flux density are defined by

\[
n(r, t) = \sum_{\text{stable clusters}} n^{(A)}(r, t), \quad j(r, t) = \sum_{\text{stable clusters}} j^{(A)}(r, t) .
\]

(4.22)

It then follows simply from the reaction-diffusion equations together with Eq. (4.20) that

\[
\frac{\partial}{\partial t} n(r, t) + \nabla \cdot j(r, t) = 0 ,
\]

(4.23)

i.e., conservation of molecular number. A more direct proof is also possible.

For reactive gaseous systems, it is common to assume a separation of chemical and kinetic relaxation time scales. The nonreactive cross sections are typically much larger than the reactive ones so the approach to kinetic equilibrium is correspondingly faster. Consequently

\[
f^{(A)}(r, p_1, t) = \exp(-\beta F(A)(r, p_1, t)) \exp \left[ -\beta \left( \frac{(p_1 + p_2 - M(A_1) + M(A_2)) \omega}{2(M(A_1) + M(A_2))} \right) \right] \]

\[
\times \left[ \frac{(2\pi \hbar)^2}{\beta M(A_1) M(A_2)} \right]^{1/2} \ .
\]

(4.24)

where \( \beta = (kT)^{-1} \), \( Q(A) \) is the internal partition function for the bound states of molecule \( A \), \( u = u(r, t) \) is the streaming velocity of the fluid at the point \( r \) and the reduced mass \( \mu_{A_1 A_2} = M(A_1) M(A_2) / [M(A_1) + M(A_2)] \). Clearly the rate constants are independent of \( u \).

Following the usual arguments\(^{33}\) utilizing "microscopic reversibility" for the \( T \) or \( S \) matrices together with energy conservation through the collision, we obtain the "detailed balance" identities

\[
k_i[(A_1)(A_2)] \rightarrow (B_1)(B_2)] = \left( \frac{\mu_{A_1 A_2}}{\mu_{B_1 B_2}} \right)^{1/2} \frac{Q(A_1) Q(A_2)}{Q(B_1) Q(B_2)} \left< \frac{\hat{\delta}(A_1)}{P_1} \right> \left< \frac{\hat{\delta}(A_2)}{P_2} \right> \left< \frac{\hat{\delta}(B_1)}{P_1} \right> \left< \frac{\hat{\delta}(B_2)}{P_2} \right> \ .
\]

(4.25)

The energies used in calculating the \( Q \)'s are referred to an absolute zero of energy. More commonly the ground state energy for each cluster is used and a modified \( Q \) results. Then we make the replacement

\[
Q(A_1) Q(A_2) = \frac{Q(A_1) Q(A_2)}{Q(B_1) Q(B_2)} e^{\Delta E_g} ,
\]

(4.26)

where \( \Delta E_g \) is the difference between total ground state energies of reactants and products.

V. AN EXAMPLE AND CONCLUDING REMARKS

It is instructive to consider a specific example of a dilute reacting gaseous system to illustrate the various concepts introduced, especially the combinatorial ones. Suppose there are three monatomic constituents denoted \( a, b, c \), and up to six diatomic constituents denoted \( ab, \ldots \) formed from these. We assume that no stable species of more than two atoms exist.

We allow all possible (up to nine) bimolecular reactions with a monatom and a diatom as reactants and products, i.e.,

\[
ab + c \rightarrow ab + b \quad ab + b \rightarrow a + bb \quad a + bc \rightarrow ac + b \quad ac + a \rightarrow aa + cc
\]

(5.1)

\[ab + ac \rightarrow aa + bb \quad bc + b \rightarrow b + cc \]

(5.2)

If the diatoms exist as stable species. In addition, we allow (up to six) bimolecular reactions with two diatoms as reactants and products, i.e.,

\[
ab + ab \rightarrow aa + bb \quad bc + bc \rightarrow bb + cc
\]

(5.3)

The exclusion of breakup implies, e.g., that

\[
ab + c \neq a + b + c \quad ab + ac \neq ab + a + c
\]

(5.4)

The exclusion of long lived activated complexes and of recombination imply, for example, that

\[
a + b \neq ab \quad ab + c \neq ab + c
\]

(5.5)
In presenting the reactive Boltzmann equations, it is convenient to adopt the following diagrammatic notation:
\[
\frac{d}{dt} \langle \hat{d}(a_1) \hat{d}(a_2) \rangle = \left\{ \begin{array}{ll}
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_2) \hat{d}(a_1) \rangle & \left( a_2 \rightarrow b_1 \right) + \left( a_2 \rightarrow c_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( b_1 \rightarrow c_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( a_2 \rightarrow b_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( b_1 \rightarrow c_1 \right) \\
\end{array} \right.
\]

Then for this system, Eq. (3.29) become
\[
\frac{d}{dt} \langle \hat{d}(a_1) \hat{d}(a_2) \rangle = \left\{ \begin{array}{ll}
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_2) \hat{d}(a_1) \rangle & \left( a_2 \rightarrow b_1 \right) + \left( a_2 \rightarrow c_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( b_1 \rightarrow c_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( a_2 \rightarrow b_1 \right) \\
\langle \hat{d}(a_1) \hat{d}(a_2) \rangle + \langle \hat{d}(a_1) \hat{d}(a_2) \rangle & \left( b_1 \rightarrow c_1 \right) \\
\end{array} \right.
\]

and so on. Here ⊕ is used to denote dynamically equivalent collisions. Although only a sample of equations and terms have been given, we have included explicitly all appearances of terms corresponding to the reactions \( a + bb \rightarrow ab + a \), \( c + ab \rightarrow bc + a \), \( aa + bb \rightarrow ab + ab \) and the corresponding reverse reactions. It is thus readily verified that the combinatorial coefficients appearing are consistent with the fact that all of these processes preserve molecular number (as is true for any others).

We illustrate Eq. (4.17) by

\[
\frac{\partial}{\partial t} n^{(a)} + \frac{\partial}{\partial z} \cdot \mathbf{j}^{(a)}
\]

\[
= k_f (a_1 + b_1 c_1 - a_1 b_1 + c_1) n^{(ab)} n^{(c)} - k_r (a_1 b_1 + c_1 - a_1 + b_1 c_1) n^{(a)} n^{(bc)} + k_f (a_1 + b_1 c_1 - a_1 c_1 + b_1) n^{(ac)} n^{(b)}
\]

\[
- k_r (a_1 c_1 + b_1 - a_1 + b_1 c_1) n^{(ab)} n^{(c)} + k_f (a_1 + b_1 c_1 - a_1 + b_1 c_1) n^{(a)} n^{(bc)} + k_r (a_1 b_1 + c_1 - a_1 + a_1 b_1 + b_1) n^{(ac)} n^{(b)}
\]

\[
+ k_f (a_1 + a_2 c_1 - a_1 a_2 + c_1) n^{(a)} n^{(bc)} - k_r (a_1 a_2 + c_1 - a_1 + a_1 c_1) n^{(a)} n^{(bc)} + k_f (a_1 b_1 + a_2 - a_1 b_1 + b_2) n^{(ac)} n^{(b)}
\]

In Eqs. (4.19) and (4.20), have a factor $n(ab, ba) = 2$ (there is only one equivalence class here) since dynamically equivalent $a_1 a_2 b_1 b_2 - a_2 a_1 b_1 b_2$ and $a_1 a_2 b_1 b_2$, $a_1 b_2 b_1 a_2$ produce equal contributions to the rate. For similar reasons a factor of 2 appears in the corresponding expressions for $k_r(a_1 a_2 c_1 - a_2 a_1 c_1)$, $k_r(a_1 c_1 + c_2 - a_1 + c_1 c_2)$, and $k_r(a_1 b_1 + b_2 c_2 - a_1 c_1 + b_1 b_2)$.

In conclusion, we remark that the use of an arrangement channel space representation has enabled us to provide a rigorous derivation of the reactive quantum Boltzmann equations. This derivation is free from built approximations or assumptions in defining chemical composition components of the full density matrix or the reduced species density matrices and free from the rather intuitive extraction of collision terms from the right-hand side of the conventional hierarchy as required previously. A consequence of our approach is that one must use a combinatorially more complex hierarchy and mathematically more sophisticated scattering theory. The resulting Boltzmann equations are more detailed than derived previously as evidenced by the appearance of the combinatorial factors mentioned above.

We have restricted our attention here to model a dilute gaseous system incorporating bimolecular reactions but excluding breakup or recombination. In applying the Boltzmann equations to real systems where breakup and recombination have negligible effect on the kinetics, these processes must be consistently and strictly excluded (modification of the interaction potentials have been described). In practice, we expect to take scattering data for the real system and unitarily truncate this to exclude unwanted channels at the same time preserving all the properties demonstrated in Sec. IV. Future work will be directed towards developing equations incorporating breakup and recombination effects and other features such as the effect of isomerization which may be significant).

APPENDIX A

Given some reactive gaseous system, we describe in Sec. III one method of obtaining a corresponding model system where breakup and recombination are strictly excluded. The idea is to add a suitable $N$-body potential which either (a) restricts the system to part of coordinate space corresponding to some fixed number of molecular clusters (approaching infinity on the rest) or (b) partitions coordinate space into dynamically disconnected regions corresponding to different numbers of clusters. In both cases the potential should be chosen so as not to significantly interfere with the nonreactive and rearrangement bimolecular collision dynamics at thermal energies. Recombination is excluded at all energies but this will not significantly affect the gas kinetics by virtue of the low density and thus low frequency of three-body recombination collisions.

It is important to note that within the context of this model, the blocks $H^0(\|A\|)$ for fixed $\|A\|$ provide representations of the restricted subsystems (to which the blocks $H^0(\|A\|)$ are related) by means of the reduced density matrices (in appropriate asymptotic regions) support an infinite number of bound states in each cluster. By hypothesis, the low lying states (predominantly populated at thermal energies) differ little from the corresponding states of the physical system.

APPENDIX B

Consider the $T$-matrix elements $T^{(A_1)(A_2),(B_1)(B_2)}$. Various labelings of the channels are assigned to equivalence classes by requiring the corresponding $T$'s be dynamically equivalent. For example, if $\sigma$ denotes a permutation of labels of atoms of the same type then $T^{(A_1)(A_2)}$, $T^{(B_1)(B_2)}$ and $T^{(A_1)(A_2)}$, $T^{(B_1)(B_2)}$ are in the same class. This result is used in Eqs. (3.25) and (4.17). There are however other equivalences, e.g., $T^{(A_1)(A_2),(B_1)(B_2)}$ and $T^{(A_1)(A_2),(B_1)(B_2)}$ describe the same process.

Let $S_1(\|A\| \parallel \|B\|)$ denote the number of distinct unordered labelings of clusters with atomic contents $\|A\|$ and $\|B\|$. Thus, $S_1(\|A\| \parallel \|B\|) = S_{A_1A_2A_3A_4}S_{B_1B_2B_3B_4}$, where the symmetry number $S_{A_1A_2A_3A_4}$ is 2, if $\|A\| = \|B\| = 1$ otherwise. We can partition the total number $S_1(\|A\| \parallel \|B\|)$ into sets of labelings $(A_1)(A_2)$, $(B_1)(B_2)$ into these $N(\|A\| \parallel \|B\|)$, say, equivalence classes $j = 1$ to $N$ in two natural ways. First, for some canonical choice of $(A_1)(A_2)$ labelling, appropriately partition the $(B_1)(B_2)$ labellings into sets of $m_j(\|A\| \parallel \|B\|)$.
elements \( j = 1 \) to \( N \) so
\[
\frac{\partial}{\partial t} \mathbf{n}_j(\|A_j\| \|B_j\|) = \mathbf{s}_j(\|B_j\| \|B_j\|).
\]
Thus, allowing all \((A_j|A_j)\) labelings, there are a total of
\[
\mathbf{s}_j(\|A_j\| \|B_j\|) \mathbf{n}_j(\|A_j\| \|B_j\|)
\]
labelings in equivalence class \( j \). Alternatively, for some canonical choice of
\((B_j|B_j)\) labeling, we could appropriately partition the
\((A_j|A_j)\) labelings into sets of \( \mathbf{n}_j(\|A_j\| \|B_j\|)
\]
elements \( j = 1 \) to \( N \). Thus for consistency
\[
\mathbf{s}_j(\|A_j\| \|A_j\|) \mathbf{n}_j(\|A_j\| \|A_j\|) = \mathbf{s}_j(\|B_j\| \|B_j\|),
\]
\( j = 1 \) to \( N \),
\[
\text{e.g.,}
\|
\]
\[
\| A_j \| = ab, \quad \| A_j \| = ac, \quad \| B_j \| = 4,
\]
\[
\| B_j \| = ac, \quad \| B_j \| = bc, \quad \| S_n(abc) \| = 2.
\]
Let \( j = 1 \) include \((a_1b_1c_1)(a_1c_1c_2)(a_2c_1b_2)(b_2c_2)\). Then
\[
\mathbf{n}_1(\|A_j\| \|B_j\|) = 1,
\]
however \( \mathbf{n}_2(\|A_j\| \|B_j\|) = 2 \) since
\[
(a_2b_1c_1)(a_2c_1b_2)(b_2c_2)
\]
is also in this equivalence class.

Here there are only two equivalence classes and \( j = 2 \) includes
\((a_1b_1c_1)(a_1b_2c_1)(a_2b_1c_2)(b_2c_1)\). Thus,
\[
\mathbf{n}_2(\|A_j\| \|B_j\|) = 1,
\]
however \( \mathbf{n}_2(\|A_j\| \|B_j\|) = 2 \) since
\[
(a_2b_1c_1)(a_2b_2c_2)(b_2c_1)
\]
is also in \( j = 2 \).