ASPECTS OF REACTIVE MODERATELY DENSE GAS
QUANTUM KINETIC THEORY

by

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Abstract

This thesis consists of three parts.

In Part I, a two-Liouville space theory of reactive gases is formulated in an effort to understand and by-pass the strong orthogonality approximation standardly used in reactive gas kinetic theories. The formulation is based on a two-Liouville space scattering formalism developed in this thesis. The present work follows an approach very similar to the presentation by Lowry and Snider (J. Chem. Phys. 61, 2320 (1974)). Kinetic equations for arbitrary bound clusters are derived within the structure of the two-Liouville space scattering theory. Bound clusters for an arbitrary number of particles are systematically treated in the present work and defined as the asymptotic bound fragments in the $N$-particle asymptotic Liouville space. A method of closure, which is quite different from the conventional BBGKY procedure, is introduced to yield a compact set of kinetic equations for the clusters. A comparison with the Lowry-Snider theory is given.

In Part II, a Hilbert-Schmidt representation of Ursell operators is given. It is found that the connected quantum Ursell operators are closely related to the Hilbert-Schmidt kernel of Faddeev (for three particles), and its generalization to the description of the collision of an arbitrary number of particles. This important feature permits the formulation of a general Hilbert-Schmidt representation of Ursell operators by expressing the latter in terms of Hilbert-Schmidt kernels. As a consequence, it is seen how the virial coefficients can be evaluated using Hilbert-Schmidt expansions. In particular, second virial coefficient is explicitly expressed in terms of the Hilbert-Schmidt expansion of the resolvent operator. Square integrable states associated with the resonance poles have been found of use in carrying out this expansion. The method depends on distinguishing between the functional analysis properties
of the resolvent operator and the analytic function properties of its matrix elements.

In Part III, a renormalized quantum Boltzmann equation (R. F. Snider, J. Stat. Phys. 61, 443 (1990)) has been generalized to include the presence of bound states. This has involved the introduction of three coupled equations, one each for the renormalized particle, the bound pair and the unbound pair correlations. The latter is responsible, at equilibrium, for the unbound part of the second virial coefficient. Chapman Enskog solutions to this set of equations are obtained in two schemes. One for moderately dense gas in which there are no bound states, the other in the presence of bound states. The Wigner representation for quantum mechanical operators are used throughout to separate the macroscopic and microscopic properties of the state of system. The resulting expressions for the transport coefficients in the first scheme have contributions arising from particles that are free and from pair correlations. In the second, there are also contributions from the bound pairs.
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Preface

On the first days of my arriving at UBC in the summer of 1992, Professor Snider suggested that I generalize his newly obtained renormalized quantum Boltzmann equation to include the presence of bound states for a moderately dense reactive gas system. This is equivalent to the introduction of pair correlations into the Lowry-Snider theory of reactive gases. In that theory, as well as in other formal theories of reactive gases, such as those by Klimontovich and by McLennan, a channel strong orthogonality assumption is standardly used. An exception to this practice is the rigorous two-Hilbert space reactive gas theory of Hoffman, Kouri and their coworkers. That theory does not depend on the channel strong orthogonality assumption but is based on the BKLT scattering theory, which is different from the scattering theory used by Lowry and Snider, and others. Motivated by the two-Hilbert space treatment, this thesis develops a two-Liouville space reactive gas theory in an effort to understand and by-pass the strong orthogonality approximation. This is the content of Part I of this thesis.

It was soon realized that in order to treat the pair correlations on an equal footing with the free singlets and the bound pairs in a reactive gas theory, it was needed to develop a time dependent multichannel scattering theory that might include a correlated pair as a colliding partner. In particular, a hamiltonian governing the time evolution of a correlated pair is first required. Since at equilibrium pair correlations are related to the resonance poles of the S-matrix, the theory of resonance scattering was examined in hope of identifying a hamiltonian for a correlated pair. Not very much progress has been made in developing a multichannel scattering theory that might describe the collision of a correlated pair with another fragment. Nevertheless
a Hilbert-Schmidt representation of equilibrium pair correlations through the Ursell operator was found, and a set of non-classic square integrable states associated with the resonance poles of the resolvent operator was identified in this process. These results are presented in Part II.

Progress in formulating a moderately dense reactive gas kinetic theory was made in the summer of 1995. The original difficulty of incorporating a correlated pair as a collision partner was by-passed by introducing the concept of interacting pairs through an exact operator relation, Kato's chain rule, which was later found to be identical to what Snider and Lowry had discovered in formulating their quantum kinetic theory of dimer recombination and decay. Also in that summer, a previously introduced solution to the renormalized quantum Boltzmann equation was reexamined and improved by introducing a separate equation for the pair correlations. This solution, together with the solution and transport coefficients for the case where there are bound states, is presented in Part III.
Part I

A Two-Liouville Space Quantum Kinetic Theory of Reactive Gases
A typical gas contains $N \sim 10^{23}$ particles. A quantum mechanical first principles description of the time dependence of such a gas necessarily involves the time-dependent Schrödinger equation\(^1\), or equivalently the quantum Liouville equation\(^2\), of $N$ particles, which in practice is unsolvable. Quantum kinetic theory provides a simplified description of the $N$-particle reactive gas in terms of reduced density operators, in particular the singlet and pair density operators. The time evolution of the reduced density operators is usually assumed to be completely describable in terms of free motion and few-body scattering theory. With an appropriate closure assumption, such as assuming only binary collisions and molecular chaos, a closed kinetic equation can be derived, for example the Boltzmann equation\(^3\), from the $N$-particle quantum Liouville equation. Equations for macroscopic variables (such as the hydrodynamic equations) can be derived from the kinetic equations. Expressions for the macroscopic transport coefficients, such as the viscosity and thermal conductivity, in terms of microscopic properties of atoms or molecules, then follow from the hydrodynamical equations.

In a chemically reactive gas system one usually deals with not only monomers but also dimers, trimers etc., here generally referred to as clusters. Thus an appropriate description requires a set of kinetic equations for the time evolution of the clusters. A new problem is that chemical reactions can interchange the identities of the various chemical species, which makes a fundamental treatment of the system not only technically demanding, but also conceptually difficult. A multichannel quantum scattering theory\(^4\) is then required to describe the various types of collision processes such as elastic,
break up and rearrangement collisions, which may occur in the reactive gas system.

Faddeev\textsuperscript{5} pointed out that the three-body Lippmann-Schwinger\textsuperscript{6} equation does not have a unique solution for energies higher than the two-particle threshold because at such energies the homogeneous equation has binary scattering state solutions. From the point of view of the theory of integral equations, the kernel of the Lippmann-Schwinger equation becomes non-compact under these conditions and the equation is no longer of Fredholm type\textsuperscript{7}. Faddeev has resolved the problem by dividing the three-body scattering system into a combination of rearrangement channels. As a result, the kernel of Faddeev's equation is compact, or in diagrammatical language, connected\textsuperscript{8} (after an iteration). Kouri and coworkers\textsuperscript{9} have generalized Faddeev's idea of channel divisions and developed a systematic method to produce a set of integral equations, the BKLT equations, whose kernels are connected for an arbitrary number of particles. The application of the Faddeev scattering theory to kinetic theory was first considered by Lowry and Schieve\textsuperscript{10}.

Another problem in the multichannel scattering theory is that different rearrangement channels are in general not orthogonal to each other\textsuperscript{11,12}. In particular, the set of states for the unbound three-particle channel span the total Hilbert space of the three particles. Consequently that channel cannot be orthogonal to any other channel. An intuitive treatment for solving such a non-orthogonality problem is to assume strong orthogonality. This is often adopted in multichannel scattering theory. However, such a problem can be handled rigorously by introducing a two-Hilbert space scattering formalism, whose abstract theory has been developed by Kato\textsuperscript{13}, Birman\textsuperscript{14}, and by Chandler and Gibson\textsuperscript{12}.

The kinetic theory of chemically reactive gases is an old subject\textsuperscript{15,16}. But
the formal kinetic theory of reactive gases in terms of reduced density operators and multichannel scattering theory was not considered until the early seventies, partly due to technical difficulties. Olmsted and Curtiss\textsuperscript{17} treated the presence of bound states as a perturbation to the pair particle distribution functions. Eu\textsuperscript{18} has considered a gas mixture at sufficiently low energy that three-particle breakup does not occur but three-body rearrangement collisions are important. A three-body collision operator with bound state effects has also been constructed by McLennan\textsuperscript{19}. Klimontovich \textit{et al.}\textsuperscript{20} have formulated a reactive fluid theory at the three-body level. In most of the above-mentioned work, Bogoliubov's factorization ansatz\textsuperscript{21} has been adopted to close the BBGKY equations\textsuperscript{21,22} at an appropriate level. A kinetic theory of a dimer and monomer mixture has been treated by Lowry and Snider\textsuperscript{23,24}. They introduced a novel counting procedure to obtain reduced density operators from the $N$-particle density operator in a consistent manner, which reflect the presence of monomers and dimers. A reactive Boltzmann ansatz has been developed to close the kinetic equations in an appropriate way to end up with two kinetic equations of Waldmann-Snider\textsuperscript{25,26} type. Hoffman, Kouri and coworkers\textsuperscript{27,28} formulated a rigorous reactive quantum fluid theory in terms of the BKLT scattering theory\textsuperscript{9}. Their theory reduces to that of Lowry and Snider\textsuperscript{23} at the appropriate level of approximation. Of most immediate concern for the present work is the non-orthogonality problem, a problem whose existence in kinetic theory was first recognized by Lowry and Snider\textsuperscript{23}.

Most formal reactive gas kinetic theories employ the conventional one-Hilbert space multichannel scattering theory and thus must deal with the non-orthogonality problem. Moreover, the non-orthogonality problem manifests itself in kinetic theory in a more complicated manner than it does
in scattering theory. The role of the non-orthogonality problem in kinetic theory is twofold. First is the scattering channel non-orthogonality in the conventional multichannel treatment. Second is more profound, in that it concerns the validity of the kinetic description. The problem is whether the $N$ interacting particles can really be factorized into many mutually isolated few-particle clusters at a particular time. An intuitive approximation used by Lowry and Snider$^{23}$ is the strong-orthogonality assumption, which essentially assumes that this can be done and so simplifies the structure of the kinetic equations. Such an approximation appears physically reasonable for a dilute gas system. However the strong-orthogonality approximation is inherently in error and its continued use could hinder one's further understanding of the kinetics of a reactive gas system. Particularly so for a reactive moderately dense gas system, where the number of conceptual and technical problems increases dramatically. Thus it is necessary to have a good understanding of the role of non-orthogonality in kinetic theory before one approaches more intricate problems. Since this thesis deals with aspects of reactive moderately dense gas kinetic theory, a part of this project is to analyze and hopefully remove the non-orthogonality problem in kinetic theory. The present approach, partly motivated by the work of Hoffman and Evans$^{29,30}$, is mainly through a two-Liouville space scattering theory. To this end, Part I is devoted to a two-Liouville space theory of reactive gases which aims at removing the strong-orthogonality approximation used by Lowry and Snider.

Part I is divided into three chapters. A two-Liouville space scattering theory is formulated in Chapter I-2. The purpose of such a formulation is to develop a rigorous formalism appropriate for kinetic theory applications. The formulation is guided by existing physical scattering theory in superoperator notation$^{31,32,23}$, rather than emphasizing mathematical theorems and
proofs. Since the two-Liouville space scattering theory is based on a two-Hilbert space scattering theory, it is necessary to discuss the latter first. Thus a two-Hilbert space scattering theory is also presented in Chapter 1-2, both to establish notation and to clarify the various concepts. Notably the asymptotic Hilbert space is distinguished from the total Hilbert space and the bound fragments are defined only in the asymptotic space. The two-Liouville space scattering formalism provides a sound basis on which to formulate a two-Liouville space reactive gas kinetic theory. This is done in Chapter 1-3. The present work has thus removed the strong-orthogonality approximation used by Lowry and Snider with clusters defined rigorously in the asymptotic space. Clusters for an arbitrary number of particles are systematically treated in the present work. Such a generalization might be applicable to molecular beam induced metal cluster dynamics, where metal clusters of 2-10 particles or larger are frequently encountered\textsuperscript{33,34}. The Lowry-Snider counting procedure is relevant for the asymptotic channel reduction. A method of closure, which is quite different from the conventional BBGKY procedure but is analogous to that of Lowry and Snider, is introduced to yield a compact set of kinetic equations for the clusters. A comparison with the Lowry-Snider theory is given in a discussion.
A two-Liouville space scattering theory is formulated in this chapter after introducing a two-Hilbert space scattering theory. Abstract two-Hilbert space theories have been formulated by Kato$^{13}$, Chandler and Gibson$^{12}$ and others$^{35,14}$. There is a certain flexibility in selecting identification operators and channel spaces, and more so in the case of an application to a particular problem. The theories have been successfully applied to equilibrium statistical mechanics by Osborn and co-workers$^{36}$, with care being exerted to obtain connected kernels in the time independent formalism as emphasized by Faddeev$^5$. For kinetic theory applications it is necessary to develop a two-Liouville space scattering theory because quantum kinetics is conveniently described in Liouville spaces, due to the presence of statistical mixed states. This formulation involves a number of technical problems such as the definition of appropriate operator spaces and superoperators. The selection of superoperators is not unique, and physical considerations are indispensable for making a useful choice. The trace class topological norm discussed by Jauch and co-workers$^{31}$, and by Snider and Sanctuary$^{32}$ for single channel scattering theory in operator space has been adopted and certain physical arguments about asymptotic channel diagonality are assumed in order to obtain a two-Liouville space theory in a manner consistent with existing Liouville space multichannel scattering treatments$^{23}$. Transition superoperators are not defined as in the original work of Chandler and Gibson but rather in a manner convenient for application to kinetic theory. The resulting two-Liouville space formalism provides a suitable basis for gas kinetic theory, clarifying various concepts and simplifying the structure of the kinetic
This Chapter is divided into four sections. Section I-2.1 is devoted to the kinematical description of the channels and their spaces. In addition to the usual $n$-particle Hilbert space, the notion of channels and asymptotic channels, together with their associated channel spaces and asymptotic channel spaces, are introduced both from a mathematical and from a physical point of view. The difference between a channel and an asymptotic channel arises as to whether the independent fragments defining the channel are not or are bound fragments. Identification operators mapping asymptotic channel spaces to channel spaces have been introduced to connect the two kinds of spaces. A time dependent two-Hilbert space scattering theory is described in Section I-2.2 with the emphasis on Møller operators and scattering operators. The proof of the existence of the Møller operators and their adjoints is beyond the scope of this work, depending usually on completeness conditions, so the existence of such operators is assumed. However, a brief discussion of asymptotic completeness is given in order to enhance the physical understanding of the problem. A two-Liouville space scattering theory is formulated in Section I-2.3. This formalism is mainly guided by the chemical conceptualization of the problem rather than by mathematical arguments and proofs. The notation is chosen to be appropriate for kinetic theory application. Various Møller superoperators as well as transition superoperators are of primary importance for kinetic theory and this is the main objective of the development. Some discussions are collected in Section I-2.4.

I-2.1 Kinematics of Multichannel Scattering

a) The $n$-particle Hilbert Space $\mathcal{H}^{(n)}$
Consider a system of \( n \) indistinguishable particles. Its time dependence is governed by a self-adjoint hamiltonian \( H^{(n)} \) generating a one-parameter strongly continuous abelian group of unitary evolution operators

\[
U^{(n)}(t) = \exp(-iH^{(n)}t),
\]

where and throughout this chapter \( \hbar \) is set equal to 1. The hamiltonian consists of a kinetic energy operator \( K^{(n)} \) and a potential operator \( V^{(n)} \), which is assumed to be pairwise additive and of short range,

\[
\begin{align*}
H^{(n)} &\equiv K^{(n)} + V^{(n)} \\
&= K^{(n)} + \sum_{i>j} V_{ij}.
\end{align*}
\]

These operators act on a Hilbert space \( \mathcal{H}^{(n)} \) which can be regarded as the linear span of all square integrable functions \( \Psi^{(n)} \) of \( \mathbb{R}^{3n} \) or more generally as the direct product

\[
\mathcal{H}^{(n)} = \bigotimes_{i=1}^{n} \mathcal{H}_i,
\]

of the separable Hilbert spaces \( \mathcal{H}_i \), one for each particle \( i \).

**b) Channel Hilbert Spaces \( \mathcal{H}_{C^n} \)**

For an \( n \) indistinguishable particle system there are many topologically distinct ways to divide the labelled \( n \) particles into sets of particles, generally referred to here as fragments. These mathematical divisions are in a sense just like the partitioning of the cluster expansion of the partition function for a *monatomic gas*. Each particular way of partitioning the \( n \) particles will be called a clustering and its result constitutes a rearrangement channel \( C^n \). Each channel \( C^n \) has a set of \( l \) fragments (sets of particles) and each
fragment will at times be called a subchannel, denoted as $C^{n}_m$, so that

$$C^n = \{C^n_1, \ldots, C^n_m, \ldots, C^n_l\} \equiv \{C^n_m\}. \quad (1.4)$$

Each fragment consists of a set of labelled particles, $C^n_m = \{i, j, \ldots, s\}$ (which could be just a single labelled particle). There are channel hamiltonians and channel spaces. A channel hamiltonian $H_{C^n}$ is given by the kinetic energy operator $K^{(n)}$ and mutual potential interactions among the particles within each fragment.

$$H_{C^n} \equiv K^{(n)} + \sum_{C^n_m} \sum_{k>j} V_{jk}, \quad \forall j, k \in C^n_m$$

$$= \sum_{m=1}^{l} H_{C^n_m}$$

$$= \sum_{C^n_m} H_{C^n_m}, \quad (1.5)$$

where the last form emphasizes a summation convention. In general the channel hamiltonian $H_{C^n}$ acts on a subspace $\mathcal{H}_{C^n}$ of the full Hilbert space $\mathcal{H}^{(n)}$.

$$\mathcal{H}_{C^n} \subseteq \mathcal{H}^{(n)}. \quad (1.6)$$

These channel subspaces $\mathcal{H}_{C^n}$ are in general not orthogonal to each other, that is, there are states

$$\Psi_{C^n} \in \mathcal{H}_{C^n} \quad \text{and} \quad \Psi_{D^n} \in \mathcal{H}_{D^n}, \quad (1.7)$$

such that

$$\langle \Psi_{C^n} | \Psi_{D^n} \rangle \neq 0. \quad (1.8)$$

In particular, the subspace for the channel that has $n$ fragments ($n$ non-interacting particles) is identical to the total Hilbert space $\mathcal{H}^{(n)}$, thus it can not be orthogonal to any other channel space.
c) Asymptotic Channel Spaces $H_{C^n}$

It is necessary to introduce certain important concepts for our further discussion of two-Hilbert space scattering theory. First is the concept of asymptotic. The word *asymptotic* means times long before all fragments enter inter-fragment interacting regions or long after all fragments exit inter-fragment interacting regions. The mathematical time limits $t \to \mp \infty$ are appropriately associated with asymptotic. Second is the concept of a bound fragment. A bound fragment is a fragment that does not break up asymptotically. Third is the concept of an asymptotic channel. An asymptotic channel is a channel that has only bound fragments. For simplicity let us consider only a single bound state in each bound fragment. Therefore each asymptotic channel can be characterized by a set of freely moving bound fragments, which are described by a one-parameter unitary group

$$U_{C^n}(t) = \exp(-iH_{C^n}t) = \exp(-iH_{C^n}t) \otimes \cdots \otimes \exp(-iH_{C^n}t),$$

where the asymptotic channel hamiltonian $H_{C^n}$ is the kinetic energy operator $K_{C^n}$ modified by a constant $\varepsilon_{C^n}$ corresponding to the sum of binding energies of bound fragments in the asymptotic channel $C^n$

$$H_{C^n} = \sum_{m=1}^{l} (K_{C_m} - \varepsilon_{C^n}) \quad \forall j, k \in C^n$$

$$= K_{C^n} - \varepsilon_{C^n},$$

and has an absolutely continuous spectrum. $H_{C^n}$ is a self-adjoint operator whose domain is dense in a separable Hilbert space $H_{C^n}$ which consists of all $L^2$ functions $\Phi_{C^n}$ in $R^{3l}$, with $l$ the number of fragments in the asymptotic channel $C^n$. $H_{C^n}$ has form

$$H_{C^n} = \bigotimes_{C_m^n} H_{C_m^n} \quad \forall C_m^n \in C^n,$$
where $H_{C^n}$ is an asymptotic fragment Hilbert space which is a linear span of all square integrable functions in $R^3$. The asymptotic hamiltonian $H_{C^n}$ has a simpler structure than that of the channel hamiltonian $H_{C^n}$ due to the assumption of a single bound state for each bound fragment.

It is to be understood from the strongly continuous group Eq.(1.9) that the asymptotic channel evolution will not mix one asymptotic channel with another one. If channel mixing does happen, the process can no longer be treated as an asymptotic one. This lack of mixing among the different asymptotic channels implies their mutual orthogonality. To further understand this asymptotic channel orthogonality, one offers the following two arguments: i) Experimentally one can only prepare the state of an $n$ particle system at one single channel at a time and physical observations always confirm that the state of the system ends up in only one particular asymptotic channel after scattering, thus the state of the system can not asymptotically be in more than one channel at a time\(^{35}\), thus requiring the asymptotic channel spaces to be mutually orthogonal. ii) At asymptotic times, the particles belonging to different fragments are so far apart that their corresponding potential interactions dies out as a strong operator limit, thus the different asymptotic channels are orthogonal to each other. This picture of asymptotic physical separation may be helpful for the understanding of asymptotic orthogonality. The orthogonality of asymptotic channel spaces follows rigorously from the scattering boundary condition which requires the role of the asymptotic hamiltonian (the vanishing of certain potential interactions) and a time limiting process [see Eq. (1.25)].

Since the difference between a channel and an asymptotic channel lies in the difference between whether the fragments are not or are bound, It is important to noted that except for the $n$-body total bound states, no other
bound state of fewer particles is uniquely defined in the $n$-particle Hilbert space $\mathcal{S}^{(n)}$. A bound state with fewer than $n$ particles is only uniquely defined in an appropriate subspace $\mathcal{S}_{C_m}^{(n)}$ where the associated hamiltonian $H_{C_m}^{(n)}$ has a unique spectral decomposition. For example the bound pair (12) is uniquely defined in the two particle space $\mathcal{S}_{12}^{(2)}$. Consequently, except for the $n$-body total bound states, the bound state projections in the $n$-particle Hilbert space $\mathcal{S}^{(n)}$ are not mutual orthogonal and the spectral decompositions of $H^{(n)}$ according to bound states in $\mathcal{S}^{(n)}$ are not unique. Thus, the identity of a bound state of fewer than $n$ particles in the Hilbert space $\mathcal{S}^{(n)}$ is not strictly valid. In contrast, the bound fragment is defined through the notion of asymptotic in an appropriate subspace $H_{C_m}^{(n)}$ where the associated hamiltonian $H_{C_m}^{(n)}$ has a unique spectral decomposition. The asymptotic channel spaces are mutually orthogonal and bound fragments are uniquely defined objects only in the asymptotic channel space.

**d) The Asymptotic Space $H^{(n)}$**

In order to make multichannel scattering theory appear simple and conceptually concise, it is convenient to construct an asymptotic space, which is the direct sum of all asymptotic channel spaces

$$H^{(n)} = \bigoplus_{C_n} H_{C_n}, \quad \forall C_n \in C^n$$

where $C^n$ is a collection of all asymptotic channels. It is this construction that leads to the two-Hilbert space scattering theory. A function in $H^{(n)}$ consists of a direct sum of functions in each asymptotic channel

$$\Phi^{(n)} = \bigoplus_{C_n} \Phi_{C_n}, \quad \forall \Phi_{C_n} \in H_{C_n}.$$
An asymptotic hamiltonian is defined through the asymptotic channel hamiltonians and the concept of asymptotic space

\[
H^{(n)} \Phi^{(n)} = \bigoplus_{C^n} H_{C^n} \Phi_{C^n}.
\] (I.14)

e) Identification Operators

In order to relate the asymptotic space \( H^{(n)} \) to the familiar \( n \)-body Hilbert space \( \mathcal{H}^{(n)} \), a linear identification operator \( J^{(n)} \) is defined, which maps \( H^{(n)} \) into \( \mathcal{H}^{(n)} \)

\[
J^{(n)} : H^{(n)} \rightarrow \mathcal{H}^{(n)},
\] (I.15)
as

\[
J^{(n)} \Phi^{(n)} = \sum_{C^n} \Psi_{C^n},
\] (I.16)

where \( \Psi_{C^n} \) are functions in the channel Hilbert space \( \mathcal{H}_{C^n} \) [see Eq. (I.7)]. The identification operator also maps the domain of \( H^{(n)} \) into the domain of \( H^{(n)} \),

\[
J^{(n)} : D(H^{(n)}) \rightarrow D(H^{(n)}),
\] (I.17)

while the adjoint operator

\[
J^{(n)^\dagger} : \mathcal{H}^{(n)} \rightarrow H^{(n)}
\] (I.18)
is then a bounded linear operator.

The detailed channel structure can be emphasized by defining a channel identification operator

\[
J_{C^n} : H_{C^n} \rightarrow \mathcal{H}^{(n)},
\] (I.19)
according to

\[
J_{C^n} \Phi_{C^n} = \Psi_{C^n},
\] (I.20)
and its adjoint
\[ J_{C^n}^\dagger : \mathcal{H}^{(n)} \rightarrow H_{C^n}. \]  

Specifically \( J_{C^n} \) is related to \( J^{(n)} \) by
\[
J^{(n)} \Phi^{(n)} = \sum_{C^n} J_{C^n} \Phi_{C^n} = \sum_{C^n} \Psi_{C^n}. \]

This completes the kinematical descriptions of the channels and spaces in an \( n \) indistinguishable particle system. A two-Hilbert space scattering theory is to be introduced by using this structure.

### 1-2.2 A Two-Hilbert Space Scattering Theory

The purpose of a theory is to describe and predict experimental observations. The processes of a scattering experiment are the following: i) prepare particles in a certain asymptotic channel far from the interaction region; ii) let the particles (fragments) collide with each other in the interaction region; iii) observe the final state of the particles and note what transition or rearrangement has occurred. Observations are conducted in a region where the mutual interaction among different asymptotic channels, denoted as \( V_{C^n,D^n} \), die out in a strong operator limit associated with the time limit
\[
\lim_{t \to \pm \infty} ||V_{C^n,D^n}|| \rightarrow 0. \]

The observations are described by a set of self-adjoint operators \( D^{\pm}_{C^n} \) with domain dense on the scattering subspace \( \mathcal{H}^{(n)}_{\infty} \)
\[
\mathcal{H}^{(n)}_{\infty} = \mathcal{H}^{(n)} \ominus \mathcal{B}^{(n)}. \]
where \( \mathfrak{A}^{(n)} \) is the subspace of the \( n \)-particle total bound states, such that
\[
\forall \Psi \in \mathfrak{H}^{(n)}
\]
\[
D^\pm_{C_n} \Psi = \begin{cases} 
\Psi & \text{if } \exists \Phi_{C_n} \in H_{C_n}, \lim_{t \to \infty} \| U(t) \Psi - U(t) \Phi_{C_n} \| \to 0 \\
0 & \text{otherwise}
\end{cases}
\tag{1.25}
\]

Physically \( D_{C_n}^- \) is an observable which verifies whether a scattering state \( \Psi \) will asymptotically develop into a state in the asymptotic channel \( C^n \). Whereas \( D_{C_n}^+ \) is an observable which verifies that if a scattering state \( \Psi \) has asymptotically evolved from a state in asymptotic channel \( C^n \). Eq. (1.25) will be referred to as the scattering boundary condition. Under the same scattering boundary condition different asymptotic channel spaces are mutually orthogonal.

\( Q^\pm_{C_n} \) are sets of orthogonal spectral projections of \( D^\pm_{C_n} \)
\[
Q^+_C Q^-_B = Q^-_C Q^+_B = \delta_{C_n,B_n}
\tag{1.26}
\]

With these spectral projection operators \( Q^\pm_{B_n} \) it is not necessary to refer to the physical observables \( D^\pm_{C_n} \) any further. A central problem in scattering theory is to prove the asymptotic completeness condition
\[
\sum_{C_n} Q^+_C = \sum_{C_n} Q^-_C
\tag{1.27}
\]

and the strong completeness condition (asymptotic condition)
\[
\sum_{C_n} Q^+_C = \mathfrak{H}^{(n)} = \sum_{C_n} Q^-_C.
\tag{1.28}
\]

These are the most difficult problems in scattering theory. We will not go into the details of the proofs but sketch out the following physical aspects of these conditions. Physically the particles are prepared in an initial channel (set of fragments) and end up in a final channel at a time asymptotically
after the collision Eq.(1.25). An immediate consequence is that the different channels are mutually exclusive asymptotically and the evolution of the states in a channel is governed by the asymptotic channel evolution operator Eq.(1.9). The justification of these statements depend certainly on the form of the potentials. Moreover the set of subspaces, Eq.(I.11), associated with the evolution group, Eq.(I.9), is sufficiently large so as to accommodate all scattering states asymptotically. These completeness conditions imply the existence of channel Møller operators

$$\Omega_{C^n}^\pm \equiv \lim_{t \to \pm \infty} e^{iH^{(n)}_C}J_{C^n}e^{-iH^{(n)}_C}.$$  

(I.29)

The channel Møller operator $\Omega_{C^n}^\pm$ maps an incoming state $\Phi_{C^n}^\pm$ into a scattering state $\Psi_{C^n}^{(+)}$.

The ranges $R(\Omega_{C^n}^\pm)$ are mutually orthogonal subspaces of $\mathcal{H}_{\infty}^{(n)}$.

$$\sum_{C^n} \Omega_{C^n}^\pm \Omega_{D^n}^\pm = \sum_{C^n} Q_{C^n}^\pm \delta_{C^n,D^n} = \mathcal{H}_{\infty}^{(n)}. $$  

(I.30)

The asymptotic channels are orthogonal to each other

$$\Omega_{C^n}^\pm \Omega_{D^n}^\pm = P_{C^n}^\pm \delta_{C^n,D^n}, $$  

(I.31)

where $P_{C^n}^\pm$ are asymptotic channel projection operators and defined on the asymptotic space $H^{(n)}$. The $P_{C^n}^\pm$ are mutually orthogonal to each other

$$P_{C^n}^\pm P_{D^n}^\pm = P_{C^n}^\pm \delta_{C^n,D^n}, $$  

(I.32)

It is useful to define a Møller operator $\Omega_{\pm}^{(n)}$ mapping from Hilbert space $\mathcal{H}^{(n)}$ to asymptotic Hilbert space $H^{(n)}$.

$$\Omega_{\pm}^{(n)} \equiv \lim_{t \to \pm \infty} e^{iH^{(n)}_j}J^{(n)}e^{-iH^{(n)}_j}. $$  

(I.33)
The Møller operator $\Omega_+^{(n)}$ ($\Omega_-^{(n)}$) maps an incoming (outgoing) state $\Phi_+^{(n)}$ ($\Phi_-^{(n)}$) into a scattering state $\Psi_+^{(n)}$ ($\Psi_-^{(n)}$)

$$\Psi_+^{(n)} = \Omega_+^{(n)} \Phi_+^{(n)}.$$  \hfill (I.34)

These Møller operators have properties such as partial isometry

$$\Omega_\pm^{(n)\dagger} \Omega_\pm^{(n)} = I^{(n)},$$  \hfill (I.35)

and completeness

$$\Omega_\pm^{(n)} \Omega_\pm^{(n)\dagger} = Q_n^{(n)},$$  \hfill (I.36)

where $I^{(n)}$ is the identity on $H^{(n)}$ and $Q_n^{(n)}$ is an orthogonal projection of $S_n^{(n)}$ onto the range $R(\Omega_\pm^{(n)})$ of the Møller operator.

In parallel to Eq.(I.22), two types of Møller operators $\Omega_{C^n}^{\pm}$ and $\Omega_\pm^{(n)}$ are related to each other by

$$\Omega_\pm^{(n)} = \sum_{C^n} \Omega_{C^n}^{\pm}.$$  \hfill (I.37)

In the two-Hilbert space formalism the scattering operator is defined $S^{(n)} : H^{(n)} \rightarrow H^{(n)}$ in a manner similar to its definition in a single channel scattering theory

$$S^{(n)} = \Omega_-^{(n)\dagger} \Omega_+^{(n)}.$$  \hfill (I.38)

The channel scattering operators $S_{C^n,D^n} : H_{D^n} \rightarrow H_{C^n}$ are defined as

$$S_{C^n,D^n} = \Omega_{C^n}^{-1\dagger} \Omega_{D^n}^+.$$  \hfill (I.39)

The operators $S_{C^n,D^n}$ are the channel matrix elements of the scattering operator $S^{(n)}$

$$S^{(n)} = \bigoplus_{C^n,D^n} S_{C^n,D^n}.$$  \hfill (I.40)
The unitarity of the $S^{(n)}$ requires that

$$
S^{(n)}S^{(n)\dagger} = \bigoplus_{A^n,B^n} S_{A^n,B^n} S_{C^n,D^n}^\dagger \\
= \bigoplus \Omega_{A^n}^\dagger (I^{(n)} - Q_{b^n}) \Omega_{C^n} \\
= \bigoplus P_{A^n}^\dagger \delta_{A^n,B^n} \\
= I^{(n)}, \tag{1.41}
$$

$$
S^{(n)\dagger}S^{(n)} = \bigoplus_{A^n,B^n} S_{A^n,B^n}^\dagger S_{C^n,D^n} \\
= \bigoplus \Omega_{A^n}^\dagger (I^{(n)} - Q_{b^n}) \Omega_{C^n}^\dagger \\
= \bigoplus P_{A^n}^\dagger \delta_{A^n,B^n} \\
= I^{(n)}, \tag{1.42}
$$

where $Q_{b^n}$ is the $n$-particle totally bound state projection operator. $I^{(n)}$ is the identity operator in space $\mathcal{H}^{(n)}$. Eqs.(1.30), (1.31) and (1.39) have been used.

One of the advantages of the two-Hilbert space scattering theory is that the multichannel scattering theory looks like single channel scattering theory. It is to be mentioned that the center-of-mass motion can be systematically removed without changing the structure of the theory.

These are the essentials of two-Hilbert space theory. The next section deals with a Liouville space generalization of the two-Hilbert space theory.

**I-2.3 A two-Liouville Space Scattering Theory**

A two-Liouville space scattering formalism suitable for kinetic theory is developed in this section. Based on the various hamiltonians and associated spaces introduced in the last section, the corresponding Liouville operators and their associated Liouville spaces are defined first, followed by various
evolution superoperators. A Møller superoperator is constructed after giving an identification superoperator and its adjoint. A non-symmetrical transition superoperator is defined from an asymptotic Liouville space back to itself, a form which is different from the multichannel treatment usually used in kinetic theory. Such non-symmetrical transition superoperators are found convenient for formulating kinetic theory in the asymptotic channel Liouville spaces, see Chapter I-3. Finally channel Møller superoperators and various channel transition superoperators are defined in a manner suitable for kinetic theory descriptions.

A Liouville operator is a linear superoperator defined through the full hamiltonian $H^{(n)}$

$$L^{(n)}\rho^{(n)} \equiv H^{(n)}\rho^{(n)} - \rho^{(n)}H^{(n)},$$

(1.43)

where the density operator $\rho^{(n)}$ is an operator on the Hilbert space $\mathcal{H}^{(n)}$. As discussed by Jauch and co-workers$^{31}$, and by Snider and Sanctuary$^{32}$, a trace norm for $\rho^{(n)}$

$$\text{Tr}\rho^{(n)} < \infty \quad \forall n < \infty$$

(1.44)

is crucial both to the existence of Møller superoperators and to the convergence of kinetic operators. Here $\rho^{(n)}$ is assumed to be a trace class operator on the Hilbert space $\mathcal{H}^{(n)}$. The linear span of all operators $\rho^{(n)}$ on $\mathcal{H}^{(n)}$ defines a Liouville space $\mathcal{L}^{(n)} = \mathcal{H}^{(n)} \otimes \mathcal{H}^{(n)}$. The set of density operators $\rho^{(n)} \in \mathcal{L}^{(n)}$ forms a convex subset of $\mathcal{L}^{(n)}$ and has the form of $\mathcal{H}^{(n)} \otimes \mathcal{H}^{(n)}$.

It is natural to further define a channel Liouville operator through the channel hamiltonian $H_{C^n}$

$$L_{C^n}\rho_{C^n} \equiv H_{C^n}\rho_{C^n} - \rho_{C^n}H_{C^n},$$

(1.45)

where channel density operator $\rho_{C^n}$ is a trace class operator on the channel Hilbert space $\mathcal{H}_{C^n}$ equivalently an element of the channel Liouville space.
\( \mathcal{L}_{C^n} = \mathcal{H}_{C^n} \otimes \mathcal{H}_{C^n} \). \( \mathcal{L}_{C^n} \) is a subspace of the Liouville space \( \mathcal{L}^{(n)} \)

\[
\mathcal{L}_{C^n} \subseteq \mathcal{L}^{(n)}. 
\]  
(1.46)

Like the non-orthogonality of the channel Hilbert spaces \( \mathcal{H}_{C^n} \) in the last section, these channel Liouville spaces \( \mathcal{L}_{C^n} \) are not necessarily mutual orthogonal.

Similarly an asymptotic channel Liouville operator \( L_{C^n} \) is defined through an asymptotic channel hamiltonian \( H_{C^n} \)

\[
L_{C^n} \varrho_{C^n} \equiv H_{C^n} \varrho_{C^n} - \varrho_{C^n} H_{C^n}, \quad \forall \varrho_{C^n} \in L_{C^n},
\]  
(1.47)

where an asymptotic channel density operator \( \varrho_{C^n} \) is a trace class operator on the asymptotic channel Hilbert space \( H_{C^n} \). The linear span of all operators on \( H_{C^n} \) forms an asymptotic channel Liouville space \( L_{C^n} \).

It seems obvious to define an asymptotic Liouville operator \( L^{(n)} \) through the asymptotic hamiltonian

\[
L^{(n)} \varphi^{(n)} = H^{(n)} \varphi^{(n)} - \varphi^{(n)} H^{(n)}, \quad \forall \varphi^{(n)} \in L^{(n)}.
\]  
(1.48)

where the asymptotic density operator \( \varphi^{(n)} \) is a trace class operator on the Hilbert space \( H^{(n)} \) and an element of \( L^{(n)} \equiv H^{(n)} \otimes H^{(n)} \). Mathematically the matrix elements of a density operator \( \varphi^{(n)} \) have two channel indices and both diagonal and off-diagonal elements in channel label \( C^n \)'s occur. From the asymptotic condition Eq.(1.28) discussed in the last section and mimicking Evans, Hoffman and Kouri\(^{37} \), it is argued that asymptotically the fragments are well resolved into a particular channel long before a collision and a scattering state can only lead to one asymptotic channel at a time long after a collision. Therefore the off-diagonal elements in channel labels \( C^n \) in \( \varphi^{(n)} \) are
taken to be identically zero and \( \varphi^{(n)} \) reduces to a simple form

\[
\varphi^{(n)} = \bigoplus_{C^n} \varphi_{C^n}.
\]  

Consequently, instead of being defined by Eq.(I.48), the asymptotic Liouville operator \( L^{(n)} \) is further restricted to be diagonal in channel label \( C^n \) and

\[
L^{(n)} \varphi^{(n)} = \bigoplus_{C^n} L_{C^n} \varphi_{C^n}.
\]

This argument of asymptotic diagonality leads to a two-Liouville space scattering formalism which parallels the existing Liouville space multichannel scattering theory in Lowry and Snider's work\(^{23}\).

The full evolution of the n-body system is governed by a unitary superoperator \( U_L^{(n)}(t) : \mathcal{L}^{(n)} \rightarrow \mathcal{L}^{(n)} \)

\[
U_L^{(n)}(t) = e^{-iL^{(n)}t}.
\]  

While the asymptotic evolution is determined by an asymptotic evolution superoperator \( U_L^{(n)}(t) : L^{(n)} \rightarrow L^{(n)} \)

\[
U_L^{(n)}(t) = e^{-iL^{(n)}t}.
\]

The connection between the Liouville space \( \mathcal{L}^{(n)} \) and the asymptotic Liouville space \( L^{(n)} \) is carried out by an identification mapping \( \mathcal{J}^{(n)} \)

\[
\mathcal{J}^{(n)} \varphi^{(n)} \equiv J^{(n)} \varphi^{(n)} J^{(n)}\dagger, \quad \forall \varphi^{(n)} \in L^{(n)}.
\]

Then the n particle, two-Liouville space Møller superoperator is defined as

\[
\Omega^{(n)} \equiv \lim_{t \to -\infty} U_L^{(n)\dagger}(t)\mathcal{J}^{(n)} U_L^{(n)}(t)
= \lim_{t \to -\infty} e^{iL^{(n)}t} \mathcal{J}^{(n)} e^{-iL^{(n)}t}.
\]
A transition superoperator $\mathcal{T}^{(n)} : L^{(n)} \rightarrow L^{(n)}$ is defined as

$$\mathcal{T}^{(n)} \equiv \mathcal{V}^{(n)\dagger} \Omega^{(n)},$$

(I.55)

where the superoperator $\mathcal{V}^{(n)} : \mathcal{L}^{(n)} \rightarrow \mathcal{L}^{(n)}$ is defined as

$$\mathcal{V}^{(n)} \equiv \mathcal{L}^{(n)} \mathcal{J}^{(n)} - \mathcal{J}^{(n)} \mathcal{L}^{(n)},$$

(I.56)

and

$$\mathcal{V}^{(n)\dagger} \equiv \mathcal{J}^{(n)\dagger} \mathcal{L}^{(n)} - \mathcal{L}^{(n)} \mathcal{J}^{(n)\dagger},$$

(I.57)

where the adjoint operator $\mathcal{J}^{(n)\dagger}$ is assumed to exist as a bounded mapping.

The channel identification mapping $\mathcal{J}_{C^n}$ from the asymptotic channel Liouville space $L_{C^n}$ to the Liouville space $\mathcal{L}^{(n)}$

$$\mathcal{J}_{C^n} : L_{C^n} \rightarrow \mathcal{L}^{(n)}$$

(I.58)

is defined by

$$\mathcal{J}_{C^n} \varphi_{C^n} = \mathcal{J}_{C^n} \varphi_{C^n} \mathcal{J}_{C^n}^\dagger, \quad \forall \varphi_{C^n} \in L_{C^n}.$$ (I.59)

The channel identification mapping $\mathcal{J}_{C^n}$ is related to $\mathcal{J}^{(n)}$ through asymptotic density operators

$$\mathcal{J}^{(n)} \varphi^{(n)} = \sum_{C^n} \mathcal{J}_{C^n} \varphi_{C^n}$$

$$= \sum_{C^n} \rho_{C^n},$$

(I.60)

and for asymptotic Liouville operators

$$\mathcal{J}^{(n)} \mathcal{L}^{(n)} = \sum_{C^n} \mathcal{J}_{C^n} \mathcal{L}_{C^n}$$

$$= \sum_{C^n} \mathcal{L}_{C^n} \mathcal{J}_{C^n},$$

(I.61)
using the relation (I.49) and (I.50) have been used. In a similar way, the
adjoint of the channel identification mapping $J_{C_n}^\dagger$ is related to $J^{(n)}_{C_n}^\dagger$

$$J^{(n)}_{C_n}^\dagger \rho^{(n)} = \bigoplus_{C_n} J_{C_n}^\dagger \rho^{(n)}$$

$$= \bigoplus_{C_n} \varphi_{C_n}. \quad (I.62)$$

The asymptotic channel evolution is described by a unitary superoperator

$$U_{Lcn}(t): L_G^n \longrightarrow L_{C^n}$$

$$U_{Lcn}(t) = e^{-i L_{C^n}t}. \quad (I.63)$$

One may notice that an asymptotic channel Liouville operator $L_{C^n}$ has a
much simpler structure than that of $L^{(n)}$ because $L_{C^n}$ acts only on $L_{C^n}$,
an asymptotic Liouville space consisting of states of the channel $C^n$'s $I$-fragments, each of which evolves only via free motion. With these definitions
a channel Møller superoperator is defined as

$$\Omega_{C^n} \equiv \lim_{t \to -\infty} U_{L}^{(n)\dagger}(t) J_{C^n} U_{Lcn}(t)$$

$$= \lim_{t \to -\infty} e^{i L^{(n)} t} J_{C^n} e^{-i L_{C^n}t}. \quad (I.64)$$

The channel Møller superoperators have certain properties such as asymp­
totic channel orthogonality,

$$\Omega_{C^n}^\dagger \Omega_{B^n} = \delta_{C^n B^n} P_{C^n}, \quad (I.65)$$

completeness,

$$\sum_{C^n} \Omega_{C^n} \Omega_{C^n}^\dagger = \sum_{C^n} Q_{C^n}$$

$$= Q^{(n)}, \quad (I.66)$$

and the intertwining relations

$$L^{(n)} \Omega_{C^n} = \Omega_{C^n} L_{C^n}, \quad (I.67)$$
where $\delta_{C^nB^n}$ is the Kronecker delta and $P_{C^n}$ are the asymptotic channel projection superoperators on $\mathcal{L}^{(n)}$, the asymptotic Liouville space. $\mathcal{Q}^{(n)}$ is an orthogonal projection of the full $n$-particle Liouville space $\mathcal{L}^{(n)}$ onto the range $\mathcal{R}(\Omega^{(n)})$ of the Møller superoperator. The asymptotic channel orthogonality relations imply probability conservation for a scattering initially in a particular asymptotic channel $C^n$. Eq. (1.66) is a part of strong completeness, which means that the closure of the direct sum of $\mathcal{Q}^{(n)}$ and $Q_{\nu^n}$, the $n$-bound projection superoperator, is the identity $\mathcal{J}^{(n)}_L$ for the total $n$-particle Liouville space $\mathcal{L}^{(n)}$. The strong completeness relations are hard to prove due to the possible existence of singular spectra with infinite multiplicity. Faddeev$^5$ and others$^{38,39}$ have established the strong completeness in Hilbert space for a three-particle collision problem. Here it is taken as an assumption. The intertwining relations imply energy conservation and are useful in kinetic theory calculations.

The asymptotic channel transition superoperators $T_{C^n,B^n} : L_{B^n} \rightarrow L_{C^n}$ can be defined as

$$T_{C^n,B^n} \equiv \mathcal{V}^{\dagger}_{C^n}\Omega_{B^n}$$  \hspace{1cm} (I.68)

with

$$\mathcal{V}_{C^n} \equiv \mathcal{L}^{(n)}\mathcal{J}_{C^n} - \mathcal{J}_{C^n}\mathcal{L}^{(n)},$$  \hspace{1cm} (I.69)

and

$$\mathcal{V}^{\dagger}_{C^n} \equiv \mathcal{J}^{\dagger}_{C^n}\mathcal{L}^{(n)} - \mathcal{L}^{(n)}\mathcal{J}^{\dagger}_{C^n}$$  \hspace{1cm} (I.70)

as restricted forms of Eqs. (I.56) and (I.57). The channel transition superoperators $T_{C^n,B^n}$ describe rearrangement scattering from the asymptotic channel $B^n$ to the asymptotic channel $C^n$. There are also channel transition superoperators emphasizing the final operator state interactions

$$T_{C^n} \equiv \mathcal{V}^{\dagger}_{C^n}\Omega^{(n)}$$

27
\[ \mathcal{T} = \sum_{B^n} \mathcal{T}^n_{\text{B}}, \quad (1.71) \]

The transition superoperator \( \mathcal{T}^{(n)} \) can be expressed in terms of the channel transition superoperators \( \mathcal{T}_{\text{C}n} \) according to

\[ \mathcal{T}^{(n)} = \bigoplus_{\text{C}n} \mathcal{V}_{\text{C}n}^{\dagger} \Omega^{(n)} \quad (1.72) \]

\[ = \bigoplus_{\text{C}n} \mathcal{T}_{\text{C}n}. \quad (1.73) \]

### I-2.4 Discussion

The structure of the two-Hilbert spaces defined here is different from those given by Chandler and Gibson\(^{12}\). Their asymptotic channel hamiltonians are chosen the same as the channel hamiltonians \( \mathcal{H}_{\text{C}n} = \mathcal{H}_{\text{C}n} \). Then the asymptotic channel spaces are coincident with the channel spaces \( \mathcal{H}_{\text{C}n} = \mathcal{S}_{\text{C}n} \).

This choice certainly simplifies the notation of the two-Hilbert space theory. However, the selection in this work has two advantages. First, the asymptotic channel hamiltonians and spaces defined here emphasize the fragments rather than the detailed internal states of each fragment and simplify the structure of the Møller operator. This treatment is much more consistent with the basic concepts of a multichannel scattering theory, in particular, that the asymptotic hamiltonian has an absolutely continuous spectrum. Secondly, choosing asymptotic channel spaces different from channel spaces gives scattering theory some flexibility to incorporate certain unbound but highly correlated states, which are not the eigenstates of any channel hamiltonian into a kinetic theory description. An example of such a state is an \( L^2 \) resonance wavefunction\(^{40}\), which might provide a rigorous formalism from the scattering point of view for a long-lived reaction complex. The form of the asymptotic
channel space allows also the inclusion of secondary asymptotic channels, say \( \{D^n\} \), by using Kato's chain rule

\[
\Omega_{D^n}^\pm = \Omega_{D^n}^\pm \Omega_{D^n,C^n}^\pm,
\]

where secondary channel hamiltonian \( H_{D^n} \) includes a part of the potential interaction between the particles belonging to different bound fragments. Møller operator \( \Omega_{D^n,C^n}^\pm \) maps the states of the asymptotic channel \( C^n \) to the states of secondary asymptotic channel \( D^n \). A superoperator relation which is equivalent to Kato's chain rule has been rediscovered independently by Snider and Lowry

\[
\mathcal{T}_{ba} = \frac{1}{3} \sum_m \mathcal{T}_{bm} \Omega_m,
\]

where \( b \) is an arbitrary final channel and \( a \) is the initial three-fragment channel of a three-body scattering system. The secondary asymptotic channel formalism, particularly the concept, has considerable potential for being used to formulate a moderately dense reactive gas kinetic theory. An attempt at such a formulation is given in Part III of this thesis (see Chapter III-2). After all, the effects of our asymptotic channel states can be made exactly the same as those of Chandler and Gibson's by properly choosing the identification operators. The present choice of asymptotic channels and states is similar to that of Osborn, but Osborn does not consider the extra set of channels and channel spaces as is done here.

Superpositions among different channel labels naturally arise in scattering wavefunctions \( \Psi^{(n)} \) which are compatible with the total hamiltonian \( H^{(n)} \) and its evolution group \( U^{(n)}(t) \). It is to be noted that the notion of channels in the interacting region is not the same as that in the asymptotic region. A scattering wavefunction may just be associated with a channel label but it cannot belong to any channel in the interacting region. An
asymptotic wavefunction is usually determined by the method of preparation and/or measurements of the scattering system and always belongs to one of the asymptotic channels. The asymptotic wavefunction is compatible with the asymptotic channel Hamiltonian $H_C$ and its evolution group $U_C$. Therefore the superpositions among different asymptotic channels do not have a physical justification in terms of state preparation or measurement. The decoherence among the topologically distinct channel states at asymptotic times is indispensable in a detection process. The same argument has been applied to exclude the off-diagonalities in asymptotic channels from the asymptotic density operator $\rho_n$, Eq.(1.49). In contrast, the off-diagonality in channel labels naturally present in the (full) scattering density operator $\rho(n)$ associated with coherences among channels are consistent with the Liouville superoperator $L(n)$ and the corresponding evolution group $U_L(n)(t)$. The statistical presence of certain off-diagonal elements at equilibrium have been discussed by Krishnan and Snider\textsuperscript{43}.

A number of different transition operators have been discussed in Chandler and Gibson's work, while the transition superoperators defined here are not parallel to any in their work. The form of transition superoperators in this work, Eqs.(1.55) and (1.68), is similar in form to that used in kinetic theories\textsuperscript{26,32,23}. The validity of the latter has been discussed\textsuperscript{18,44,45}. Similar non-symmetrical multichannel transition operators have been used by Kouri and Levin\textsuperscript{46}, and Lovelace\textsuperscript{47}, see also the monographs by Schmid and Ziegelmann\textsuperscript{7}, and by Glöckle\textsuperscript{8}.

The explicit form of the identification operators is not necessary to be specified unless one deals with a practical problem. Nevertheless some discussion regarding their form is in order. One example given by Chandler and
Gibson\textsuperscript{12} for their form is that

\[ J^{(n)} \Phi^{(n)} = \sum_{C^n} \Psi_{C^n}, \] \hspace{1cm} (I.76)

and

\[ J^{(n)\dagger} \Psi^{(n)} = \bigoplus_{C^n} P_{C^n} \Psi^{(n)} \] \hspace{1cm} (I.77)

where the projection operators \( P_{C^n} \) commute with the channel hamiltonians \( H_{C^n} \) and are in general non-orthogonal to each other. It is possible to use the \( Q_{C^n} \) projectors, Eq.(1.28), which have the following nice properties: Firstly \( Q_{C^n} \) are properly defined in the interacting space \( \gamma^{(n)} \). Secondly they are mutually orthogonal to each other and commute with the total hamiltonian. Finally each \( Q_{C^n} \), by definition, selects out the set of scattering states which will lead to the desired asymptotic channel \( C^n \) in the infinite future.

The existence of the adjoint of a Møller operator is a much stronger requirement than the existence of a Møller operator\textsuperscript{31,12}. This property is required in order to write the Møller superoperators in terms of Møller operators, namely

\[ \Omega_{C^n} \varphi_{C^n} = \Omega_{C^n} \varphi_{C^n} \Omega_{C^n}^{\dagger}. \] \hspace{1cm} (I.78)

The existence of the adjoint of Møller operator is assumed in the discussions of various properties of Møller operators. While the major definitions such as Møller superoperators and transition superoperators do not depend on this assumption. Some recent progress on the existence of the Møller operator and the strong completeness can be found in the book by Cycon, Froese, Kirsch and Simon\textsuperscript{48} and is also discussed in the book by Yafaev\textsuperscript{49}.
Chapter 1-3
A Two-Liouville Space Kinetic Theory of Reactive Gases

The formal theory of the kinetic theory of reactive gases has received considerable attention since the early seventies. Olmsted and Curtiss\textsuperscript{17} looked at the presence of bound states as a perturbation to the two and three particle distribution functions, $f^{(2)}$ and $f^{(3)}$. They used a perturbational closure to the BBGKY equations\textsuperscript{21,22} and found corrections to the transport coefficients from dimer formation and decay. A dimer rearrangement reaction in a low energy system has been considered by Eu\textsuperscript{18} from the three particle scattering point of view. His framework allows an arbitrary number of bound states in the gas mixture while the collision energy is small so as not to induce break up reactions. A three-body collision operator has also been constructed by McLennan\textsuperscript{19}. He treats both reactive and non-reactive collisions on an equal footing. The effect on the transport coefficients has been addressed in the generalized framework of the Green-Kubo formalism\textsuperscript{50}. The resulting equations at equilibrium coincide with those of Osborn and coworker's\textsuperscript{36}, which is formulated in terms of a two-Hilbert space scattering theory. Klimontovich \textit{et al.}\textsuperscript{20} have independently formulated a reactive fluid theory at the three-body level. A modified version of Bogoliubov's factorization ansatz\textsuperscript{21} has been adopted in most of the above-mentioned work to close the BBGKY equations at the two and three particle levels. A quantum theory of a dimer and monomer mixture has been introduced by Lowry and Snider\textsuperscript{23}. That work involved a new statistical counting procedure which accommodates arbitrary numbers of atoms and molecules in a consistent manner. A reactive Boltzmann ansatz, notably different from the conventional BBGKY method, was developed to close the kinetic equations in an appropriate way. The problem
in kinetic theory arising from the non-orthogonality of the freely moving fragments was recognized for the first time. The resulting theory was formulated in terms of a set of kinetic equations of Waldmann-Snider\textsuperscript{25,26} type. Their formalism has been applied to give a kinetic theory of dimer formation and decay\textsuperscript{24}. A rigorous reactive quantum fluid theory has also been formulated by Hoffman, Kouri and coworkers\textsuperscript{27}. Their theory is cast in a channel coupling array formalism with great care taken to handle the spurious solutions which are inherently associated with the BKLT equations\textsuperscript{9} and other integral equations such as AGS\textsuperscript{51} equations, except the Faddeev\textsuperscript{5} equation. The molecular picture is realized through channel clustering. Kinetic equations are derived by reducing their $N$-particle channel array von Neumann equation into a set of appropriate few-body channel array equations in the spirit of the BBGKY. It has been shown that this theory reduces, in form, to that of Lowry and Snider\textsuperscript{23} at the appropriate level of approximation.

A comprehensive review paper of this field has been presented by Hoffman and Evans\textsuperscript{29}. One of the most important features among all theories is whether the emphasis is on the atomic picture or the molecular picture. The former takes atomic density operators as the basic building blocks and treats possible associations of atoms as perturbations. The latter puts atomic and molecular density operators on an equal footing. The advantage of the molecular picture over the atomic one has been properly addressed in the aforementioned review\textsuperscript{29}. This molecular picture has been rigorously implemented at equilibrium by Osborn\textsuperscript{36} in terms of a multispecies cluster (monomer and dimer) expansion for the grand partition function. His structure of the interplay between monomers and dimers is similar to that given by Lowry and Snider.

The non-orthogonality problem of reactive gas kinetics is expected to be
present in all treatments which employ the conventional one-Hilbert space multichannel scattering theory. The first serious discussion of the problem from the kinetic theory point of view was due to Lowry and Snider\textsuperscript{23}. The origins of the non-orthogonality problem are twofold. First is the problem associated with channel non-orthogonality in the conventional multichannel scattering treatment. Second is a more profound problem which is due to the validity of the kinetic description. One can ask how well the kinetic equations expressed in terms of reduced density operators $\rho^{(1)}, \rho^{(2)}$ describe the whole gas? More specifically, can one really factorize the $N$-particle system into a few isolated particles at a time?

The kinetic factorizability is discussed before commenting on the non-orthogonality of the scattering channels. An immediate answer to the factorizability question is in the negative because there are interactions between the particles which prevent the factorization. But a kinetic theory is inherently a theory based on sound physical approximations. From this point of view the factorization of an $N$ particle system into few particle systems has a sound physical basis for an approximate treatment of dilute gases with reasonable (short range) potentials. For example, the Boltzmann equation\textsuperscript{3} provides a sound physical basis for the description of a dilute gas. In the case of moderately dense gases, various correlations play important roles. It is believed that by explicitly accounting for the correlations in the reduced density operators\textsuperscript{52}, a kinetic theory can provide a physically reasonable description of a reactive moderately dense gas. An attempt at formulating such a theory is given in Part III, using the secondary asymptotic channel formalism. The solution for a limited set of kinetic equations is also given for the purpose of calculating transport coefficients.

The problem of non-orthogonality in conventional multichannel scatter-
ing theory can be resolved by using the two-Liouville space scattering theory formulated in the previous chapter. The two-Liouville space formalism allows a rigorous description of time-dependent quantum mechanical scattering, incorporating both channel orthogonality and completeness relations. The notion of asymptotic channels and subchannels is compatible with the general statistical counting of microstates in an \( N \)-particle system. Tracing over asymptotic channels is then parallel to the reduction of an \( N \)-particle system to a few-particle problem. Thus the two-Liouville space scattering theory provides a physically sound basis for the kinetic theory of reactive gases. In particular, the strong orthogonality assumption of Lowry and Snider is overcome by the use of the two-Liouville space theory.

The organization of this chapter is the following. The reduction of the full density operator \( \rho^{(N)} \) into reduced density operators is discussed in Section I-3.1. Such a reduction is necessary for formulating kinetic equations. The derivation utilizes the structure of \( N \)-particle asymptotic channels in the spirit of Faddeev\(^5\) and of two-Liouville space theory, while the essential procedure is that of Lowry and Snider. The resulting reduced statistical operators are found to be an extension of those of Lowry-Snider when ignoring apparent difference in definitions and notation. This arises from the fact that the results of the Lowry-Snider partition have a one to one correspondence with those of the asymptotic channel division. Clusters, such as monomers, dimers and trimers, are defined as asymptotic observables\(^53\) of the \( N \) particle asymptotic space in Section I-3.2. A generalized set of equations for the clusters are derived within the framework of a multiple two-Liouville space theory. The philosophy of that derivation differs from the usual BBGKY method but is similar to that developed by Lowry and Snider. The equations of monomer and dimer are reduced, in form, to those of Lowry and
Snider\textsuperscript{23} by further approximation. It is found that the two-Liouville space formalism provides a suitable description for a reactive gas system. The extension to multi-particle clusters is useful since it might provide a rigorous theoretical basis for the dynamical evolution of various metal clusters produced in molecular beam experiments\textsuperscript{33,34}. A discussion is given in Section I-3.3.

I-3.1 Channel Reduction of the Density Operator

Kinetic theories usually deal with reduced distribution functions or reduced density operators to give a simplified description of the \( N \)-particle system. Different theories may have different reduction procedures. Lowry and Snider\textsuperscript{23} developed a method of incorporating monomers and dimers on an equal footing. The method starts from a state \( \rho_{M;D}^{(N)} \) at a particular time characterized by the \( M \) monomers and \( D \) dimers.

\[
\rho_{M;D}^{(N)} = g(N, M, D)^{-1} M^{-M} D^{-D} \sum_{\{\alpha, \beta\}} \prod_{i \in \alpha} \rho_f(i) \prod_{(j,k) \in \beta} \rho_b(j,k)
\]  

where \( \alpha \) is the list of particles which are monomers and \( \beta \) is the list of pairs of particles which are bound pairs (dimers).

\[
g(N, M, D) = \frac{N!}{M!D!2^D} \tag{I.80}
\]

is all the possible ways of partitioning \( N \) indistinguishable particles into \( M \) monomers and \( D \) dimers. Then the reduced density operator \( \rho^{(n)} \) is the partial trace over all but a subset of \( n \) particles.

\[
\rho^{(n)}(1, \cdots, n) = \left( \begin{array}{c} N \\ n \end{array} \right) \text{Tr}_{n+1, \cdots, N} \rho^{(N)} \tag{I.81}
\]

The spirit of the above reduction procedure is to be implemented here while being consistent with the two-Liouville space description. Specifically the above reduction is expressed in terms of asymptotic channels.
It is necessary to introduce some notation which facilitates the connection between the kinetic description and the quantum mechanical two-Liouville space scattering theory. Recall that the particles are assumed to be indistinguishable but labelled. This detailed information is inherently contained in the channels and fragments but is unwanted in certain statistical descriptions. Hence the molecular content of fragment \( C^m \), denoted as \( \tilde{C}^m \), is the chemical binding information regardless of the detailed atomic labels and order. A molecule \( \tilde{C}^m \) can be the same as a molecule \( \tilde{B}^m \), while the corresponding fragments \( C^m \) and \( B^m \) may not be the same (having different particle labels and thus belonging to different labelled channels). Two fragments \( C^m \) and \( B^m \) are said to be compatible fragments if they have the same molecular content \( \tilde{C}^m = \tilde{B}^m \), and two channels \( C^n \) and \( B^n \) are compatible channels, \( \tilde{C}^n = \tilde{B}^n \) if they have the same set of molecular species and the same number of molecules of each molecular species, regardless of the detailed atomic labels. For instance, in a three particle system, channel (12),3 and (13),2 are compatible channels, moreover fragment (12) in the first channel and fragment (13) in the second channel are compatible fragments. The set of all compatible channels is denoted as \( \tilde{C}^n \equiv \{ \tilde{C}^n \} \). The number of compatible channels is denoted as \( | \tilde{C}^n | \). Similarly the set of all compatible fragments \( \{ \tilde{C}^m \} \) in a channel \( C^n \) is denoted as \( \tilde{C}^m \equiv \{ \tilde{C}^m \} \), and the number of \( \tilde{C}^m \) molecules in the channel \( C^n \) is \( | \tilde{C}^m | \). Finally, the number of particles in the fragment \( C^m \) is denoted as \( | C^m | \). Obviously

\[
\sum_{C^m \in C^n} | C^m | = n. \tag{1.82}
\]

number of particles in the scattering system. It is to be noticed that the aforementioned notation is applicable also to the description of asymptotic channels and asymptotic subchannels (fragments).
Physically, for a given total $N$ particles, a reduction of the $N$ particle density operator can only be visualized in asymptotic space where the $N$ particles may fall apart in various pieces. It is naturally assumed that the $N$-particle density operator is a functional of various asymptotic channel density operators. This assumption takes the density operators of various molecular species as initial building blocks. A reduction is to be performed in two separate steps, namely specification and partial trace. From the asymptotic channel point of view a given kinetic system can have one specified configuration at a time. This means a given set of monomers, dimers, trimers and so on, say $\tilde{C}^N$, with known numbers of each species. The instantaneous chemical reaction at that particular time is assumed to be negligible. Since all particles are indistinguishable, the $N$-particle density operator includes all possible asymptotic channels $C^N$ having the same molecular content, namely $\tilde{C}^N$, thus

$$\varphi_{\tilde{C}^N}^{(N)} = |\tilde{C}^N|^{-1}\left(\prod_{\tilde{C}_m^N} |\tilde{C}_m^N|^{-|\tilde{C}_m^N|}\right) \bigoplus \prod_{C^N \in \tilde{C}^N} \varphi_{C^N},$$

(I.83)

where $|\tilde{C}^N|$ is the number of channels that are compatible to $C^N$

$$|\tilde{C}^N| = \frac{N!}{\prod_{\tilde{C}_m^N} |\tilde{C}_m^N| ! (| \tilde{C}_m^N |)!^{|\tilde{C}_m^N|}},$$

(I.84)

and $|\tilde{C}_m^N|$ is the number of fragments compatible to the fragment $C_m^N$ in channel $C^N$. $\varphi_{C_m^N}(i,j,\ldots,s)$ is the fragment density operator for the set of labelled particles $i,j,\ldots,s$ normalized

$$\text{Tr}_{i,j,\ldots,s} \varphi_{C_m^N}(i,j,\ldots,s) = |\tilde{C}_m^N|,$$

(I.85)

to the total number of the compatible molecular species $\tilde{C}_m^N$. The sum is
over all channels compatible to \( \tilde{C}^N \). The trace normalization of \( \varphi_{\tilde{C}^N}^{(N)} \) is

\[
\text{Tr}_{1,\ldots,N} \varphi_{\tilde{C}^N}^{(N)} = 1. \tag{1.86}
\]

The reduced density operator \( \varphi^{(n)} \) is defined as a partial trace over \( N - n \) particles in \( \varphi_{\tilde{C}^N}^{(N)} \),

\[
\varphi^{(n)}(1, \ldots, n) \equiv \left( \begin{array}{c} N \\ n \end{array} \right) \text{Tr}_{n+1,\ldots,N} \varphi_{\tilde{C}^N}^{(N)}, \tag{1.87}
\]

with norm

\[
\text{Tr}_{1,\ldots,n} \varphi^{(n)}(1, \ldots, n) = \left( \begin{array}{c} N \\ n \end{array} \right) \tag{1.88}
\]

the binomial coefficient \( \left( \begin{array}{c} N \\ n \end{array} \right) \) as the number of ways of selecting \( n \) unlabelled particles from \( N \) indistinguishable particles.

As defined, \( \varphi^{(n)}(1, \ldots, n) \) is equivalent to assigning the distinct particles 1, \( \ldots \), \( n \) into various fragments in all possible ways allowed by the channel structure of \( \tilde{C}^N \). In the case of \( \varphi^{(1)}(1) \),

\[
\varphi^{(1)}(1) \equiv \left( \begin{array}{c} N \\ 1 \end{array} \right) \text{Tr}_{2,\ldots,N} \varphi_{\tilde{C}^N}^{(N)}
\]

\[
= N | \tilde{C}^N |^{-1} \left( \prod_{m \in \tilde{C}^N} | \tilde{C}^N_m |^{-1} \right) \bigoplus_{C^N_m \in \tilde{C}^N \setminus \tilde{C}^N} | \tilde{C}^N - | C^N_m | \Bigg| \cdot \left( \prod_{\tilde{C}^N_m \notin \tilde{C}^N} | \tilde{C}^N_{m'} |^{-1} \right)
\]

\[
| \tilde{C}^N_{m'} |^{-1} \sum_{j,\ldots,s \in \{2,\ldots,N\}} \text{Tr}_{j,\ldots,s} \varphi_{C^N_m}(1, j, \ldots, s)
\]

\[
= \bigoplus_{C^N_m \in \tilde{C}^N \setminus \tilde{C}^N} \frac{| C^N_m |!}{(N - 1) \cdots (N - | C^N_m | + 1)} \sum_{j,\ldots,s \in \{2,\ldots,N\}} \text{Tr}_{j,\ldots,s} \varphi_{C^N_m}(1, j, \ldots, s)
\]

\[
= \bigoplus_{C^N_m \in \tilde{C}^N \setminus \tilde{C}^N} | C^N_m | \varphi_{C^N_m}(1) \tag{1.89}
\]
where $\tilde{C}^{N-|C^N_m|}$ denotes a daughter compatible channel which differs from $\tilde{C}^N$ (the parent compatible channel) by a (compatible) fragment $\tilde{C}^N_m$. Similarly $\tilde{C}^{N-|C^N_m|}$ denotes a set of all compatible daughter channels $\{\tilde{C}^{N-|C^N_m|}\}$. The number of elements in the set is

$$|\tilde{C}^{N-|C^N_m|}| = \frac{(N - |C^N_m|)!}{\prod_{\tilde{C}^N_m, \tilde{C}^N_m \neq \tilde{C}^N_m} ((|C^N_m| + 1)! |\tilde{C}^N_m| - 1)! (|C^N_m|)!^{k^N_m| - 1}}.$$ (I.90)

The counting relation

$$\sum_{j, \cdots, s \in \{2, \cdots, N\}} \text{Tr}_{j, \cdots, s} \varphi_{C^N_m}(1, j, \cdots, s) = (N - 1) \cdots (N - |C^N_m| + 1) \frac{\text{Tr}_{1, \cdots, |C^N_m|} \varphi_{C^N_m}(1, 2, \cdots, |C^N_m|)}{|C^N_m| - 1)!}.$$ (I.91)

has been used in Eq. (I.89). $\varphi_{C^N_m}(1)$ is defined as

$$\varphi_{C^N_m}(1) = \text{Tr}_{1, \cdots, |C^N_m|} \varphi_{C^N_m}(1, 2, \cdots, |C^N_m|),$$ (I.92)

and is so normalized that

$$\text{Tr}_{1} \varphi(1) = \sum_{\tilde{C}^N_m \in \tilde{C}^N} |C^N_m| \text{Tr}_{1} \varphi_{C^N_m}(1) = \sum_{\tilde{C}^N_m \in \tilde{C}^N} |C^N_m| \tilde{C}^N_m = N.$$ (I.93)

Therefore a single density operator inherently contains not only the single free density operator contribution in case the fragment $C^N_m$ is a single particle, but also the operator contributions from various molecular species that are allowed by $\tilde{C}^N$. This simply reflects the fact that each particle has a certain probability of being located in each fragment allowed by the physically selected $\tilde{C}^N$.  

40
A completely general expression for the $n$ particle reduced density operator is

$$
\varphi^{(n)}(1, \ldots, n) = \left( \begin{array}{c} N \\ n \end{array} \right) |\tilde{\mathcal{C}}^N|^{-1} \left( \prod_{\mathcal{C}_m^N} |\tilde{\mathcal{C}}_m^N|^{-|\mathcal{C}_m^N|} \right) \bigoplus_{\mathcal{C}_m^N \in \mathcal{C}^N} \left( \prod_{\mathcal{C}_m^N} |\tilde{\mathcal{C}}_m^N|^{-|\mathcal{C}_m^N|} \right)^{l(C_m^N)} \times \sum_{\{i_{C_m^N}, \ldots, i_{C_m^N}\} \in \{1, \ldots, n\}} \text{Tr}_{\{s\}} \prod_{\mathcal{C}_m^N \in \mathcal{C}^N} \varphi_{C_m^N}(i_{C_m^N}, \ldots, i_{C_m^N}, s_{C_m^N}^1, \ldots, s_{C_m^N}^k).
$$

(1.94)

Here $\{i_{C_m^N}, \ldots, i_{C_m^N}\}$ is the set of $l(C_m^N) \leq |C_m^N|$ particles which belong to the given set $\{1, \ldots, n\}$, while $\{s_{C_m^N}^1, \ldots, s_{C_m^N}^k\}$ is the set of

$$
k = |C_m^N| - l
$$

(1.95)

particles (ghosts) which belong to the set of $\{n+1, \ldots, N\}$. $\{s\}$ is the collection of all sets of ghosts

$$
\{s\} = \bigcup_{C_m^N} \{s_{C_m^N}^1, \ldots, s_{C_m^N}^k\}.
$$

(1.96)

It is noted that $\varphi_{C_m^N}$ in Eq. (1.94) is required to satisfy

$$
\varphi_{C_m^N}(i_{C_m^N}, \ldots, i_{C_m^N}, s_{C_m^N}^1, \ldots, s_{C_m^N}^k) = 0
$$

(1.97)

whenever $\{i_{C_m^N}, \ldots, i_{C_m^N}\} = \emptyset$. $t_{C_m^N}$ is the total number of subchannels of the type of $\tilde{\mathcal{C}}_m^N$ which contain at least one particle from the given set $\{1, \ldots, n\}$. The direct sum in Eq.(1.94) is essentially over all possible partitions of $n$ particle labels into subchannels $C_m^N \in C^N \in \tilde{\mathcal{C}}^N$, and for each partition, there is a numerical factor arising from the sum $(\sum_{\{s_{C_m^N}^1, \ldots, s_{C_m^N}^k\} \in \{n+1, \ldots, N\})$
over all possible partitions of \( N - n \) ghost particle labels into subchannels \( C_N^m \in C^N \in \tilde{C}^N \). The restrictions to the summations are

\[
0 \leq l \leq \left| C^N_m \right|, \quad 0 \leq l \leq n \quad (I.98)
\]
\[
l_{\max} = \min(n, \left| C^N_m \right|) \quad (I.99)
\]
\[
0 \leq t_{\tilde{C}^N_m} \leq n \quad (I.100)
\]
\[
0 \leq t_{\tilde{C}^N_m} \leq \left| \tilde{C}^N_m \right| \quad (I.101)
\]
\[
\sum_{C_N^m \in C^N} l(C^N_m) = n \quad (I.102)
\]
\[
0 \leq k(C^N_m) \left| C^N_m \right| \leq N. \quad (I.103)
\]

The factor \(| \tilde{C}^N - \sum_{C_N^m} t_{\tilde{C}^N_m} | C^N_m | | \) is

\[
| \tilde{C}^N - \sum_{C_N^m} t_{\tilde{C}^N_m} | C^N_m | | = \frac{(N - \sum_{C_N^m} t_{\tilde{C}^N_m} | C^N_m |)!}{\prod_{C_N^m} \left( \left| \tilde{C}^N_m \right| - t_{\tilde{C}^N_m} \right)! (\left| C^N_m \right|)!^{\left| C^N_m \right| - t_{\tilde{C}^N_m}}} \quad (I.104)
\]

So far the derivation is completely general and strictly rigorous. The expressions can be simplified in a variety of ways according to the physical situation. For example if a system supports only monomers and dimers, and has large \( N \) (usually \( N \sim 10^{20} \)) and therefore large \( \left| \tilde{C}^N_m \right| \)'s,

\[
\varphi^{(1)}(1) = \varphi_f(1) \oplus 2 \varphi_b(1), \quad (I.105)
\]
\[
\varphi^{(2)}(12) = \frac{1}{2} \varphi^{(1)}(1) \varphi^{(1)}(2) \oplus \varphi_b(12), \quad (I.106)
\]
\[
\varphi^{(3)}(123) = \frac{1}{6} \varphi^{(1)}(1) \varphi^{(1)}(2) \varphi^{(1)}(3)
\]
\[
\quad \oplus \frac{1}{3} \left[ \varphi^{(1)}(1) \varphi_b(23) \oplus \varphi^{(1)}(2) \varphi_b(13) \oplus \varphi^{(1)}(3) \varphi_b(12) \right] \quad (I.107)
\]

and

\[
\varphi^{(4)}(1234) = \frac{1}{24} \varphi^{(1)}(1) \varphi^{(1)}(2) \varphi^{(1)}(3) \varphi^{(1)}(4)
\]
\[\begin{align*}
&\oplus \frac{1}{12} [\varphi^{(1)}(1)\varphi^{(1)}(2)\varphi_b(34) \oplus \varphi^{(1)}(1)\varphi^{(1)}(3)\varphi_b(12)] \\
&\oplus \varphi^{(1)}(1)\varphi^{(1)}(4)\varphi_b(23) \oplus \varphi^{(1)}(2)\varphi^{(1)}(3)\varphi_b(14) \\
&\oplus \varphi^{(1)}(2)\varphi^{(1)}(4)\varphi_b(13) \oplus \varphi^{(1)}(3)\varphi^{(1)}(4)\varphi_b(12)] \\
&\oplus \frac{1}{6} [\varphi_b(12)\varphi_b(34) \oplus \varphi_b(13)\varphi_b(24)\varphi_b(14)\varphi_b(23)]. \quad (I.108)
\end{align*}\]

These are exactly the Lowry and Snider expressions\textsuperscript{23} except that here the reduced density operators are treated as operators in the asymptotic channel Liouville space. A general expression under the aforementioned conditions can be written

\[\varphi^{(n)}(1, \ldots, n) = \bigoplus \frac{2^n-f}{n!} \prod_{i \in \alpha} \varphi^{(1)}(i) \prod_{(j,k) \in \beta} \varphi_b(jk) \quad (I.109)\]

where \(f\) is the number of fragments, and \(\alpha, \beta\) have the same interpretations as in the Eq.(I.79) but with \(N\) being reduced to \(n\).

**I-3.2 Kinetic Equations for Clusters**

Quantum mechanically the fragment Hamiltonians \(H_{C_m}\) do not commute with the total Hamiltonian of the system \(H^{(n)}\). Thus the physical observables which commute with \(H^{(n)}\) are not in general compatible\textsuperscript{54} with the physical observables which commute with the fragment Hamiltonians \(H_{C_m}\). Consequently it is very difficult to simultaneously identify individual atomic or molecular properties in the Liouville operator space \(\mathcal{L}^{(n)}\) (\(2 \leq n \leq N\)) except for those that are associated with the \(n\)-bound states. Strictly speaking, atomic and molecular identities are not well defined in the interaction region. Mathematically, various channel spaces \(\mathcal{H}_{C^n}\) and fragment spaces \(\mathcal{H}_{C_m}\) are in general not orthogonal to each other. As a result atomic and molecular projection operators are not orthogonal to each other either. In contrast,
by construction, the various asymptotic channel spaces $H_{C^n}$ and asymptotic subchannel (fragment) spaces $H_{C^n_m}$ are orthogonal to each other. The states in the asymptotic channel spaces are physically realizable\textsuperscript{55}, have been called physical states\textsuperscript{56}. They can physically be prepared, observed, and initially prescribed. These are crucial properties for a kinetic description. A natural way to identify atomic and molecular properties is thus via the asymptotic channel space. Thus the two-Liouville space formalism is a suitable device for resolving the dilemma of channel non-orthogonality and asymptotic channel orthogonality, thus providing a description that reflects a correct chemical picture.

In some cases the experimental arrangement can be very different from that of a collision process, for instance, the reaction-diffusion processes of simple gases or gas mixtures. In such a case the experimental preparation and consequent observations (measurements) are usually conducted at a very coarse level. Experimentally, only the time evolution of certain clusters such as monomers, dimers, trimers etc., can be monitored. Here a cluster, denoted $C_m$ is defined as an asymptotic bound fragment of the $N(\sim 10^{23})$ particle kinetic system. Note that the superscript $N$ has been omitted for convenience. Hence a cluster is a special kind of bound fragment that is associated with the $N$- (the total number of particles in the system) body asymptotic channel spaces. Technically the $N$-particle problem is treated in terms of few-body ($n \sim 2 - 10$ particles) collision theory. Specifically, the time dependence of a cluster is governed by a kinetic equation whose dynamical processes are treated in terms of few-body collisions. Thus the present goal is to derive kinetic equations for the various clusters. A chemical picture for the present problem is that: Most of the time a cluster $C_m$ is free from collisions with any another cluster(s) in the $N$-body system. While from time to time it suffers
from an isolated $n$-particle collision. Here the number of particle involved in the collision is arbitrary $|C_m| + 1 \leq n \leq N$. But the more fragments a collision involves, the less probability it can occur. Hence each cluster $C_m$ is part of all asymptotic channels $C^n$, $(N \geq n \geq |C_m|)$ that contain the labelled cluster $C_m$ as a subchannel. As for the outcome of the $n$-body collision, it can be of any type, such as break-up, elastic, rearrangement, recombination and decay, and is determined by quantum mechanical scattering theory. Based on this chemical picture, a time dependent cluster density operator $\varphi_{C_m}(t)$ is defined as

$$\varphi_{C_m}(t) = \sum_{n \geq |C_m|} \bigoplus_{C^n} \left( \begin{array}{c} n \\ |C_m| \end{array} \right) \text{Tr}_{|C_m|+1\ldots,n} \mathcal{J}_{C^n}^\dagger \left[ \rho^{(n)}(t) \right]_{n\text{-body}},$$  \hspace{1cm} (I.110)

where the incomplete direct sum $\bigoplus_{C^n}$ is denoted as a partial direct sum over those asymptotic channels which contain the labelled cluster $C_m$

$$\bigoplus_{C^n} \equiv \bigoplus_{\{C^n\mid C^n \cap C_m \neq \emptyset\}}.$$  \hspace{1cm} (I.111)

The adjoint of the identification $\mathcal{J}_{C^n}^\dagger$ is given in Chapter I-2. And the normalization factor is

$$\left( \begin{array}{c} n \\ |C_m| \end{array} \right) = \left( \begin{array}{c} N \\ |C_m| \end{array} \right) \left( \begin{array}{c} N \\ n \end{array} \right)^{-1} \frac{(N - n + 1) \cdots (N - |C_m|)}{(n - |C_m|)!}. \hspace{1cm} (I.112)$$

The statistical counting could have been explicitly listed in the right hand side of Eq.(I.110), instead it is contained in the reduced density operator $\rho^{(n)}$. The hypothesis of Eq.(I.110) essentially resolves the statistical problem into the problem of many isolated $n$-body quantum mechanics.

It is reasonable to write $\left[ \rho^{(n)}(t) \right]_{n\text{-body}}$ of a scattering problem as

$$\left[ \rho^{(n)}(t) \right]_{n\text{-body}} = \mathcal{O}^{(n)} \left[ \varphi^{(n)}(t) \right]_{n\text{-body}},$$  \hspace{1cm} (I.113)
where the Møller superoperator has been defined in Chapter I-2. \( \varphi^{(n)}(t) \) \( n \text{-body} \) is the asymptotic channel density operator Eq.(I.94) excluding all fragments (subchannels) that contain ghost particles \( \{s\} \), i.e.

\[
\{s\} = \emptyset.
\]  

Hence \( \varphi^{(n)}(t) \) \( n \text{-body} \) has a simple form

\[
\left[ \varphi^{(n)}(t) \right]_{n \text{-body}} = \bigoplus_{C} D(\hat{C}^N, n, \hat{C}_m^n) \frac{1}{n!} \prod_{c_m^n} (|C_m^n|) \varphi_{C^n_m}(t),
\]  

where \( D(\hat{C}^N, n, \hat{C}_m^n) \) is the remaining counting factor from Eq. (I.94)

\[
D(\hat{C}^N, n, \hat{C}_m^n) = \prod_{\hat{C}_m^n} \frac{(|\hat{C}_m^n| - |\hat{C}_m^n|)^{C_m^n - C_m^n}}{|\hat{C}_m^n|},
\]  

with constraint

\[
\sum_{\hat{C}_m^n} |C_m^n| \varphi_{C^n_m} = n.
\]  

This factor is close to unity for large \( N \) and \( |\hat{C}_m^n| \),

\[
\lim_{N \to \infty} D(\hat{C}^N, n, \hat{C}_m^n) \to 1.
\]  

Thus a desired expression for \( \left[ \varphi^{(n)}(t) \right]_{n \text{-body}} \) which is consistent with the two-Liouville space description is obtained

\[
\varphi^{(n)}(t) = \bigoplus_{C} \frac{1}{n!} \prod_{c_m^n} (|C_m^n|) \varphi_{C^n_m}(t).
\]  

The \( \left[ \_ \right]_{n \text{-body}} \) has been omitted in Eq.(I.119) for simplicity. The constants \( \frac{1}{n!} \prod_{c_m^n} (|C_m^n|) \) can be absorbed into the normalization if desired. The first few terms in Eq.(I.119) read explicitly

\[
\varphi^{(1)}(1) = \varphi_f(1),
\]  

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\( \varphi^{(2)}(12) = \frac{1}{2} \varphi_f(1) \varphi_f(2) \oplus \varphi_b(12), \) 
\( \varphi^{(3)}(123) = \frac{1}{6} \varphi_f(1) \varphi_f(2) \varphi_f(3) \]
\( \oplus \frac{1}{3} [\varphi_f(1) \varphi_b(23) \oplus \varphi_f(2) \varphi_b(13) \oplus \varphi_f(3) \varphi_b(12)] \]
\( \oplus \varphi_b(123), \) 
\( \varphi^{(3)}(123) = \frac{1}{6} \varphi_f(1) \varphi_f(2) \varphi_f(3) \)
\( \oplus \frac{1}{6} [\varphi_f(1) \varphi_f(2) \varphi_b(34) \oplus \varphi_f(1) \varphi_f(3) \varphi_b(24) \oplus \varphi_f(1) \varphi_f(4) \varphi_b(23)] \]
\( \oplus \varphi_f(2) \varphi_f(3) \varphi_b(14) \oplus \varphi_f(2) \varphi_f(4) \varphi_b(13) \oplus \varphi_f(3) \varphi_f(4) \varphi_b(12)] \]
\( \oplus \frac{1}{6} [\varphi_b(12) \varphi_b(34) \oplus \varphi_b(13) \varphi_b(24) \oplus \varphi_b(14) \varphi_b(23)] \)
\( \oplus \frac{1}{4} [\varphi_f(1) \varphi_b(234) \oplus \varphi_f(2) \varphi_b(134)] \)
\( \oplus \varphi_f(3) \varphi_b(124) \oplus \varphi_f(4) \varphi_b(123)] \)
\( \oplus \varphi_b(1234). \)

The \( n \)-bound channels can be removed from consideration since they are not involved in a scattering problem.

From Eq.(1.110) the kinetic equation for a cluster evolution is then written as
\( i \frac{\partial \varphi_{C_m}}{\partial t} = \sum_{n \geq |C_m|} \left[ \begin{array}{c} n \\ C_m \end{array} \right] \text{Tr}_{|C_m|+1, \ldots, n} \mathcal{J}_{C_m}^{n} \left[ i \frac{\partial \rho^{(n)}}{\partial t} \right]_{n\text{-body}}, \) 

where \([i \frac{\partial \rho^{(n)}}{\partial t}]_{n\text{-body}}\) denotes an isolated \( n \)-body problem and the label \([ \cdots ]_{n\text{-body}}\) will be dropped for simplicity from now on.

Since the right hand side of Eq.(1.124) involves only the \( n \)-particle channel space operators, the rest of the task is to deal with the purely quantum
mechanical process involving an isolated set of \( n \) particles. For an isolated \( n \)-particle system the quantum Liouville equation is

\[
i\frac{\partial \rho^{(n)}}{\partial t} = \mathbf{L}^{(n)} \rho^{(n)}, \tag{I.125}
\]

therefore the right hand side of Eq.(1.124) becomes

\[
\sum_{n \geq|C_m|} \sum_{C^n} \left( \begin{array}{c} n \\ C_m \end{array} \right) \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \left( i \frac{\partial \rho^{(n)}}{\partial t} \right) = \mathcal{J}_{C_m |C_m|}^{\dagger} \mathbf{L}_{C_m |C_m|} \rho^{(|C_m|)} + \sum_{n > |C_m|} \sum_{C^n} \left( \begin{array}{c} n \\ C_m \end{array} \right) \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \left( \mathbf{L}^{(n)} \rho^{(n)} \right). \tag{I.126}
\]

For \( n =|C_m| \)

\[
\mathcal{J}_{C_m |C_m|}^{\dagger} \mathbf{L}_{C_m |C_m|} \rho^{(|C_m|)} = \mathbf{L}_{C_m |C_m|} \rho^{(|C_m|)}. \tag{I.127}
\]

The further manipulations for \( n > |C_m| \) in the Eq.(1.126) are

\[
\mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \left( \mathbf{L}^{(n)} \rho^{(n)} \right) = \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \mathbf{L}_{C^n} \rho^{(n)} + \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \left( \mathbf{L}^{(n)} - \mathbf{L}_{C^n} \right) \rho^{(n)} \tag{I.128}
\]

\[
= \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{J}_{C^n}^{\dagger} \Omega^{(n)} \rho^{(n)} \tag{I.129}
\]

where the first term in the right-hand-side of Eq. (I.128) vanishes upon tracing. Various superoperators appeared in Eqs.(I.128) and (I.129) have been defined in Chapter I-2. These lead, from Eq.(I.124), to a compact set of kinetic equations for the clusters \( C_m \)

\[
i \frac{\partial \varphi^{C_m}}{\partial t} = \mathbf{L}_{C_m |C_m|} \varphi^{C_m |C_m|} + \sum_{n > |C_m|} \sum_{C^n} \left( \begin{array}{c} n \\ C_m \end{array} \right) \mathrm{Tr}_{|C_m|+1,\ldots,n} \mathcal{T}_{C^n} \varphi^{(n)}. \tag{I.130}
\]

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These equations are compact and completely general. By using the relation between transition superoperators

$$T_{C^n} = \sum_{B^n} T_{C^n, B^n},$$  
(I.131)

Eq.(I.130) can be rewritten to emphasize the initial reaction channels $B^n$ as

$$i \frac{\partial \varphi_{Cm}}{\partial t} = L_{Cm | Cm} | \varphi_{Cm | Cm} | +$$

$$\sum_{n>|C_m|} \bigg( \bigg( \prod_{B_m^n \in B^n} | B_m^n | \bigg) \bigg)_{|C_m |} \bigg( \prod_{B_m^n \in B^n} \varphi_{B_m^n}(t) \bigg), \quad (I.132)$$

where Eqs.(I.119) has been used. As an illustration, the first few terms of a monomer equation are listed explicitly as follows

$$i \frac{\partial \varphi_{f1}}{\partial t} = L_{f1 f1} +$$

$$\sum_{n>|C_m|} \bigg( \bigg( \prod_{B_m^n \in B^n} | B_m^n | \bigg) \bigg)_{|C_m |} \bigg( \prod_{B_m^n \in B^n} \varphi_{B_m^n}(t) \bigg),$$

$$\begin{align*}
&+ \text{Tr}_2 T_{12,13} \varphi_{f1} \varphi_{f2} \\
&+ \frac{1}{2} \text{Tr}_2 T_{123,123} \varphi_{f1} \varphi_{f2} \varphi_{f3} \\
&+ \left[ \text{Tr}_2 T_{123,3(12)} \varphi_{f3} \varphi_{b12} + \text{Tr}_2 T_{123,2(13)} \varphi_{f2} \varphi_{b13} + \text{Tr}_2 T_{123,1(23)} \varphi_{f1} \varphi_{b23} \right] \\
&+ \frac{1}{2} \text{Tr}_2 T_{1(23),123} \varphi_{f1} \varphi_{f2} \varphi_{f3} \\
&+ \left[ \text{Tr}_2 T_{1(23),3(12)} \varphi_{f3} \varphi_{b12} + \text{Tr}_2 T_{1(23),2(13)} \varphi_{f2} \varphi_{b13} + \text{Tr}_2 T_{1(23),1(23)} \varphi_{f1} \varphi_{b23} \right] \\
&+ \frac{1}{6} \text{Tr}_2 T_{1234,1234} \varphi_{f1} \varphi_{f2} \varphi_{f3} \varphi_{f4} \\
&+ \frac{1}{3} \left[ \text{Tr}_2 T_{1234,34(12)} \varphi_{f3} \varphi_{f4} \varphi_{b12} + \text{Tr}_2 T_{1234,24(13)} \varphi_{f2} \varphi_{f4} \varphi_{b13} + \text{Tr}_2 T_{1234,34(14)} \varphi_{f2} \varphi_{f3} \varphi_{b14} + \text{Tr}_2 T_{1234,14(23)} \varphi_{f1} \varphi_{f4} \varphi_{b23} + \text{Tr}_2 T_{1234,13(24)} \varphi_{f1} \varphi_{f3} \varphi_{b24} + \text{Tr}_2 T_{1234,12(34)} \varphi_{f1} \varphi_{f2} \varphi_{b34} \right] \\
&+ \frac{2}{3} \left[ \text{Tr}_2 T_{1234,13(24)} \varphi_{b12} \varphi_{b13} \varphi_{b24} + \text{Tr}_2 T_{1234,12(34)} \varphi_{b13} \varphi_{b24} + \text{Tr}_2 T_{1234,13(24)} \varphi_{b12} \varphi_{b13} \varphi_{b24} \right] \\
&+ \left[ \text{Tr}_2 T_{1234,1(234)} \varphi_{f1} \varphi_{b234} + \text{Tr}_2 T_{1234,2(134)} \varphi_{f2} \varphi_{b134} \right]
\end{align*}$$

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\[\begin{align*}
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{1234,3(124)} \mathcal{P}_{f3} \mathcal{P}_{b124} + \text{Tr}_{2,3,4} \mathcal{T}_{1234,4(123)} \mathcal{P}_{f4} \mathcal{P}_{b123} \\
\oplus & \frac{1}{6} \text{Tr}_{2,3,4} \mathcal{T}_{12(34),1234} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{f4} \\
\oplus & \frac{1}{3} \left[ \text{Tr}_{2,3,4} \mathcal{T}_{12(34),34(12)} \mathcal{P}_{f3} \mathcal{P}_{f4} \mathcal{P}_{b12} + \text{Tr}_{2,3,4} \mathcal{T}_{12(34),24(13)} \mathcal{P}_{f2} \mathcal{P}_{f4} \mathcal{P}_{b13} \right] \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{12(34),23(14)} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{b14} + \text{Tr}_{2,3,4} \mathcal{T}_{12(34),14(23)} \mathcal{P}_{f1} \mathcal{P}_{f4} \mathcal{P}_{b23} \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{12(34),13(24)} \mathcal{P}_{f1} \mathcal{P}_{f3} \mathcal{P}_{b24} + \text{Tr}_{2,3,4} \mathcal{T}_{12(34),12(34)} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{b34} \\
\oplus & \frac{2}{3} \left[ \text{Tr}_{2,3,4} \mathcal{T}_{12(34),(12)(34)} \mathcal{P}_{b12} \mathcal{P}_{b534} + \text{Tr}_{2,3,4} \mathcal{T}_{12(34),(13)(24)} \mathcal{P}_{b13} \mathcal{P}_{b24} \right] \\
\oplus & \frac{1}{6} \text{Tr}_{2,3,4} \mathcal{T}_{13(24),1234} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{f4} \\
\oplus & \frac{1}{3} \left[ \text{Tr}_{2,3,4} \mathcal{T}_{13(24),34(12)} \mathcal{P}_{f3} \mathcal{P}_{f4} \mathcal{P}_{b12} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),24(13)} \mathcal{P}_{f2} \mathcal{P}_{f4} \mathcal{P}_{b13} \right] \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{13(24),23(14)} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{b14} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),14(23)} \mathcal{P}_{f1} \mathcal{P}_{f4} \mathcal{P}_{b23} \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{13(24),13(24)} \mathcal{P}_{f1} \mathcal{P}_{f3} \mathcal{P}_{b24} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),12(34)} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{b34} \\
\oplus & \frac{2}{3} \left[ \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(12)(34)} \mathcal{P}_{b12} \mathcal{P}_{b534} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(13)(24)} \mathcal{P}_{b13} \mathcal{P}_{b24} \right] \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(14)(23)} \mathcal{P}_{b14} \mathcal{P}_{b23} \\
\oplus & \left[ \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(1234)} \mathcal{P}_{f1} \mathcal{P}_{b234} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(2134)} \mathcal{P}_{f2} \mathcal{P}_{b134} \right] \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(3124)} \mathcal{P}_{f3} \mathcal{P}_{b124} + \text{Tr}_{2,3,4} \mathcal{T}_{13(24),(4123)} \mathcal{P}_{f4} \mathcal{P}_{b123} \\
\oplus & \frac{1}{6} \text{Tr}_{2,3,4} \mathcal{T}_{14(23),1234} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{f4} \\
\oplus & \frac{1}{3} \left[ \text{Tr}_{2,3,4} \mathcal{T}_{14(23),34(12)} \mathcal{P}_{f3} \mathcal{P}_{f4} \mathcal{P}_{b12} + \text{Tr}_{2,3,4} \mathcal{T}_{14(23),24(13)} \mathcal{P}_{f2} \mathcal{P}_{f4} \mathcal{P}_{b13} \right] \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{14(23),23(14)} \mathcal{P}_{f2} \mathcal{P}_{f3} \mathcal{P}_{b14} + \text{Tr}_{2,3,4} \mathcal{T}_{14(23),14(23)} \mathcal{P}_{f1} \mathcal{P}_{f4} \mathcal{P}_{b23} \\
\oplus & \text{Tr}_{2,3,4} \mathcal{T}_{14(23),(1324)} \mathcal{P}_{f1} \mathcal{P}_{f3} \mathcal{P}_{b24} + \text{Tr}_{2,3,4} \mathcal{T}_{14(23),(1234)} \mathcal{P}_{f1} \mathcal{P}_{f2} \mathcal{P}_{b34} \\
\end{align*}\]
Similarly the first few terms of a dimer equation are

\[
\frac{1}{i} \frac{\partial \rho_{12}}{\partial t} = L_{12} \rho_{12} + \frac{1}{2} \left[ Tr_{3,4} T_{1(12),3(12)} \rho_{34}\rho_{34} + Tr_{3,4} T_{1(12),3(12)} \rho_{34}\rho_{34} + Tr_{3,4} T_{1(12),3(12)} \rho_{34}\rho_{34} + Tr_{3,4} T_{1(12),3(12)} \rho_{34}\rho_{34} \right]
\]

(I.133)
\[ \begin{align*}
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(12)(34) \rho_{12} \rho_{34} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34)(13)(24) \rho_{13} \rho_{24} \right] \\
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(14)(23) \rho_{14} \rho_{23} \right] \\
&\bigoplus \frac{3}{2} \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34,1)(234) \rho_{1} \rho_{234} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34,2)(134) \rho_{2} \rho_{134} \right] \\
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34,3)(124) \rho_{3} \rho_{124} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34,4)(123) \rho_{4} \rho_{123} \right] \\
&\bigoplus \frac{1}{4} \text{Tr}_{3,4} \mathcal{T}_{12}(34)(1234) \rho_{1} \rho_{2} \rho_{3} \rho_{4} \\
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(12) \rho_{3} \rho_{4} \rho_{b12} \rho_{b12} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34)(13) \rho_{2} \rho_{4} \rho_{b13} \rho_{b13} \right] \\
&\bigoplus \text{Tr}_{3,4} \mathcal{T}_{12}(34)(14) \rho_{1} \rho_{3} \rho_{b14} \rho_{b14} \\
&\bigoplus \frac{3}{2} \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34,1)(234) \rho_{1} \rho_{234} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34,2)(134) \rho_{2} \rho_{134} \right] \\
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34,3)(124) \rho_{3} \rho_{124} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34,4)(123) \rho_{4} \rho_{123} \right] \\
&+ \cdots \\
\end{align*} \]

The set of terms for the trimer equation is similarly

\[ \frac{1}{i} \frac{\partial \rho_{123}}{\partial t} = L_{123} \rho_{b123} \]

\[ + \frac{1}{6} \text{Tr}_{3,4} \mathcal{T}_{12}(34)_{1,1234} \rho_{1} \rho_{2} \rho_{3} \rho_{4} \]

\[ + \frac{1}{3} \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(12) \rho_{3} \rho_{4} \rho_{b12} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34)(13) \rho_{2} \rho_{4} \rho_{b13} \right] \\
&\bigoplus \text{Tr}_{3,4} \mathcal{T}_{12}(34)(14) \rho_{1} \rho_{3} \rho_{b14} \rho_{b14} \\
&\bigoplus \frac{2}{3} \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(12) \rho_{12} \rho_{b34} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34)(13) \rho_{13} \rho_{b24} \right] \\
&\bigoplus \text{Tr}_{3,4} \mathcal{T}_{12}(34)(14) \rho_{1} \rho_{2} \rho_{b34} \rho_{b23} \\
&\bigoplus \left[ \text{Tr}_{3,4} \mathcal{T}_{12}(34)(1234) \rho_{1} \rho_{234} \right. \\
&\left. + \text{Tr}_{3,4} \mathcal{T}_{12}(34)(2134) \rho_{2} \rho_{134} \right] \]

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Only terms up to four particles have been systematically listed. The terms for more particles are lengthy but straightforward. The equations describe all possible channel reactions, including elastic, break up, rearrangement, recombination and decay.

**I-3.3 Discussion**

Eq.(I.130) is the main result of this chapter. The derivation of this equation involves two important aspects. i) First is the reduction of the \( N \)-particle density operator into various cluster contributions. The reduction is equivalent to tracing over asymptotic channels which has been discussed in Chapter I-2. Since the asymptotic channel structures have a one to one correspondence with the Lowry-Snider partition\(^{23}\), the asymptotic channel reduction is essentially equivalent to that of Lowry and Snider when limited to monomers and dimers. Therefore the asymptotic channel reduction is an alternative way to view the Lowry-Snider form for the kinetic theory of recombination and decay. It has been shown by Evans\(^{30}\) that the kinetic theory of Hoffman and Kouri\(^{27}\), which is based on the BKLT\(^{9}\) scattering theory, also leads to exactly the same set of coefficients as those of Lowry and Snider for the monomer and dimer case. In equilibrium statistical mechanics, a monomer and dimer cluster expansion for the grand partition function has been given by Osborn\(^{36}\). His method relies on the \( Q^+_{CN} \) projectors rather than on the counting of asymptotic channels. ii) The second aspect regards the method of closure of the kinetic equations. In the Lowry-Snider theory the closure is achieved through the cluster (monomer and dimer) projection operators.
which act on the total interacting Liouville space to select out the monomer and dimer density operators involved in an isolated $n$-atom collision, see for example their Eqs.(64), (66) and (79). That method is significantly different from the usual BBGKY procedure. In this work, after the $N$-particle density operator is broken down into reduced cluster density operators defined in the asymptotic channel Liouville spaces, the time evolution of a cluster $C_m$ is due to all possible isolated $n$-body collisions ($n \geq |C_m|$), each of which is described by the $n$-body two-Liouville space theory of Chapter I-2. The two-Liouville space structure has been utilized in two different ways. For the reduction of the $N$-particle density operator an $N$-particle two-Liouville space has been used. In contrast, multiple two-Liouville spaces characterized by $2 \leq n \leq N$ have been employed to formulate the cluster kinetic equations (I.124).

Notably the clusters are defined as asymptotic bound fragments in the asymptotic channel Liouville spaces $L_{CN}$ rather than in the total Liouville spaces $L^{(N)}$. The corresponding density operators $\rho_{C_m}$, from the chemical kinetics point of view, involves the density operators of multiple two-Liouville spaces [see Eq.(I.110)]. The assumption of equation (I.110) leads to the kinetic equation (I.130) for the clusters $C_m$ by using the two-Liouville space formalism of Chapter I-2. A primitive chemical interpretation of Eq.(I.130) is that the clusters in a gas are isolated free molecules most of the time but can suffer collisions from time to time.

The assumption of strong orthogonality used by Lowry and Snider is removed by using the two-Liouville space theory of Chapter I-2. The separation between interacting Liouville space and the asymptotic Liouville spaces makes it possible to define a set of clusters in the asymptotic Liouville space which are mutually orthogonal to each other, both from the physical point of
view and by definition. The concept of cluster is built upon the asymptotic subchannels of the \( N \)-particle system without resorting to the projection operators used by Lowry and Snider, Klimontovich and co-workers\(^7\). The two-Liouville space theory introduced here provides a different approach to the reactive gas quantum kinetic problem.

As an extension to the Lowry-Snider theory, clusters of all orders are systematically included in the present treatment. An application of this feature might be found in molecular (laser) beam induced metal cluster dynamics, where metal clusters of \( n = 2 - 10 \) atoms or larger are frequently encountered\(^{33,34} \). As formulated in Eq.(1.130), this formal generalization does not demand very much extra labour.

The kinetic equations for the monomer and dimer derived by Lowry and Snider are based on the chemical reaction of recombination, decay and rearrangement collisions limited to the physically most probable reactive processes

\[
M + M \leftrightarrow M + M \\
M + D \leftrightarrow M + D \\
D + D \leftrightarrow D + D \\
M + M + M \leftrightarrow M + D \\
M + M + D \leftrightarrow D + D.
\]

Their arguments are physically sound and practically necessary in order to simplify their formalism. In this work no particular restriction on collision processes is imposed. The transition superoperators in Eq.(I.130) include all possible channel reactions that may be encountered in the usual chemical
kinetics, for example those in a four-particle scattering problem

\begin{align*}
M + M + M + M & \leftrightarrow M + M + M + M \\ (#1.141) \\
M + M + M + M & \leftrightarrow M + M + D \\ (#1.142) \\
M + M + M + M & \leftrightarrow D + D \\ (#1.143) \\
M + M + D & \leftrightarrow M + M + D \\ (#1.144) \\
M + M + D & \leftrightarrow D + D \\ (#1.145) \\
D + D & \leftrightarrow D + D. \\ (#1.146)
\end{align*}

Appropriate terms in Eq.(1.130) can be easily chosen for a specific application. For instance if the number of the collision fragments are restricted to three and the types of clusters are limited to monomer, dimer and trimer, the terms in Eq.(1.130) can be selected to represent the following set of collisions

\begin{align*}
T + T + T & \leftrightarrow T + T + T \\ (#1.147) \\
D + T + T & \leftrightarrow D + T + T \\ (#1.148) \\
M + T + T & \leftrightarrow M + T + T \\ (#1.149) \\
T + T & \leftrightarrow T + T \\ (#1.150) \\
M + T + T & \leftrightarrow D + D + T \\ (#1.151) \\
T + T & \leftrightarrow M + D + T \\ (#1.152) \\
D + D + T & \leftrightarrow D + D + T \\ (#1.153) \\
M + D + T & \leftrightarrow M + D + T \\ (#1.154) \\
M + D + T & \leftrightarrow D + D + D \\ (#1.155) \\
M + M + T & \leftrightarrow D + T \\ (#1.156) \\
M + M + D & \leftrightarrow M + T \\ (#1.157) \\
M + M + T & \leftrightarrow M + M + T \\ (#1.158)
\end{align*}
\begin{align*}
M + T & \leftrightarrow M + T \quad \text{(I.159)} \\
M + T & \leftrightarrow D + D \quad \text{(I.160)} \\
D + D + D & \leftrightarrow D + D + D \quad \text{(I.161)} \\
D + D & \leftrightarrow D + D \quad \text{(I.162)} \\
D + D & \leftrightarrow M + M + D \quad \text{(I.163)} \\
M + M + D & \leftrightarrow M + M + D \quad \text{(I.164)} \\
M + D & \leftrightarrow M + D \quad \text{(I.165)} \\
M + D & \leftrightarrow M + M + M \quad \text{(I.166)} \\
M + M + M & \leftrightarrow M + M + M \quad \text{(I.167)} \\
M + M & \leftrightarrow M + M. \quad \text{(I.168)}
\end{align*}

The last seven terms correspond to the equations given by Sze, Ali and Snider\textsuperscript{58}, in which the trimer is further excluded, the number of fragments is limited to three or less, and the number of atoms limited to four or less. When restricted to the subset of collision processes Eqs.(I.136-I.140), the monomer and dimer equations (I.133) and (I.134) coincide, in form, with those of Lowry and Snider. An extensive set of reactive collisions has also been considered by Hoffman, Kouri\textsuperscript{27}, and Evans\textsuperscript{30}. Their equations also reduce down, in form, to those of Lowry and Snider for this limited set of collision processes.

A two-Hilbert space formulation of the quantum statistical mechanics of reactive fluids has been formulated by Evans\textsuperscript{30}, see also Hoffman and Evans\textsuperscript{29}. Their work was one of the major motivations for the consideration of a two-Liouville space formalism. The channel spaces in their work are not the asymptotic channel spaces discussed in Chapter I-2, but rather the BKLT\textsuperscript{9} channel states, which are divided into physical and spurious parts. All colli-
sion processes are realized within the physical subspaces of the channel space by use of a projection and do not involve the $N$-particle total Hilbert space. Their kinetic theory is developed from an earlier work by Hoffman, Kouri and Top\textsuperscript{27}. Their resulting kinetic equations have been compared with those of Lowry and Snider.

A generalization of the present work to describe a moderately dense gas mixture, which necessarily involves correlations, can be accomplished in one of two ways. One way is to explicitly include long-lived metastable states in the multichannel scattering. However, in order for a time dependent scattering treatment of such quantities, it is necessary to create a set of Hamiltonians which govern the time evolution of the metastable states. How to formulate such an extra set of Hamiltonians and how they would fit into the normal treatment of the system is not clear to us at present. Another way is to modify the set of asymptotic channels to include a set of secondary asymptotic channels. This method has been used by Bencze and Chandler\textsuperscript{41} in quantum scattering theory. A formulation along this line is attempted in Part III (see Chapter III-2), which is devoted to a quantum kinetic theory of moderately dense gases.

Internal states of each cluster can be easily included either by properly choosing the identification superoperators or by slightly modifying the asymptotic channels, or by a combination of both. The present form of asymptotic channel states and identification superoperators simplifies the presentation of the kinetic equations and is readily adaptable to various practical applications.
Part II

Theory of Statistical Correlations and Resonance States
Chapter II-1
Introduction to Part II

The most successful kinetic theory of gases is that based on the Boltzmann equation\(^3\). This theory includes the derivation of the hydrodynamic equations for a dilute gas and the evaluation of macroscopic transport coefficients, such as viscosity and thermal conductivity from atomic and molecular properties. To a certain extent, modern kinetic theory has been a massive effort to generalize the Boltzmann equation in a variety of ways in order to provide suitable descriptions for particular physical observations. Two of the most important generalizations are to deal with polyatomic gases and dense gases (other important extensions of the theory are to deal with rarefied gases and plasmas). The equations for polyatomic gases, such as the Wang Chang-Uhlenbeck-de Boer equation\(^{59}\) and the Waldmann-Snider equation\(^{60,26}\), are quantum mechanical generalizations of the Boltzmann equation. Dense gas kinetic theory involves a number of different aspects, such as the non-locality of the collisions\(^{152,61,62}\), three body and higher order collisions\(^{152,153,17,63,159}\), formation and reaction of stable molecules\(^{156,23,27,19,20,18}\) and the effects of pair- or higher order correlations. Snider\(^{52}\) has proposed a density-corrected quantum Boltzmann equation to explicitly account for the contribution of pair correlations to the singlet density operator. The Boltzmann collision ansatz has been used to derive a closed equation for the full singlet density operator. In an effort to extend Snider's idea to take into account the effect of a correlated pair colliding with a third particle or molecule, we tried to develop a quantum scattering theory to describe this phenomenon. Since non-equilibrium statistical mechanics has its root in equilibrium statistical mechanics, the properties of the pair-particle Ursell operator\(^{64}\), which de-
scribes statistical pair correlations at equilibrium, was the starting point for this investigation.

Historically, Beth and Uhlenbeck$^{65}$ related the second virial coefficient to the phase shifts of a binary collision. This has led to alternate expressions involving the $S$-matrix, the Jost function and the on-shell $T$-matrix$^{66,67,68}$. It has also led to relating pair correlations to the time delay$^{69,70,71}$ and to a general $S$-matrix formulation of equilibrium statistical mechanics$^{72}$. Nussenzveig$^{73}$ represents the effect of the pair correlation in terms of functions of the poles of the $S$-matrix. The poles of the $S$-matrix are associated with bound state and scattering resonances$^{74}$. This implies that the pair correlations may be associated with resonance phenomena, a subject intensively studied in quantum scattering theory$^{74,75,76}$. Unfortunately resonance theory as usually formulated involves decay and growth phenomena that does not easily fit into conventional quantum mechanics. Due to this inherent mathematical difficulty, there is even a problem in agreeing on the definition of what is a resonance$^{77}$. The immediate barrier for making any application of resonance theory to kinetic theory is that a resonance state, as usually defined as a Gamow state$^{78,74}$, is non-normalizable. Formal research on resonance theory has been confined to looking for artificial normalizations of the Gamow state$^{79,80}$. However the resulting formalisms with non-Hilbert space norms have very limited merit for application since true physical states and physical processes are in Hilbert space, or equivalently in Liouville space for an operator formalism. In an effort to formulate a multichannel scattering theory that might include resonance pairs as one of the colliding partners, so as to incorporate correlations in the kinetic theory of moderately dense gases, a way of associating a resonance pole with a Hilbert space element$^{40}$ was found. The new state was called a correlated state because of its direct...
connection to pair correlations. Our work involved the interplay of operator (functional) analysis and analytic function theory. Our analysis suggested that the non-normalizable Gamow state might be a result of an inappropriate interpretation of the Schrödinger operator. Poles of matrix elements of the resolvent of the hamiltonian were found to be of two classes, one class of poles were called correlated-state poles since they are associated with the pair particle interaction potential while the other class of poles were called structural poles, since they are associated with the free resolvent operator. The effects of the two sets of poles were not separable in the model problem that was examined and this unpleasant feature complicates the possible development of a kinetic theory aimed at including the effects of pair correlations by means of correlated states. An alternative approach to deal with our original problem of formulating moderately dense gas kinetic theory has been explored by introducing secondary asymptotic channels. Such an approach allows a time dependent scattering theory including correlations, see Chapter III-2. As another by-product of this search for a new resonance pair scattering theory, a Hilbert-Schmidt representation of Ursell operators has been found which parallels the S-matrix formulation of statistical mechanics given by Dashen, Ma and Bernstein\textsuperscript{72}. As the S-matrix formulation is based on the one species grand partition function this is an atomic picture of statistical mechanics. The Hilbert-Schmidt representation is based on the same expansion of the grand partition function and uses atomic Ursell operators, which correspond to connected graphs\textsuperscript{81}. It is found that the connected quantum Ursell operators are closely related to the Hilbert-Schmidt kernel of Faddeev\textsuperscript{5} and its generalization to the collisions of an arbitrary number of particles. This important feature permits the formulation of a general Hilbert-Schmidt representation of the Ursell operators in terms of Hilbert-Schmidt kernels.
Part II is divided into two chapters. Chapter II-2 is devoted to a formulation of a general Hilbert-Schmidt representation of equilibrium statistical mechanics. Osborn's two-species cluster expansion for the grand partition function is first generalized to an arbitrary species expansion by using the two-Liouville space scattering theory of Part I. The resulting multispecies expansion of the grand partition function is then shown to be equivalent to an atomic expansion by reexpressing channel Ursell operators in terms of atomic Ursell operators using the asymptotic completeness theorem of Faddeev\textsuperscript{5} and the condition of chemical equilibrium. An expression for an Ursell operator in terms of resolvent operators is obtained by means of a Laplace transform\textsuperscript{82}. The Hilbert-Schmidt representation of an Ursell operator is finally achieved after applying Faddeev's analysis to the combination of resolvent operators. Functional analysis and analytic function theory are employed in Chapter II-3 to formulate the new resonance theory and to evaluate the second virial coefficient by a set of $L^2$ resonance states. A separable potential is used in our model to arrive at analytical expressions. Conventional resonance theories are critically reviewed and their connection to our resonance state theory discussed. Most of material in Chapter II-3 is from Ref. (40).
Chapter II-2
Hilbert-Schmidt Representation of Ursell Operators

In this chapter a Hilbert-Schmidt representation of Ursell operators is formulated. The main purpose of such a formulation is to provide a practical method for the quantum mechanical evaluation of the equation of state of a non-ideal gas system and to explore possible applications to moderately dense gas kinetic theory. The standard starting point for evaluating the equation of state of a non-ideal gas is usually the cluster expansion of the grand partition function, a classic approach developed by Ursell and Mayer. The corresponding quantum mechanical cluster expansion is due to Kahn and Uhlenbeck. Their method applies equally well for classical mechanics. The cluster expansion is certainly the most efficient method known so far that can be used to break the \( N \sim 10^{23} \) identical particle system into few-body systems which can be dealt with few-body classical or quantum mechanics. However the cluster expansion suffers from slow convergence at higher density, and is of questionable validity at densities close to condensation. Lee and Yang explored the properties of \( \Xi(z) \), the grand partition function as a function of fugacity extended to the complex \( z \)-plane. A phase transition is predicted by their theory if \( \Xi(z) \) has a root \( z_0 \) arbitrarily close to the positive real axis. Hill and others introduced multispecies fugacity expansions. This important development has the flexibility to account explicitly for stable molecules formed due to strong interatomic forces. Hill has argued that the molecular picture is equivalent to the atomic picture expansion since terms in the molecular fugacity expansion can give rise to higher order terms in the atomic fugacity expansion. However it has been shown that molecular fugacity expansions have better convergence behaviour than
the corresponding atomic ones. It was noticed by Hill that his definition of cluster is arbitrary because classical phase space does not allow a unique division among molecules, metastable species and elementary atoms. This difficulty has also been discussed by Ebeling, Kraeft and Kremp\textsuperscript{89}. As argued in Part I, the various bound states can only be rigorously defined in a many-particle system in terms of asymptotic channels. Dashen, Ma and Bernstein\textsuperscript{72} obtain a Feynman-Dyson expansion for the grand partition function and their use of Feynman diagrams allows a separation between a "dynamical part" and a "statistical part"\textsuperscript{72}. The validity of their method is based on the connectedness of Feynman diagrams. The resulting expression for the correlations agrees exactly with those derived using a quantum cluster expansion. A modern scattering theory formulation of a monomer-dimer mixture has been given by Osborn\textsuperscript{36}. His method relies on the asymptotic completeness theorem of the multichannel scattering theory of Faddeev\textsuperscript{5}. An elegant two-Hilbert space formalism for the multispecies fugacity expansion has been provided by Hoffman and Evans\textsuperscript{29}. Their formalism is based on the method used in a rigorous reactive quantum kinetic theory developed by Hoffman, Kouri and their coworkers\textsuperscript{27,28}, which is in turn based on the BKLT multichannel scattering theory\textsuperscript{9}.

The classical evaluation of the equation of state is in terms of virial coefficients, which are related to Ursell operators. Diagrammatic representations are used to classify the large numbers of configurations. The first quantum mechanical calculation of the second virial coefficient was due to Beth and Uhlenbeck\textsuperscript{65}, in terms of quantum scattering phase shifts. Since the phase shifts are related to the $S$-matrix, the Jost function, and the on-shell $T$-matrix, various alternative expressions of this result have been reported\textsuperscript{66,70,68}. Smith\textsuperscript{69} relates phase shift to the time delay and general-
ized this to time delay matrices for general realistic collisions. Thus the pair particle Ursell operator can be expressed in terms of a time delay. Higher order Ursell operators can also be expressed in terms of a time delay formalism. For example, the general $S$-matrix formulation of equilibrium statistical mechanics is basically in terms of the time delay. The most elegant formalism for the virial coefficients using the time delay method has been given by Osborn. In his work the correlations of dimer-dimer, monomer-dimer and monomer-monomer are related to the corresponding time delays on an equal footing. Despite the various developments, the evaluation of the second virial coefficient in analytical form can only be done for a limited class of potentials. It is even more difficult to evaluate higher order virials in analytical form due to the fact that in general the quantum mechanical many-body problem still cannot be solved analytically. Therefore reliable numerical methods are indispensable for solving realistic problems. Meanwhile, functional analysis has been used for establishing the reliability of the numerical methods. The Hilbert-Schmidt method is an extremely powerful method for solving quantum mechanical two-particle scattering problems. However it has rarely been used in formal statistical mechanics. Necessarily, calculating higher order virial coefficients rests on three- or more body quantum scattering theory, where the Faddeev analysis becomes obligatory. Here the Faddeev analysis is employed to formulate a Hilbert-Schmidt representation of equilibrium statistical mechanics by expressing the Ursell operators in terms of Hilbert-Schmidt operators.

The resulting formalism is in a form ready for direct computation. An example of such a computation is given in the following chapter.

This chapter is divided into three sections. Section II-2.1 is devoted to a multispecies cluster expansion for the grand partition function. This expan-
sion is an extension of Osborn's monomer-dimer expansion and is based on the two-Liouville space scattering theory of Part I. It is noted that the present concept of asymptotic space is slightly different from that of Chandler and Gibson, and of Osborn, see the discussion in Chapter I-2. Essentially, the bound fragments are defined only in asymptotic channels, which are characterized by the number of scattering particles \( n \) (\( 2 \leq n \leq N \)). The clusters are special bound fragments which are defined only in the asymptotic channels of an \( N \)-particle scattering problem, with \( N \) being the total number of particles in the (kinetic) system, see Section I-3.2. The equivalence of a multi-species expansion and an atomic expansion of the grand partition function at equilibrium is established by reexpressing channel Ursell operators in terms \( n \)-particle Ursell operators through the use of asymptotic completeness. A Hilbert-Schmidt representation of statistical mechanics through Ursell operators is presented in Section II-2.2. Ursell operators are first expressed in terms of various resolvents by the Laplace transform. An appeal to functional analysis allows the recognition that certain operators are of Hilbert-Schmidt type so that a Hilbert-Schmidt representation can be introduced. In the case of the three-particle Ursell operator, the Faddeev analysis of three-body scattering is utilized for obtaining the Hilbert-Schmidt expansion. Detailed analyses stop at the three-particle system in this thesis. Discussions and notes are collected in Section II-2.3. A brief derivation of Faddeev equations can be found in Appendix A.

II-2.1 Multispecies Cluster Expansion for the Grand Partition Function

Particles in a gas are correlated at thermal equilibrium due to the potential interactions between them. The amount of correlation increases as the
gas become denser. A moderately dense gas at equilibrium is described, in an atomic picture, by the virial equation of state

\[ P \beta = n_1 + B_2(T)n_1^2 + B_3(T)n_1^3 + \cdots, \]  
(II.1)

where \( \beta^{-1} = kT \). The quantities \( B_2(T), B_3(T), \cdots \), are called the second, third, \cdots, virial coefficients respectively and depend on the temperature \( T \) and particle interaction potentials. They are independent of density \( n_1 \) and/or pressure \( P \). The derivation of expressions for the virial coefficients in terms of quantum mechanical hamiltonians is one of the major (solved) tasks of statistical mechanics.

In the rest of this section, instead of starting from an atomic grand partition function theory, a multispecies grand partition function expansion of the equation of state (in the molecular picture) is first presented. The latter is then shown to be equivalent to an atomic picture expansion by using asymptotic completeness and chemical equilibrium.

Consider an \( N \)-particle system in thermal equilibrium and assume Boltzmann statistics are applicable. The \( N \) particles at a given temperature \( T \) and volume \( V \) may exist in a particular channel, say \( C^N \). Channel \( C^N \) has \( \tilde{C}_m^N \) clusters of type \( C_m \), each containing \( \tilde{C}_m^N \) particles, so that

\[ \sum_{\tilde{C}_m^N} \tilde{C}_m^N \| C_m \| = N. \]  
(II.2)

The density of cluster \( C_m \), which has been defined in Section I-3.2, is given by

\[ n_{C_m} = \frac{\tilde{C}_m^N}{V}. \]  
(II.3)

The first objective is to give a multicluster equation of state in the form of

\[ P \beta = \sum_n \sum_{\tilde{C}_n} a_{\tilde{C}_n}(T) \prod_{\tilde{C}_m} n_{C_m}^{\tilde{C}_m^N}. \]  
(II.4)
Define an \( n \) (\( 1 \leq n \leq N \)) particle channel probability operator \( W_{\mathcal{C}^n} \) as

\[
W_{\mathcal{C}^n} = Q_{\mathcal{C}^n} e^{-\beta H^{(n)}},
\]

(II.5)

where \( Q_{\mathcal{C}^n} \) is an orthogonal channel projection superoperator, one for each channel (including the \( n \)-particle total bound channel). In the case of a scattering channel, \( Q_{\mathcal{C}^n} \) is defined in terms of the channel Møller superoperator \( \Omega_{\mathcal{C}^n} \) in Chapter I-2,

\[
Q_{\mathcal{C}^n} = \Omega_{\mathcal{C}^n} \Omega_{\mathcal{C}^n}^{\dagger}.
\]

(II.6)

A compatible channel (see Section I-3.2) probability operator \( W_{\tilde{\mathcal{C}}^n} \) is defined as

\[
W_{\tilde{\mathcal{C}}^n} = \frac{1}{n!} \left( \prod_{\tilde{\mathcal{C}}^n \in \tilde{\mathcal{C}}^n} | \tilde{\mathcal{C}}^n \rangle \langle \tilde{\mathcal{C}}^n | \right) Q_{\tilde{\mathcal{C}}^n} e^{-\beta H^{(n)}},
\]

(II.7)

where \( Q_{\tilde{\mathcal{C}}^n} \) is a collection of compatible orthogonal channel projection superoperators

\[
Q_{\tilde{\mathcal{C}}^n} = \sum_{\mathcal{C}^n \in \tilde{\mathcal{C}}^n} Q_{\mathcal{C}^n}.
\]

(II.8)

Define the partition function for compatible channel \( \tilde{\mathcal{C}}^n \)

\[
Q_{\tilde{\mathcal{C}}^n}(V, T) = \left( \prod_{\tilde{\mathcal{C}}^n \in \tilde{\mathcal{C}}^n} | \tilde{\mathcal{C}}^n \rangle \langle \tilde{\mathcal{C}}^n | \right)^{-1} \text{Tr} W_{\tilde{\mathcal{C}}^n}
\]

(II.9)

Denote \( z_{\mathcal{C}_m} \) as the fugacity associated with the cluster of type \( \mathcal{C}_m \). The multispecies grand partition function is

\[
\Xi(V, T, z_{\mathcal{C}_m}) = \sum_{\mathcal{C}^n} \sum_{\tilde{\mathcal{C}}^n} Q_{\tilde{\mathcal{C}}^n}(V, T) \prod_{\tilde{\mathcal{C}}^n \in \tilde{\mathcal{C}}^n} z_{\mathcal{C}_m}^{k_{\mathcal{C}_m}^n}.
\]

(II.10)

With such a grand partition function the equation of state can be determined from

\[
P \beta = \frac{1}{V} \ln \Xi.
\]

(II.11)
The ensemble average number $|\mathcal{C}_m|$ of each cluster of type $C_m$ can also be obtained

$$|\mathcal{C}_m| = z_{C_m} \frac{\partial}{\partial z_{C_m}} \ln \Xi.$$  \hspace{1cm} (II.12)

A second set of expansions can be introduced as

$$\Xi = \exp \left[ V \sum_n \sum b_{C_n} (V, T) \prod_{\mathcal{C} m \in \mathcal{C}_n} z_{C_m}^{|\mathcal{C}_m|} \right],$$  \hspace{1cm} (II.13)

where the cluster coefficients $b_{C_n}(V, T)$ are given in terms of Ursell operators by

$$b_{C_n}(V, T) = \left( \prod_{\mathcal{C} m \in \mathcal{C}_n} \frac{|\mathcal{C}_m|!V}{|\mathcal{C}_m|!} \right)^{-1} \text{Tr} \mathcal{U}_{\mathcal{C}_n}. \hspace{1cm} (II.14)$$

The Ursell operators are related to the $W$ operators, of which first few terms are

$$W_M = U_M \hspace{1cm} (II.15)$$
$$W_D = U_D \hspace{1cm} (II.16)$$
$$W_{M^2} = U_{M^2} + U_M^2 \hspace{1cm} (II.17)$$
$$W_T = U_T \hspace{1cm} (II.18)$$
$$W_{MD} = U_{MD} + U_M U_D \hspace{1cm} (II.19)$$
$$W_{M^3} = U_{M^3} + 3U_{M^2} U_M + U_M^3 \hspace{1cm} (II.20)$$
$$W_Q = U_Q \hspace{1cm} (II.21)$$
$$W_{M^2D} = U_{M^2D} + U_{M^2} U_D + 2U_{MD} U_M + U_M^2 U_D \hspace{1cm} (II.22)$$
$$W_{D^2} = U_{D^2} + U_D^2 \hspace{1cm} (II.23)$$
$$W_{MT} = U_{MT} + U_M U_T \hspace{1cm} (II.24)$$

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\[ W_{M^4} = U_{M^4} + 4U_{M^3}U_M + 3U_{M^2}^2 + 6U_{M^2}U_M^2 + U_M^4 \]  
\[ W_P = U_P \]  
\[ W_{MQ} = U_{MQ} + U_MU_Q \]  
\[ W_{M^2T} = U_{M^2T} + U_{M^2}U_T + 2U_{MT}U_M + U_M^2U_T \]  
\[ W_{MD^2} = U_{MD^2} + U_MU_D^2 + 2U_{MD}U_D + U_MU_D^2 \]  
\[ W_{M^3D} = U_{M^3D} + U_{M^3}U_D + 3U_{M^2D}U_M + 3U_{MD}U_M^2 + 3U_{M^2}U_MU_D + U_M^3U_D \]  

where \( M \) stands monomer, \( D \) for dimer, \( T \) for trimer, \( Q \) and \( P \) for four- and five-particle clusters respectively. The interpretation of the Ursell operators is such that \( U_M^2, U_M^3 \) are pair- and three-monomer correlations respectively; \( U_{MD}, U_{MT} \) and \( U_{MQ} \) are monomer-dimer, monomer-trimer and monomer-four-particle cluster correlations respectively.

A general expression for this series is

\[ W_{\tilde{C}^n} = \sum_{\tilde{C}^n} \frac{\prod_{\bar{C}_m \in \tilde{C}^n} |\tilde{C}_m|!}{\prod_{\bar{C}_m \in \tilde{C}^n} |\bar{C}_m|!! |\bar{C}_m^k|!!} \prod_{\bar{C}_m \in \tilde{C}^n} U_{\bar{C}_m} \]  

with the restriction on the sum that

\[ \sum_{\tilde{C}_h} |\bar{C}_m| |\bar{C}_m^k| = |\tilde{C}_m| . \]  

In words the summation is over all possible ways of dividing the number \( |\tilde{C}_m| \) [which is, e.g., 3 for the monomer and 1 for the dimer in Eq.(II.30)] of \( W \) into a sum of fragments \( \bar{C}_m^k \) with \( |\bar{C}_m^k| \) clusters of type \( C_m \). The inverse transformation expresses the Ursell operators in terms of \( W \)'s, the first few terms being

\[ U_M = W_M \]
\[ U_D = W_D \]  
\[ U_{M^2} = W_{M^2} - W_M^2 \]  
\[ U_T = W_T \]  
\[ U_{MD} = W_{MD} - W_M W_D \]  
\[ U_{M^3} = (W_{M^3} - W_M^3) - 3(W_{M^2} W_M - W_M^3) \]  
\[ U_Q = W_Q \]  

\[ U_{M^2 D} = (W_{M^2 D} - W_M^2 W_D) - 2(W_{MD} W_M - W_M^2 W_D) \]  
\[ U_{D^2} = W_{D^2} - W_D^2 \]  
\[ U_{MT} = W_{MT} - W_M W_T \]  

\[ U_{M^4} = (W_{M^4} - W_M^4) - 4(W_{M^3} - W_M^3) W_M \]  
\[ - 3(W_{M^2} - W_M^2)^2 + 6(W_{M^2} - W_M^2) W_M^2 \]  
\[ U_P = W_P \]  
\[ U_{MQ} = W_{MQ} - W_M W_Q \]  

\[ U_{M^2 T} = (W_{M^2 T} - W_M^2 W_T) - 2(W_{MT} W_M - W_M^2 W_T) \]  
\[ U_{MD^2} = (W_{MD^2} - W_M W_D^2) - 2(W_{MD} W_D - W_M W_D^2) \]  

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\[ U_{\text{MD}} = (W_{\text{MD}}^3 - W_M^3 W_D) - (W_M^3 W_D - W_M^3 W_D) \]
\[ - 3(W_M^2 - W_M^2)(W_{\text{MD}} - W_M W_D) - 3(W_M^2 W_{\text{MD}} - W_M^3 W_D) \]
\[ + 3(W_M^2 W_M W_D - W_M^3 W_D) + 3(W_M^2 W_{\text{MD}} - W_M^3 W_D) \]

Equation (II.13) leads to the multicluster expression for the equation of state

\[ P\beta = \sum_n \sum_{\tilde{c}_n} b_{\tilde{c}_n} (V, T) \prod_{\tilde{c}_n \in \tilde{c}_n} z_{\tilde{c}_n}^{|\tilde{c}_n|}. \]  

(II.49)

In order to make connection with Eq.(II.4), the density of each cluster \( n_{\text{C}_m} \) is expressed as

\[ n_{\text{C}_m} = \sum_{\tilde{c}_n} \sum_{\tilde{c}_n \in \tilde{c}_n} \tilde{c}_n | b_{\tilde{c}_n} (V, T) \prod_{\tilde{c}_n \in \tilde{c}_n} z_{\tilde{c}_n}^{|\tilde{c}_n|}. \]  

(II.50)

where Eqs. (II.3) and (II.12) have been used. This together with Eq.(II.4), leads to a series of cluster (molecular) virial coefficients

\[ a_M = 1, \]  

(II.51)

\[ a_D = 1, \]  

(II.52)

\[ a_T = 1, \]  

(II.53)

\[ a_Q = 1, \]  

(II.54)

\[ a_P = 1, \]  

(II.55)

\[ a_{M^2} = -\frac{b_{M^2}}{b_M^2}, \]  

(II.56)

\[ a_{MD} = -\frac{b_{MD}}{b_{M} b_{D}}, \]  

(II.57)

\[ a_{M^3} = -2\frac{b_{M^3}}{b_M^3} + 4\frac{b_{M^2}}{b_M^4}, \]  

(II.58)
In terms of these virial coefficients, the equation of state for a multispecies system can be written

$$P\beta = n_M + n_D + n_T + n_Q + n_P \cdots$$

$$- (\frac{b_{M^2}}{b_M^2}n_M^2 + \frac{b_{D^2}}{b_D^2}n_D^2 + \frac{b_{T^2}}{b_T^2}n_T^2 + \cdots)$$

$$- (\frac{b_{MD}}{b_M b_D}n_M n_D + \frac{b_{MT}}{b_M b_T}n_M n_T + \frac{b_{MQ}}{b_M b_Q}n_M n_Q + \frac{b_{DT}}{b_D b_T}n_D n_T + \cdots)$$

$$+ (-2\frac{b_{M^3}^2}{b_M^3} + 4\frac{b_{M^2}^2}{b_M^2})n_M^3 + \cdots$$

$$+ (-3\frac{b_{M^4}}{b_M^4} + 18\frac{b_{M^3}^2 b_{M^2}^2}{b_M^3 b_M^2} - 20\frac{b_{M^2}^3}{b_M^2})n_M^4 + \cdots.$$ (II.65)

Here the pattern is easily seen so that the higher order cluster terms can easily be added.

In order to relate this expansion to the conventional atomic expansion, Eq.(II.1), it is noticed that the n-particle partition function is the summation.
over all compatible channel partition functions

\[ Q^{(n)}(V, T) = \sum_{\mathcal{C}} Q_{\mathcal{C}}(V, T) = \frac{1}{n!} \text{Tr} e^{-\beta H^{(n)}} \]  

where the asymptotic completeness relation

\[ \sum_{\mathcal{C}} Q_{\mathcal{C}} = \mathcal{J}^{(n)} \]

has been used. The series of atomic Ursell operators can be expressed in terms of \( W^{(n)} \)

\[
\begin{align*}
U^{(1)} &= W^{(1)} \\
U^{(2)} &= W^{(2)} - W^{(1)}W^{(1)} \\
U^{(3)} &= W^{(3)} - W^{(1)}W^{(1)}W^{(1)} \\
& \quad - 3(W^{(2)} - W^{(1)}W^{(1)})W^{(1)} \\
U^{(4)} &= (W^{(4)} - W^{(1)}W^{(1)}W^{(1)}W^{(1)}) \\
& \quad - 4(W^{(3)} - W^{(1)}W^{(1)}W^{(1)})W^{(1)} \\
& \quad - 3(W^{(2)} - W^{(1)}W^{(1)})^2 + 6(W^{(2)} - W^{(1)}W^{(1)})W^{(1)}W^{(1)} \\
& \quad \ldots. 
\end{align*}
\]

The atomic expansion in terms of \( Q^{(n)}(V, T) \) and particle fugacity \( z \) can be written

\[ \Xi(V, T, z) = \sum_n Q^{(n)}(V, T)z^n. \]

That leads to the equation of state

\[ P\beta = \sum_n \beta^{(n)}(V, T)z^n, \]
where

\[ b^{(n)} = \frac{1}{Vn!} \text{Tr} U^{(n)}. \] (II.71)

The average number of particles is given by

\[ N = z \frac{\partial}{\partial z} \ln \Xi(V, T, z) = V \sum_n nb^{(n)} z^n. \] (II.72)

On inverting this series to give \( z \) in terms of the particle density \( n_1 = N/V \), the equation of state Eq. (II.1) is obtained with \( B_n \) given by \( b^{(n)} \)

\[ B_2(T) = \frac{b^{(2)}}{[b^{(1)}]^2} \] (II.73)

\[ B_3(T) = 4 \left[ \frac{b^{(2)}}{[b^{(1)}]^3} \right]^2 - 2 \frac{b^{(3)}}{[b^{(1)}]^3} \] (II.74)

\[ \ldots \ldots \]

The equivalence of the atomic expansion, Eq. (II.1) and the multispecies expansion Eq. (II.65) can be established by using the conditions of chemical reaction equilibrium in terms of chemical potentials

\[ \mu_{C_m} = |C_m | \mu_M, \] (II.75)

or equivalently in terms of fugacities

\[ z_{C_m} = z_M |C_m|. \] (II.76)

This, together with Eq. (II.50), gives a set of equations for fugacities

\[ z_M = \frac{1}{b_M} n_M - 2 \frac{b_{M}^2}{b_M^2} n_M^2 - \frac{b_{MD}}{b_M b_D} n_M n_D - \frac{b_{MT}}{b_M b_T} n_M n_T + \cdots \] (II.77)

\[ z_D = \frac{1}{b_D} n_D - 2 \frac{b_{D}^2}{b_D^2} n_D^2 - \frac{b_{MD}}{b_M b_D} n_M n_D - \frac{b_{DT}}{b_D b_T} n_D n_T + \cdots \] (II.78)
\[ z_T = \frac{1}{b_T} n_T - 2 \frac{b_{T^2}}{b_T^3} n_T^2 - \frac{b_{MT}}{b_M b_T^2} n_M n_T - \frac{b_{DT}}{b_D b_T^2} n_D n_T + \cdots \] (II.79)

With Eqs. (II.76-II.79), higher order clusters \( n_{C_n} \) can be expressed in terms of \( n_M \)

\[ n_D = b_D \frac{b_T^2}{b_M^3} n_M^2 + \left( b_{MD} \frac{b_D}{b_M^3} - 4 \frac{b_D}{b_M^3} \right) n_M^3 + \cdots, \] (II.80)

\[ n_T = \frac{b_T}{b_M^3} n_M^3 + \cdots, \] (II.81)

\[ \cdots \cdots \] (II.82)

Because the total number of particles is conserved, one has

\[ n_1 = n_M + 2n_D + 3n_T + \cdots. \] (II.83)

These lead to an equation of state compatible to Eq.(II.1)

\[ P \beta = n_1 - \left( \frac{b_D}{b_M^2} + \frac{b_{M^2}}{b_M^2} \right) n_1^2 - \left( 2 \frac{b_{M^3}}{b_M^2} - 4 \frac{b_D}{b_M^4} + 2 \frac{b_{MD}}{b_M^2} - 8 \frac{b_D}{b_M^3} \frac{b_{M^2}}{b_M^2} + 2 \frac{b_T}{b_M^2} - \cdots \right) n_1^3 + \cdots \] (II.84)

One can then identify the second and third atomic virial coefficients in terms of the molecular as

\[ B_2(T) = \frac{b_D}{b_M^2} - \frac{b_{M^2}}{b_M^2}, \] (II.85)

and

\[ B_3(T) = -2 \frac{b_{M^3}}{b_M^3} + 4 \frac{b_{M^2}}{b_M^3} + 4 \frac{b_{D^2}}{b_M^4} - 2 \frac{b_{MD}}{b_M^2} - 8 \frac{b_D}{b_M^3} \frac{b_{M^2}}{b_M^2} - 2 \frac{b_T}{b_M^2}. \] (II.86)
These are consistent with those given by Rainwater and Snider\textsuperscript{94} when restricted to a monomer-dimer mixture.

II-2.2 Hilbert-Schmidt Representation of Ursell Operators

In this section a Hilbert-Schmidt representation for the two- and three-particle Ursell operators is formulated. It is believed that the general structure presented here will hold for higher order Ursell operators, but this has not been explored within the limited scope of this thesis. This section is divided into two parts, the first dealing with the two-particle Ursell operator and the second with the three-particle Ursell operator.

a) Two-Particle Ursell Operator

At equilibrium the correlations between two particles is given by the Ursell operator

\[ U_{12}^{(2)} = e^{-\beta H^{(2)}} - e^{-\beta H_0^{(2)}}. \]  

(II.87)

Where the hamiltonians $H^{(2)}$ and $H_0^{(2)} \equiv K^{(2)}$ are, as in Part I, self-adjoint operators acting on the pair Hilbert space $F_{\mathbf{r}}^{(2)}$ with both their spectra being absolutely continuous on the positive real axis and the possibility that the spectrum of $H^{(2)}$ is also singular on the negative real axis, corresponding to a finite number of bound states. The $U_{12}^{(2)}$ is a trace class operator\textsuperscript{95,96} for a reasonable potential

\[ \text{Tr} | U_{12}^{(2)} | < \infty. \]  

(II.88)

$U_{12}^{(2)}$ is connected to the interacting and free resolvent operators $R^{(2)}$ and $R_0^{(2)}$,

\[ R^{(2)} \equiv \frac{1}{z - H^{(2)}}, \quad R_0^{(2)} \equiv \frac{1}{z - H_0^{(2)}}, \]  

(II.89)
by the Laplace transform

\[ U_{12}^{(2)} = \frac{1}{2\pi i} \int_C e^{-\beta z} R^{(2)}(z) \, dz \]  

(II.90)

involving the contour \( C \) counterclockwisely encircling the spectrum of \( H^{(2)} \) and the difference of the resolvent operators

\[ R^{(2)}(z) = R^{(2)} - R_0^{(2)} \]

\[ = \frac{1}{z - H^{(2)}} - \frac{1}{z - H_0^{(2)}}. \]  

(II.91)

The corresponding resolvents \((z - H^{(2)})^{-1}\) and \((z - H_0^{(2)})^{-1}\) are bounded operators on \( \mathcal{S}^{(2)} \) for all complex \( z \) except on the spectra of their respective hamiltonian. As a consequence, the difference in resolvents \( R^{(2)}(z) \) is defined on the complex \( z \)-plane excluding the spectrum of \( H^{(2)} \). An advantage of \( R^{(2)} \) over the resolvent operators \( R^{(2)} \) and \( R_0^{(2)} \) is that, for reasonable potentials, the operator \( R^{(2)} \) is of trace class, whereas \( R^{(2)} \) and \( R_0^{(2)} \) are not.

It is easy to show that the difference in resolvents \( R^{(2)} \) is related to the kernel

\[ K^{(2)}(z) \equiv (z - H_0)^{-1} V \]  

(II.92)

by

\[ R^{(2)}(z) = \left( \frac{1}{1 - K^{(2)}(z)} \right) K^{(2)}(z) \left( \frac{1}{z - H_0} \right). \]  

(II.93)

Moreover the kernel \( K^{(2)}(z) \) is, for \( \sqrt{2\mu z} = x + iy \) not on the real axis and for square integrable potentials, a Hilbert-Schmidt class operator\(^{42,97}\). This follows from the fact that operator \( K^{(2)}(z)^{\dagger} K^{(2)}(z) \) is of trace class, namely for a three dimensional system,

\[ \text{Tr}K^{(2)}(z)^{\dagger}K^{(2)}(z) = \int \langle p|V^2|p\rangle \frac{4\mu^2}{[(x-p)^2 + y^2][(x+p)^2 + y^2]} \, dp < \infty, \]

(II.94)
provided $V$ is a square integrable local potential, so that

$$\langle p|V^2|p \rangle = \frac{1}{\hbar^3} \int V(r)^2 \, dr$$  \hspace{1cm} (II.95)$$

is finite. As a consequence, $K^{(2)}(z)$ is a compact operator and its spectrum discrete$^{97}$, having eigenvalues $\eta_n(z)$, and a set of biorthonormal right $|\zeta_n(z)\rangle$ and left $\langle \xi_n(z)|$ eigenvectors indexed by $n$, namely

$$K^{(2)}(z)|\zeta_n(z)\rangle = \eta_n(z)|\zeta_n(z)\rangle \hspace{1cm} (II.96)$$

$$\langle \xi_n(z)|K^{(2)}(z) = \langle \xi_n(z)|\eta_n(z), \hspace{1cm} (II.97)$$

$$\langle \xi_m(z)|\zeta_n(z)\rangle = \delta_{mn}, \hspace{1cm} (II.98)$$

such that

$$\sum_n |\eta_n(z)|^2 < \infty. \hspace{1cm} (II.99)$$

The proof of the compactness of $K^{(2)}(z)$ can be extended to the real axis, see e.g. Ref.(98), by showing that the symmetrized kernel $V^{1/2}(z - H_0)^{-1}V^{1/2}$ is a Hilbert-Schmidt operator. It follows that the spectrum of $R^{(2)}(z)$ is also discrete and consequently the operator has the spectral representation

$$R^{(2)}(z) = \sum_n |\zeta_n(z)\rangle \frac{\eta_n(z)}{1 - \eta_n(z)} \langle \xi_n(z)| \frac{1}{z - H_0^{(2)}} \hspace{1cm} (II.100)$$

Thus one arrives at a Hilbert-Schmidt representation for the pair Ursell operator

$$U^{(2)}_{12} = \sum_n \frac{1}{2\pi i} \oint_C e^{-\beta z} |\zeta_n(z)\rangle \frac{\eta_n(z)}{1 - \eta_n(z)} \langle \xi_n(z)| \frac{1}{z - H_0^{(2)}} \, dz. \hspace{1cm} (II.101)$$

**b) Three-Particle Ursell Operator**
At equilibrium three-particle correlations are described by the three-body Ursell operator

\[ U_{123}^{(3)} = e^{-\beta H^{(3)}} - e^{-\beta H_0^{(3)}} - \sum_{\alpha} \left( e^{-\beta H_\alpha^{(3)}} - e^{-\beta H_0^{(3)}} \right) \]  \hspace{1cm} (II.102)

Here the full three-body hamiltonian is defined as

\[ H^{(3)} = H_0^{(3)} + V^{(3)} \]  \hspace{1cm} (II.103)

where \( H_0^{(3)} \equiv K^{(3)} \) and \( V^{(3)} \) is the three-body potential

\[ V^{(3)} = \sum_{\alpha=0}^{3} V_\alpha \]  \hspace{1cm} (II.104)

given in terms of the pair potentials

\[ V_0 \equiv 0, \] \hspace{1cm} (II.105)
\[ V_1 \equiv V_{23}, \] \hspace{1cm} (II.106)
\[ V_2 \equiv V_{13}, \] \hspace{1cm} (II.107)
\[ V_3 \equiv V_{12}. \] \hspace{1cm} (II.108)

Channel hamiltonians \( H_\alpha^{(3)} \) are defined according to

\[ H_\alpha^{(3)} = H_0^{(3)} + V_\alpha. \] \hspace{1cm} (II.109)

The three-body hamiltonians are assumed to be self-adjoint operators acting on the Hilbert space \( \mathcal{H}^{(3)} \). The spectrum of \( H^{(3)} \) is absolutely continuous on the positive real axis corresponding to three-particle scattering, and on part of the negative real axis corresponding to two-fragment scattering subsystems. As well, the spectrum of \( H^{(3)} \) can also be singular to the left of the two-particle threshold, corresponding to three-particle bound states.

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The full three-body resolvent operator is defined as

\[ R^{(3)}(z) = \frac{1}{z - H^{(3)}}, \quad (\text{II.110}) \]

where \( z \) is a parameter in the complex energy plane. \( R^{(3)}(z) \) is well defined in the whole complex energy plane excluding the spectrum of the Hamiltonian \( H^{(3)} \). Similarly, the three-body partial resolvent operators are defined as

\[ R_{\alpha}^{(3)}(z) = \frac{1}{z - H_{\alpha}^{(3)}}, \quad (\text{II.111}) \]

With the resolvent operators and the Laplace transform, the three-body Ursell operator can be expressed as

\[ U_{123}^{(3)} = \frac{1}{2\pi i} \oint_C e^{-\beta z} R^{(3)}(z) dz, \quad (\text{II.112}) \]

where contour \( C \) encircles the spectra of the three-body Hamiltonian in a counterclockwise manner and the quantity \( R^{(3)}(z) \) is the combination of resolvents

\[ R^{(3)}(z) \equiv R^{(3)}(z) - R_0^{(3)}(z) - \sum_{\alpha} \left( R_{\alpha}^{(3)}(z) - R^{(3)}_0(\alpha) \right). \quad (\text{II.113}) \]

\( R^{(3)} \) has been shown to be a connected operator\(^{99} \). Actually \( R^{(3)} \) is related to the Faddeev kernel of the three-body transition operator, which is a Hilbert-Schmidt operator, a necessary functional property for the validity of a Hilbert-Schmidt expansion. The Faddeev technique of three-body quantum scattering is utilized in the following to establish the relation between the operator \( R^{(3)}(z) \) and the Faddeev kernel.

Faddeev has found that the three-body (on-shell) Lippmann-Schwinger equation\(^6 \) does not have a unique solution because the homogeneous equations admit two-body scattering state solutions. The Lippmann-Schwinger
equation is equivalent to the three-body Schrödinger equation only for energies below the lowest two-particle threshold. At higher energy the kernel of the Lippmann-Schwinger equation becomes non-compact and the equation is no longer of Fredholm type so that the standard theory of integral equations cannot be applied. A three-body transition operator can be defined in a form analogous to the two-body transition operator

\[ T^3(z) = V^+ V^R(z) V. \]  

(II.114)

However, \( T^3(z) \) does not give the scattering cross section in the same manner as does the two-body transition operator. The three-body resolvent operator can be written in the following alternate ways:

\[ R^3(z) = R(z) \rightdagger + R(z) V^\alpha R^3(z), \]  

(11.115)

\[ = R^3(z) + R(z) T^3(z) R^3(z), \]  

(11.116)

\[ = R^3(z) + R(z) T^3(z) R^3(z), \]  

(11.117)

where

\[ V^\alpha \equiv V^3 - V_{\alpha}. \]  

(II.118)

\( R^3(z) \) is more singular than the transition operator \( T^3(z) \) because of the presence of \( R^3(z) \). In graph theory language, Eq. (11.115) has disconnected diagrams which give rise to \( \delta \)-functions in the momentum representation.

Faddeev separated the transition operator into four parts \( T^3_{\alpha}(z) \), satisfying the set of equations (see Appendix A):

\[ T^3_{\alpha}(z) = t^3_{\alpha}(z) + \sum_{\beta=0}^{3} (1 - \delta_{\alpha,\beta}) t^3_{\alpha}(z) R^3_{\beta}(z) T^3_{\beta}(z). \]  

(II.119)

Similarly, the resolvent operator can be divided up in an analogous manner

\[ R^3(z) - R^3_{\alpha}(z) = \sum_{\alpha=0}^{3} R^3_{\beta}(z) T^3_{\alpha}(z) R^3_{\alpha}(z) \]  

(II.120)
where \( t_\alpha^{(3)}(z) \) is a two-body transition operator in the three particle space

\[
t_\alpha^{(3)}(z) \equiv V_\alpha + V_\alpha R_\alpha^{(3)}(z) V_\alpha
\]

\[
= V_\alpha + V_\alpha R_\alpha^{(3)}(z) t_\alpha^{(3)}(z) \tag{II.123}
\]

\[
= (1 - V_\alpha R_\alpha^{(3)}(z))^{-1} V_\alpha. \tag{II.124}
\]

\( G_\alpha^{(3)}(z) \) are Faddeev’s resolvent operators

\[
G_\alpha^{(3)}(z) = R_\alpha^{(3)}(z) T_\alpha^{(3)}(z) R_\alpha^{(3)}(z) \tag{II.125}
\]

\[
= R_\alpha^{(3)}(z) - R_\alpha^{(3)}(z) + \sum_{\beta=0}^{3} K_{\alpha\beta}(z) G^{(3)}_{\beta}(z) \tag{II.126}
\]

\[
= R_0^{(3)}(z) t_\alpha^{(3)}(z) R_\alpha^{(3)}(z) + \sum_{\beta=0}^{3} K_{\alpha\beta}(z) G^{(3)}_{\beta}(z), \tag{II.127}
\]

with kernel \( K_{\alpha\beta}(z) \) is defined as

\[
K_{\alpha\beta}(z) = R_0^{(3)}(z)(1 - \delta_{\alpha\beta}) t_\alpha^{(3)}(z). \tag{II.128}
\]

Using Eqs. (II.113), (II.120), (II.121), (II.125) and (II.126), \( R^{(3)}(z) \) can be written as

\[
R^{(3)}(z) = \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K^{(3)}_{\alpha\beta}(z) G^{(3)}_{\beta}(z). \tag{II.129}
\]

On iterating Eq. (II.127) for the operator \( G^{(3)}_{\beta}(z) \), the infinite series expansion

\[
R^{(3)}(z) = \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K^{(3)}_{\alpha\beta}(z) G^{(3)}_{\beta}(z)
\]

\[
= \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K^{(3)}_{\alpha\beta}(z) R_0^{(3)}(z) t_\beta^{(3)}(z) R_\alpha^{(3)}(z)
\]
\[ + \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K_{\alpha\beta}^{(3)}(z) R_{0}^{(3)}(z) R_{0}^{(3)}(z) \]
\[ + \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K_{\alpha\gamma}^{(3)}(z) K_{\beta\delta}^{(3)}(z) K_{\gamma\delta}^{(3)}(z) R_{0}^{(3)}(z) t_{\nu}^{(3)}(z) R_{0}^{(3)}(z) \]
\[ + \ldots \]  \hspace{1cm} (II.130)

is obtained. By relabelling the indices, one obtains

\[ R^{(3)}(z) = \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K_{\alpha\nu}^{(3)}(z) R_{0}^{(3)}(z) t_{\nu}^{(3)}(z) R_{0}^{(3)}(z) \]
\[ + \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K_{\alpha\nu}^{(3)}(z) K_{\beta\nu}^{(3)}(z) R_{0}^{(3)}(z) t_{\nu}^{(3)}(z) R_{0}^{(3)}(z) \]
\[ + \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} K_{\alpha\gamma}^{(3)}(z) K_{\beta\gamma}^{(3)}(z) K_{\gamma\nu}^{(3)}(z) R_{0}^{(3)}(z) t_{\nu}^{(3)}(z) R_{0}^{(3)}(z) \]
\[ + \ldots \]
\[ = \sum_{\alpha=0}^{3} \sum_{\beta=0}^{3} \left( K^{(3)}(z) \frac{1}{1 - K^{(3)}(z)} R_{0}^{(3)}(z) t^{(3)}(z) R_{0}^{(3)}(z) \right)_{\alpha\beta} \] \hspace{1cm} (II.131)

where the kernel matrix \( K^{(3)}(z) \) is defined by

\[ [K^{(3)}(z)]_{\alpha\beta} = K_{\alpha\beta}^{(3)}(z), \]  \hspace{1cm} (II.132)

and \( t^{(3)}(z) \) is the diagonal matrix

\[ [t^{(3)}(z)]_{\alpha\beta} = t_{\alpha}^{(3)}(z) \delta_{\alpha\beta}. \]  \hspace{1cm} (II.133)

That the operator \( R^{(3)}(z) \) is of Hilbert-Schmidt class is established because the Faddeev kernel \( K^{(3)}(z) \) has a Schmidt norm

\[ \| K^{(3)}(z) \|_{2} = \left( \sum_{n} \| K^{(3)}(z) \phi_{n} \|^{2} \right)^{1/2} < \infty, \] \hspace{1cm} (II.134)

necessarily basis set \( \phi_{n} \) independent.
As a consequence of being of Hilbert-Schmidt class, \(K^{(3)}(z)\) is a compact (or completely continuous) operator in \(\mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)}\) and has only a discrete spectrum. Moreover \([1 - K^{(3)}(z)]^{-1}\) exists and is a meromorphic function of \(z\). Thus \(K^{(3)}(z)\) has left and right eigenfunctions and eigenvalues

\[
K^{(3)}(z)|\zeta_n^{(3)}(z)\rangle = \eta_n^{(3)}(z)|\zeta_n^{(3)}(z)\rangle \quad \text{(II.135)}
\]

\[
\langle \xi_n^{(3)}(z)|K^{(3)}(z) = \langle \xi_n^{(3)}(z)|\eta_n^{(3)}(z), \quad \text{(II.136)}
\]

\[
\langle \xi_m^{(3)}(z)|\zeta_n^{(3)}(z)\rangle = \delta_{mn}. \quad \text{(II.137)}
\]

The eigenvalues \(\eta_n^{(3)}(z)\) satisfy

\[
\sum_n |\eta_n^{(3)}(z)|^2 < \infty. \quad \text{(II.138)}
\]

\(\mathcal{R}^{(3)}\) thus admits the expansion

\[
\mathcal{R}^{(3)}(z) = \sum_n \sum_\alpha \sum_\beta \left[ |\zeta_n^{(3)}(z)\rangle \frac{\eta_n^{(3)}(z)}{1 - \eta_n^{(3)}(z)} \langle \xi_n^{(3)}(z)\rangle \right]_{\alpha\beta} R_0^{(3)}(z)t_\beta^{(3)}(z)R_0^{(3)}(z). \quad \text{(II.139)}
\]

These lead to the desired Hilbert-Schmidt representation for the three-particle Ursell operator

\[
U_{123}^{(3)} = \frac{1}{2\pi i} \oint_C e^{-\beta z} \sum_n \sum_\alpha \sum_\beta \left[ |\zeta_n^{(3)}(z)\rangle \frac{\eta_n^{(3)}(z)}{1 - \eta_n^{(3)}(z)} \langle \xi_n^{(3)}(z)\rangle \right]_{\alpha\beta} 
\times R_0^{(3)}(z)t_\beta^{(3)}(z)R_0^{(3)}(z)dz. \quad \text{(II.140)}
\]

**II-2.3 Discussion**

A multispecies expansion of the grand partition function using the two-Liouville space theory of Part I has been given in Section II-2.1. The procedure is the same as that of Osborn's, and the result, which includes three-
and more particle clusters, is a straightforward extension of Osborn's two species expansion. However, the concept of asymptotic channel and asymptotic spaces are different from those of Osborn's. In the present treatment, small bound fragments are defined only in the asymptotic channel space, see the discussion of Chapter I-1 for details.

The equivalence of the single fugacity expansion and the multispecies expansion of the grand partition function has been established in a manner similar to that done by others. The molecular picture of the grand partition function is important when dealing with a chemically reactive gas where stable molecules are usually treated as separate species. The molecular picture provides a faster convergence property for the virial expansion than does the atomic picture because, for example, a dimer-dimer correlation contributes to the fourth virial coefficient and a trimer-trimer correlation contributes to the sixth virial coefficient in the atomic picture. But this is true only for the case without reactive collisions. If reactive collisions are present, which is the case at high temperature when the energy exceeds a reactive threshold, it is the Ursell operators \( U^{(n)} \), rather than the channel fragment Ursell operator \( U^{(c)} \), that are important. In other words the atomic picture calculations are necessary for a chemically reactive system. Osborn has further used the molecular picture to express three-body correlations in terms of channel time delays, or equivalently, in terms of channel \( S' \)-matrices, a form which may need to be reorganized for practical calculations due to the mathematical nature of the three-body problem.

It is seen, for the cases that have been explored, that the connected Ursell operators \( U^{(2)} \) and \( U^{(3)} \), have a one-to-one correspondence with Hilbert-Schmidt class operators through a Laplace transform. It is believed that this is also true for the higher order Ursell operators \( U^{(4)}, U^{(5)} \) etc. Therefore
\(U^{(4)}\), see Eq. (II.68), will be closely related to the Yakubovsky equations\(^{101}\). It is well-known that quantum mechanical scattering theories written in terms of integral equations for four and more particle systems are extremely complicated\(^{101,102,51}\) because the kernels may be unconnected. The present study implies that it may be possible to have a systematic procedure for obtaining Hilbert-Schmidt class kernels for the resolvent operators associated with the higher ordered Ursell operators \(U^{(n)}\). Since the structure of the Ursell operators of finite order is well known\(^{64,96}\), the corresponding connected resolvent operator equations should have the same structure, providing our conjecture is correct. Furthermore, the connected graphs of the Ursell-Mayer expansion\(^{81}\) may have a one-to-one correspondence with the connected diagrams of Faddeev for four and more particles. These questions are left for future work.

The Hilbert-Schmidt method has been widely used in two-body quantum scattering\(^{90,91,92}\) to evaluate both scattering wave functions and collision cross sections. The Faddeev analysis has paved the way for applying the same method to three- and more particle scattering\(^{103,104}\). The method provides a powerful representation both conceptually and computationally. However it has hardly been used in formal statistical theory as far as the author knows. Here a general formalism for the Hilbert-Schmidt representation of Ursell operators is presented. The formalism may have important applications. A first and most important application is that it provides a convenient starting point for the practical calculation of the equation of state (virial coefficients), which is pursued, for the second virial coefficient, in the following chapter. A second application is to establish Levinson's theorem for two- and more particle scattering\(^{105}\) by the resolvent method. The conventional \(S\)-matrix phase shift does not work in the case of three-body scattering since three-
body breakup collisions admit no phase-shift description. A third possible application, which was the initial motivation of the work in Part II, is to moderately dense gas kinetic theory as described in the introduction to Part II, namely to formulate a scattering theory which incorporates correlated pairs as a colliding species, a common phenomenon in a dense gas system. No immediately feasible results on this line have so far been found.

Gibson\textsuperscript{106}, Baumgartl\textsuperscript{66} and Reiner\textsuperscript{107} have applied the Faddeev results to calculate the third virial coefficient. Gibson expresses the third virial coefficient in terms of Faddeev's $T$-matrix. Baumgartl treats a part of the third virial coefficient in terms of a two-particle scattering amplitude, whereas Reiner's result is more inclusive. Since none of these authors had considered a general Hilbert-Schmidt representation for the evaluation of the virial coefficients, the present approach introduces a different and hopefully effective means for that evaluation.
Chapter 11-3
Correlated State Evaluation of the Second Virial Coefficient

The second virial coefficient arises because particles are correlated in thermal equilibrium. In classical mechanics this correlation is due solely to the intermolecular potential while in quantum mechanics the detailed properties of the free and interacting Hamiltonians are needed. A classic calculation by Beth and Uhlenbeck 65 expressed the second virial coefficient in terms of phase shifts. This has led to further expressions involving the $S$-matrix, the Jost function and the on-shell $T$-matrix 66,67,68. This has also led to relating the second virial coefficient to the time delay 69,70,71 and to a general $S$-matrix formulation of equilibrium statistical mechanics 72. A Regge pole representation has also been presented 108. Of more immediate concern for the present work is Nussenzveig’s 73 representation of the second virial coefficient in terms of functions of the momenta characterizing the poles of the $S$-matrix. In contrast to evaluating the second virial coefficient in terms of the phase shift and its properties, the present work relates the second virial coefficient to the (trace of the) difference between the resolvents for the interacting and free Hamiltonians. The analytic properties of the momentum matrix elements of this difference in resolvents, in particular its poles, provides an alternative method of arriving at Nussenzveig’s representation. Since the difference in resolvents is a trace class operator, there naturally arise certain square integrable functions associated with its poles. These states are here referred to as correlated states. It is possible that they could be useful for the description of the dynamics of moderately dense gas systems.

For Boltzmann statistics in a $d$-dimensional system, the second virial coefficient for structureless particles is given as the trace over relative motion
of the Ursell function, namely

\[ B(T) = -\frac{\Lambda_r^d}{2} \text{Tr} \left[ e^{-\beta H^{(2)}} - e^{-\beta H^{(2)}_0} \right]. \]  

(II.141)

Here the thermal deBroglie wavelength for relative motion is \( \Lambda_r = h/\sqrt{2\pi\mu kT} \), \( \beta = 1/kT \), the free hamiltonian is \( H^{(2)}_0 = p^2/2\mu \) and the interacting hamiltonian also involves the potential \( V \) according to \( H^{(2)} = H^{(2)}_0 + V \). As appropriate for relative motion, the free motion is given in terms of the reduced mass \( \mu \). After separating off the contribution from any bound states, the continuum contribution to the second virial coefficient can be interpreted in terms of the difference in the density of states for the interacting and free hamiltonians, which can be evaluated in terms of the scattering phase shifts. For a three dimensional system, a decomposition into partial waves is first required so that

\[ B(T) = \frac{\Lambda_r^3}{2} \left[ \sum_n e^{-\beta\varepsilon_n} + \frac{1}{\pi} \int_0^\infty dE \sum_l (2l + 1) \frac{\partial \eta_l(E)}{\partial E} e^{-\beta E} \right], \]  

(II.142)

wherein \( n \) labels the bound states and \( l \) labels the orbital angular momentum. Since the partial wave \( S \)-matrix \( S_l(E) = e^{2i\eta_l(E)} \) is given in terms of the corresponding phase shift \( \eta_l(E) \), and the time delay is given by the energy \( E \) derivative

\[ D_l(E) = i\hbar S_l(E) \frac{\partial S_l(E)}{\partial E} = 2\hbar \frac{\partial \eta_l(E)}{\partial E}, \]  

(II.143)

it follows that the second virial coefficient can be written

\[ B(T) = -\frac{\Lambda_r^2}{2} \left[ \sum_n e^{-\beta\varepsilon_n} + \frac{1}{\hbar} \int_0^\infty dE \sum_l (2l + 1) D_l(E) e^{-\beta E} \right]. \]  

(II.144)

in terms of the time delay.

For cutoff potentials, Nussenzveig draws on the analytic properties of the partial wave \( S \)-matrices, specifically that they are meromorphic functions.
of the momentum \( p = \sqrt{2\mu E} \) having the canonical product expansion

\[
S_i(p) = e^{-2iprc/h} \prod_j \left[ \frac{1 - (p/p_{j,1}^*)}{1 - (p/p_{j,1})} \right],
\]

involving all the poles \( p_{j,1} \) of \( S_i(p) \) in the complex \( p \)-plane and the potential cutoff distance \( r_c \). With this expansion and some properties of the complementary error function expressed in the form

\[
w(y) = e^{-y^2} \text{erfc}(-iy)
\]

\[
= -i \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{t - y} dt = -i \frac{2iy}{\pi} \int_{0}^{\infty} \frac{e^{-t^2}}{t^2 - y^2} dt, \quad \Im y > 0
\]

\[
w(-y) = i \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{e^{-t^2}}{t - y} dt = i \frac{2iy}{\pi} \int_{0}^{\infty} \frac{e^{-t^2}}{t^2 - y^2} dt, \quad \Im y < 0
\]

Nussenzveig writes the second virial coefficient as

\[
B(T) = -\frac{\Lambda_r^3}{2} \sum_l (2l + 1) \left[ \frac{r_c}{\Lambda_r} + \frac{1}{2} \sum_j w(p_{j,1}^*\sqrt{\beta/2\mu}) \right],
\]

with the \( j \) sum over all poles of \( S_i(p) \).

A form for the second virial coefficient similar to that of Nussenzveig was found by Snider by explicit calculation for the 1-dimensional Yamaguchi potential

\[
V = |\chi\rangle V_0(\chi); \quad \langle p|\chi\rangle = \left( \frac{2a^3}{\pi} \right)^{\frac{1}{2}} \frac{1}{a^2 + p^2},
\]

namely

\[
B(T) = -\frac{\Lambda_r}{2} \left[ \frac{1}{2} \sum_j w \left( -q_j\sqrt{\beta/2\mu} \right) - \frac{1}{2} - w \left( ia\sqrt{\beta/2\mu} \right) \right],
\]

where the sum is over the three poles \( q_j \) of the analytically continued matrix element

\[
Q(q) \equiv \langle \chi \left| \frac{1}{(q^2/2\mu) - H^{(2)}} \right| \chi \rangle \quad \Im q > 0
\]
of the resolvent of the hamiltonian. This similarity provides a motivation for
trying to more generally relate the resolvent of the hamiltonian and its poles
to the second virial coefficient.

As a function of the self adjoint operator $H^{(2)}$, $e^{-\beta H^{(2)}}$ can be expressed
as an appropriate contour integral over the resolvent $1/(z - H^{(2)})$ of $H^{(2)}$.
It follows that the second virial coefficient can be written as the contour integral

$$B(T) = \frac{\Lambda_r^d}{4\pi i} \int_{-\infty}^{i\infty} dz \text{Tr} R^{(2)}(z)e^{-\beta z}$$

$$= \frac{\Lambda_r^d}{4\pi i \mu} \int_{-\infty+ie}^{\infty+ie} dq \text{Tr} R^{(2)}(z)e^{-\beta z}$$

(II.151)
either over the complex energy parameter $z = q^2/2\mu$ or its equivalent complex
momentum parameter $q$ of the trace over

$$R^{(2)}(z) \equiv \left[ \frac{1}{z - H^{(2)}} - \frac{1}{z - H_0^{(2)}} \right],$$

(II.152)
the difference of the resolvents for the interacting and free motion hamiltonians. The contour must lie to the left of the spectra (eigenvalues and
generalized eigenvalues) of both $H^{(2)}$ and $H_0^{(2)}$ for the $z$ integral and equivalently, above the spectra for the $q$ integral with the small positive number $\epsilon$ constraining $q$ to have a positive imaginary component. The spectrum for $H_0^{(2)}$ is simply identified as the positive real axis, but $H^{(2)}$ may have bound states which lie on the negative real axis with their equivalent momenta positive imaginary, so the contours must be chosen appropriately. As operators, $H_0^{(2)}$, $H^{(2)}$ and $R^{(2)}(z)$ have certain properties associated with these spectra. But if a matrix element of $R^{(2)}(z)$ is taken, then this can be analyzed as an analytic function of $z$. Specifically the momentum representation $\langle p | R^{(2)}(z) | p' \rangle$ is of particular interest. The trace is of course easily calculated as $\text{Tr} R^{(2)}(z) = \int \langle p | R^{(2)}(z) | p \rangle dp$. 

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Analytic continuation of the momentum representation matrix elements of the difference $R^{(2)}(z)$ of resolvent operators leads to a set of $L^2$ states. These arise from the residues of certain poles in the complex $z$-plane. These $L^2$ states are called correlated states because of their association with the pair Ursell operator. Since the poles of the resolvent in the lower half complex momentum plane are usually associated with resonance phenomenon, the correlated states can be interpreted as normalizable resonance states. The quantum mechanical theory of resonance scattering has a long history. Gamow first introduced the notion in using the escape from a square well potential to model alpha particle decay. The scattering physical boundary conditions, such as being regular at the origin and purely outgoing at large distance, were imposed on resonance states by Siegert. The resulting Gamow states grow exponentially at large distance

$$\lim_{r \to \infty} \phi_n \to e^{ik_n r}$$

for $k_n$ in the lower half complex momentum plane. Berggren uses a regularization method to scale the Gamow states so as to obtain a "norm" for them. The analytic continuation method given by Romo can give the same norm as Berggren's for the Gamow states. However these artificially normed Gamow states have very limited physical application since true physical states are well-defined (normalizable) elements of Hilbert space. Kapur and Peierls proposed a different treatment of resonance phenomenon by separating inner and outer regions. Wigner and Eisenbud took over this idea and developed their $R$-matrix scattering theory. Further development along this line was due to Feshbach. He employed an elegant projection operator method to achieve a separation of states with different physical characteristics. These treatments have many physical applications. The problem
has also caught the attention of the mathematical community. Complex scaling\cite{117,118} and Rigged-Hilbert space\cite{76} theories provide a somewhat more mathematical treatment of resonance phenomenon.

This chapter consists of four sections. Section II-3.1 is devoted to the study of various properties of $\mathcal{R}^{(2)}(z)$ as a function of $z$. An expansion of its momentum matrix element in terms of its poles identifies certain normalizable functions which will be referred to as correlated states. This name has been introduced on the basis that $\mathcal{R}^{(2)}(z)$ itself is associated with pair particle correlations. The object of the present chapter is to explore the properties of $\mathcal{R}(z)$ and the analytic continuation of its momentum matrix elements, both for its use in evaluating the second virial coefficient and for the identification of properly normalized states that might be used to represent particle correlation in (dense) gas kinetic theory. The author sees the approach as involving the interplay between the functional analysis (operator) properties of $\mathcal{R}(z)$ and the analytic function (pole) properties of its matrix elements.

Central to the functional analysis properties of $\mathcal{R}^{(2)}(z)$ is the kernel $\mathcal{K}^{(2)}(z) \equiv (z - H^{(2)}_0)^{-1} \mathbf{V}$, see Section II-3.1. The correlated states are related to certain analytically continued eigenvectors of this kernel. The pole expansion, equivalently correlated state expansion, of the analytically continued $\langle \mathbf{p}|\mathcal{R}^{(2)}(z)|\mathbf{p}' \rangle$ can be used to reproduce Nussenzveig's\cite{73} expression for the second virial coefficient. Section II-3.2 uses the Yamaguchi potential\cite{111} to explicitly illustrate this calculation. The properties of the separable potential model is first reviewed followed by the introduction of a simple operator method for the calculation of second virial coefficient. The properties of the kernel $\mathcal{K}^{(2)}(z)$ is then examined.

A normalizable resonance state theory is introduced in Section II-3.3. Since the complex energy poles have the same values as do the resonance
energies of scattering theory, it is reasonable to associate the correlated
states with resonances. These states are \(L^2\) functions, in contrast to the
non-normalizable Gamow states\(^{74}\), which usually are regarded as resonance
states. The major difference between the present work and more standard
treatments of resonance phenomena appears to be that the present work
emphasizes the domain of definition of the Schrödinger operator so as to dis­t­
inguish operator equations from the analytic continuation of their matrix
elements. Moreover, the present work analytically continues momentum ma­
trix elements of operators whereas usually it is the \(position\) representation of
the (generalized) eigenvectors of \(H^{(2)}\) that are analytically continued, which
give the Gamow states. Because analytic continuation depends on the basis
used\(^ {119}\), different results are obtained. More discussion of these matters is
given in Section II-3.4. Most material presented in this chapter is from Ref.
(40)

II-3.1 Properties of the Difference of Resolvents

The hamiltonians \(H^{(2)}\) and \(H_0^{(2)}\) are assumed to be self-adjoint operators
acting on Hilbert space \(\mathcal{H}^{(2)}\) with both spectra being absolutely continuous on
the positive real axis together with the possibility that the spectrum of \(H^{(2)}\)
also is discrete (and bounded below) on the negative real axis, corresponding
to bound states. The associated resolvents \((z - H^{(2)})^{-1}\) and \((z - H_0^{(2)})^{-1}\)
are defined (as bounded operators on \(\mathcal{H}^{(2)}\)) for all complex \(z\) except on the
spectra of the respective hamiltonians. As a consequence, the difference in
resolvents \(\mathcal{R}(z)\) is defined on the complex \(z\)-plane excluding the spectrum
of \(H^{(2)}\). Moreover, since the image of the positive real axis for the \(z\)-plane
is the whole real axis for the momentum parameter \(q = \sqrt{2\mu z}\), this implies
that the whole real axis acts as a natural barrier for discussing either resolvent operator or \( R(z) \) as a function of \( q \). Specifically then, for any pair of normalized states \( |\phi\rangle \) and \( |\psi\rangle \), the function

\[
F(q) \equiv \langle \phi | R^{(2)}(z) | \psi \rangle
\]  

(II.154)

calculated by taking a matrix element of the difference of resolvents defined in Eq.(II.152) is defined only for \( q \) in either the upper or lower half of the complex \( q \)-plane (and further restricted to not lie on those imaginary momenta that correspond to the bound states of \( H^{(2)} \) if such exist). Because the real axis acts as a natural barrier for the operator \( R^{(2)}(z) \), it follows that there are two (different) \( F(q) \) functions, corresponding to whether the evaluation is carried out in either the upper or lower half \( q \)-plane. The function found by calculating the matrix element in the upper half \( q \)-plane will henceforth be denoted by \( F(q) \), and will be the object of interest. For contrast, when needed for comparison, \( F^{-}(q) \) will designate the other function. While the matrix element defining \( F(q) \) can only be evaluated for \( q \) in the upper half \( q \)-plane, for reasonable potentials the resulting function can be analytically continued into the lower half \( q \)-plane\(^{98}\). This analytic continuation into the lower half \( q \)-plane is NOT equal to \( F^{-}(q) \). As an analytic function of \( q \), the only singularities of \( F(q) \) in the upper half \( q \)-plane are first order poles at the bound states of \( H^{(2)} \) while its analytic continuation can have a variety of singularities in the lower half \( q \)-plane. For \( F^{-}(q) \) the role of upper and lower half \( q \)-planes is reversed. The real axis acts as a natural boundary for the evaluation of the matrix element \( \langle \phi | R^{(2)}(z) | \psi \rangle \) as a function of \( q \) and thus is responsible for the fact that \( F(q) \) and \( F^{-}(q) \) are different functions. \( F(q) \) corresponds to the usual (forward) scattering boundary conditions associated with an incoming plane wave being scattered in all directions (for three
dimensional systems). \(F^{(-)}(q)\) corresponds to the reverse, namely incoming spherical waves undergoing scattering to form an outgoing plane wave. Inherently the contour for the evaluation of the second virial coefficient, as given in Eq. (II.151), involves \(q\) in the upper half \(q\)-plane so matrix elements of the form of \(F(q)\) naturally enter into the evaluation of \(B(T)\). Thus the emphasis in the following will be on those functions of \(q\) obtained from the evaluation of \(\mathcal{R}(z)\) matrix elements having \(z = q^2/2\mu\) with \(q\) in the upper half \(q\)-plane.

The difference in resolvents, Eq. (II.152), has be expressed in Section II-2.2 in the Hilbert-Schmidt representation

\[
\mathcal{R}^{(2)}(z) = \sum_n |\zeta_n(z)| \frac{\eta_n(z)}{1 - \eta_n(z)} \langle \xi_n(z) \bigg| \frac{1}{z - H_0^{(2)}} \rangle.
\] (II.155)

In terms of this representation, the second virial coefficient can be written

\[
B(T) = \frac{\Lambda^d}{4\pi i\mu} \int_{-\infty+ic}^{\infty+ic} dq \sum_n \frac{\eta_n(z)}{1 - \eta_n(z)} \langle \xi_n(z) \bigg| \frac{1}{z - H_0^{(2)}} \rangle \zeta_n(z) e^{-\beta z}. \] (II.156)

This provides one way of expressing the second virial coefficient in terms of numerical quantities instead of the operators by which it is defined. As a contour integral over \(q\) (note that the contour lies above the real axis and also above any poles in the upper half \(q\)-plane associated with bound states of \(H^{(2)}\)) it is obvious to consider the singularities, in particular the poles, of the integrand in Eq. (II.156). Unfortunately, because of the exponential \(e^{-\beta q^2/2\mu}\), it is not possible to close the contour at \(|q| = \infty\), either in the upper or lower half \(q\)-plane even if the integrand is meromorphic, so it is not possible to carry out the complete evaluation of \(B(T)\) by residue theory. However, an understanding of the analytic properties of the integrand in Eq. (II.156) is still useful for the evaluation of the contour integral. This evaluation is now discussed.
Clearly there are poles for the integrand in Eq.(II.156) for those values of $q$ for which the eigenvalue $\eta_n(z)$ equals 1, but there can also be poles from the matrix element $\langle \xi_n(z) | (z - H^{(2)}_0)^{-1} | \xi_n(z) \rangle$. For the separable potential of Eq.(II.148), this method of evaluation is quite easy and corresponds to that used in reference$^{110}$, see Section II-3.2. Note that while $K^{(2)}(z)$, its eigenvalues, eigenvectors and also the matrix element $\langle \xi_n(z) | (z - H^{(2)}_0)^{-1} | \xi_n(z) \rangle$ are defined only for $\Im q > 0$, as analytic functions of $q$, these can all be analytically continued into the lower half $q$-plane. It is assumed in this work that the only singularities that these analytically continued functions have are simple poles.

If $q_j$ is a solution of $\eta_n(z) = 1$ for some $n$, then the eigenvector equation (II.96) for the corresponding right eigenvector $| \zeta_j \rangle$ [$\zeta_j \equiv \zeta_n(z_j)$] and the explicit form for $K^{(2)}(z)$ would imply the operator equations

$$K^{(2)}(z_j)|\zeta_j\rangle = \frac{1}{z_j - H^{(2)}_0} V|\zeta_j\rangle = |\zeta_j\rangle; \quad (H^{(2)}_0 + V)|\zeta_j\rangle = z_j|\zeta_j\rangle \quad (II.157)$$

where $z_j = q_j^2 / 2\mu$. The second form, equivalent to the first, appears to be the stationary Schrödinger equation for discrete energy eigenvalue $z_j$. In general these operator equations are invalid. See Section II-3.4 for an example of what can go wrong in what appears to be a simple calculation. Firstly, if $q_j$ is in the upper half $q$-plane, then $q_j$ must, by the self-adjoint properties of the hamiltonians, be purely imaginary and correspond to a bound state of $H^{(2)}$. In this case Eq.(II.157) is the standard and perfectly valid Schrödinger equation. On the other hand, if $q_j$ is in the lower half $q$-plane, then this eigenvector equation is an attempt to analytically continue an operator equation beyond its range of applicability. One way of understanding the inapplicability of Eq.(II.157) in such a case is to recognize that the energy $z_j$ lies on the second (unphysical) sheet of the Riemann surface of the energy parameter.
z. In contrast, the Schrödinger equation, as formulated as an operator equation in Hilbert space, does not recognize the possibility of a multisheeted Riemann surface. As a consequence, Eq.(II.157) is NOT a valid operator equation because this equation involves the splitting of the complex field into two Riemann sheets. An explicit calculation based on the Yamaguchi potential [111], given in Section II-3.3, illustrates how the operator equation is no longer valid in the analytically continued region. These comments apply to both equations in (II.157).

As analytic functions, the analytic continuation of $\eta_n(z)$ and $\langle \xi_n(z) | (z - H_0^{(2)})^{-1} | \zeta_n(z) \rangle$ can be used for the evaluation of the contour integral, Eq.(II.156), for the second virial coefficient. On the assumption that these analytic functions have only isolated first order poles, the integrand of Eq.(II.156) can be written as a sum over all its poles, according to

$$ q \sum_n \frac{\eta_n(z)}{1 - \eta_n(z)} \langle \xi_n(z) \left| \frac{1}{z - H_0^{(2)}} \right| \zeta_n(z) \rangle = \sum_j \frac{A_j}{q - q_j}. \quad (II.158) $$

Here the $j$-sum is to be over all poles and the $A_j$ are constants, independent of $q$. Technically there may be an infinite number of such poles, in which case the question of convergence of the sum may arise. Such questions are not discussed here, presumably the Mittag-Leffler expansion or its extensions can then be used, see e.g. [98]. Since the $q$-contour in Eq.(II.156) lies above all poles, the last line of Eq.(II.146) indicates that the result can be expressed in terms of $w(y)$ functions as

$$ B(T) = -\frac{\Lambda_d}{4\mu} \sum_j A_j w(-q_j \sqrt{\beta/2\mu}). \quad (II.159) $$

This result has the same structure as does Nussenzveig's [73], but the pole positions found here are related to special properties of the kernel $K^{(2)}(z)$.
and should not be immediately associated with the poles of the $S$-matrix or Jost function. It is noted that, just as in Nussenzveig's representation, this equation includes both bound state contributions (if the potential supports such states) as well as that from the continuous spectrum of $H^{(2)}$. Moreover, no constraint that the potential be cutoff has been required.

The above treatment depends on first finding the eigenvalues and eigenvectors of the kernel, before analytically continuing them into the lower half $q$-plane. It is now shown how one can get the same result more directly by looking at the momentum matrix element of $R^{(2)}(z)$. A simple calculation allows the difference in resolvents $R^{(2)}(z)$ to be written as

$$R^{(2)}(z) = \frac{1}{z - H^{(2)}_0} \left[ V + V \frac{1}{z - H^{(2)}} V \right] \frac{1}{z - H^{(2)}_0}.$$  \hspace{1cm} (II.160)

It might be noticed that the quantity inside the square brackets is the $z$ parameterized transition operator. A momentum matrix of this (three dimensional vector notation is used but that can easily be modified for systems of other dimensions) can be calculated for $q$ in the upper half $q$-plane according to

$$F(p, q, p') \equiv q(p|R^{(2)}(z)|p') = \frac{2\mu q}{p^2 - q^2} \langle p | \left[ V + V \frac{1}{z - H^{(2)}} V \right] | p' \rangle \frac{2\mu}{p'^2 - q^2}.$$  \hspace{1cm} (II.161)

As a function of three variables, $F(p, q, p') = -F(p', -q^*, p)^*$ can be considered as an analytic function of $q$ and so continued into the lower half $q$-plane. Assuming that this function has only isolated singularities that are first order poles, it is appropriate to make a pole expansion according to

$$F(p, q, p') = \sum_k \frac{F_k(p, p')}{q - q_k}.$$  \hspace{1cm} (II.162)

An immediate question is to consider whether the expansion coefficients fac-
torize in the form
\[ F_k(p, p') = \zeta_{g_k}(p) f_k \zeta_{-g_k}^*(p') \]  
(II.163)

with \( \int \zeta_{g_k}(p) \zeta_{-g_k}^*(p) dp = 1 \). This is not generally true. On comparing with the representation (II.155) of \( \mathcal{R}^{(2)}(z) \) and its subsequent analytic continuation into the full \( q \)-plane, one has the association

\[ F(p, q, p') = \sum_n \langle p|\zeta_n(z)\rangle \eta_n(z) (\xi_n(z)|p') \frac{2\mu q}{q^2 - p'^2}. \]  
(II.164)

There thus appear to be two types of poles. One set determined by \( \eta_n(z) = 1 \) and the two poles \( q = \pm p' \). By the symmetry appearing in Eq.(II.160), poles at \( q = \pm p \) should also be present, as part of the structure of \( \langle p|\zeta_n(z)\rangle \). The first set of poles will be referred to as "correlated state poles", and naturally include energies corresponding to resonances, virtual states and bound states. The four other poles at \( q = \pm p, \pm p' \), as well as any other poles which may arise from the matrix elements \( \langle p|\zeta_n(z)\rangle \) or \( \langle \xi_n(z)|p' \rangle \), will be referred to as "structural poles". Clearly, for the correlated state poles, \( F_k(p, p') \) factors as in Eq.(II.163). But for the structural poles no such factorization need occur. For this reason the pole expansion of the momentum matrix element of \( \mathcal{R}^{(2)}(z) \) is written as a sum of two types of terms

\[ F(p, q, p') = \sum_k \frac{\zeta_{g_k}(p) f_k \zeta_{-g_k}^*(p')}{q - q_k} + \sum_s \frac{X_s(p, p')}{q - q_s}, \]  
(II.165)

with the \( k \) sum over correlated state poles and \( s \) over the structural poles. Except for the poles associated with possible bound states, the correlated state poles are all in the lower half \( q \)-plane.

The second virial coefficient requires the trace of \( \mathcal{R}^{(2)}(z) \), which is expressed in terms of the pole expansion of \( F(p, q, p') \) by

\[ q \text{Tr} \mathcal{R}^{(2)}(z) = \int F(p, q, p) dp = \sum_k \frac{f_k}{q - q_k} + \sum_m \frac{x_m}{q - q_m}, \]  
(II.166)

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where
\[ \sum_m \frac{x_m}{q - q_m} = \sum_s \int \frac{X_s(p, p)}{q - q_s} dp \]  

is the decomposition of the structural contributions into a sum of pole terms, it being assumed that only first order poles arise in this decomposition. For the separable potential discussed in Section II-3.2, this is indeed the case. On the basis of this assumed form for \( TrR^{(2)}(z) \), it follows on identifying the \( q \)-contour integrals in terms of \( w(y) \) functions that

\[ B(T) = -\frac{A_r}{4\mu} \left[ \sum_k f_k w \left( -q_k \sqrt{\frac{\beta}{2\mu}} \right) + \sum_m x_m w \left( -q_m \sqrt{\frac{\beta}{2\mu}} \right) \right]. \]  

This again has Nussenzveig's form. Using the separable potential as a guide for the properties of the general case, some of the \( q_m \) will coincide with the correlated state poles \( q_k \), while others introduce new pole positions. The latter structural factors can be interpreted as the analog of Nussenzveig's cutoff contributions.

The functions \( \zeta_{q_k}(p) \) that arise from the correlated state pole expansion of \( F(p, q, p') \) in general satisfy no natural orthogonality relation, but are normalizable, well-behaved functions of momentum. These functions naturally are associated with pair particle correlations, so they are considered as the momentum representation of a set of "correlated" states \( |\zeta_{q_k}\rangle \) for the relative motion of a pair of particles. These "correlated" states have inner product normalizable position representation functions obtained from their momentum representations by standard Fourier transform,

\[ Z_k(r) = \frac{1}{\hbar^d/2} \int e^{i\mathbf{p}/\hbar \cdot \mathbf{r}} \zeta_{q_k}(\mathbf{p}) d\mathbf{p}. \]  

For \( q_k \) in the upper half \( q \)-plane, these states are exactly the bound states of \( H^{(2)} \). Considering that \( q \)-poles in the lower half plane are usually associated
with virtual states and resonances, these correlated (normalizable) states $|\zeta_{q_k}\rangle$ can be associated with virtual states and resonances. These states are very different from the usual Gamow states\textsuperscript{74} that are associated with resonances. The Gamow states grow at large distances and thus are non-normalizable in the usual Hilbert space sense. Again the correlated states with $q_k$ in the lower half plane are not eigenvectors of the hamiltonian since they arise from the pole expansion of functions that are analytically continued into the lower half $q$-plane where the operator equations are invalid. As functions that arise from making a pole expansion rather than as eigenvectors of a hamiltonian, they also have no natural orthogonality relations.

II-3.2 Separable Potential Evaluation

The one dimensional separable Yamaguchi potential\textsuperscript{111} of Eq.(II.148) is used to illustrate the expressions derived in the last section. Because this potential allows the results to be expressed in a completely analytic form, it can also serve as a check of the formulas. Furthermore, it is well known that almost all potentials can be accurately approximated by separable potentials of a certain rank\textsuperscript{47}. The discussion is divided into three parts. The first part reviews properties of the model and the simple operator methods of calculating the second virial coefficient. This is followed by examining the properties of the associated kernel operator $K^{(2)}(z)$. The last part involves carrying out the pole expansion of the general momentum matrix element of $R^{(2)}(z)$ and understanding how the different poles contribute to the second virial coefficient.

a) General Properties
Properties of the 1-dimensional Yamaguchi potential have been previously presented\textsuperscript{110,120} and used there to illustrate a number of aspects of binary collisions. The present discussion draws on some of the results of that work.

The first quantity needed for most calculations is the matrix element

\[ Q_0(q) = \langle \chi \left| \frac{1}{z - H_0^{(2)}} \right| \chi \rangle = \frac{2\mu(q + 2ia)}{q(q + ia)^2}, \quad \Re q > 0, \]  

(II.170)

of the resolvent of the free hamiltonian where \( q = \sqrt{2\mu z} \) is in the upper half plane, equivalently the "complex energy" \( z \) is on the first (physical) Riemann sheet. It follows that the matrix of the resolvent of the interacting hamiltonian is

\[ Q(q) = \langle \chi \left| \frac{1}{z - H^{(2)}} \right| \chi \rangle = \frac{Q_0(q)}{1 - V_0Q_0(q)} = \frac{2\mu(q + 2ia)}{q(q + ia)^2 - 2\mu V_0(q + 2ia)}. \]  

(II.171)

As the denominator is a cubic, there are, as an analytically continued function on the whole complex \( q \)-plane, three poles \( q_j \) of \( Q(q) \), as stated in the Introduction. The trace of \( \mathcal{R}^{(2)}(z) \) can be evaluated in terms of \( Q_0(q) \) according to

\[ \text{Tr} \mathcal{R}^{(2)}(z) = \langle \chi \left| \left( z - H_0^{(2)} \right)^{-1} \right| \chi \rangle \frac{V_0}{1 - V_0Q_0(q)} = \frac{\partial \ln[1 - V_0Q_0(q)]}{\partial z} = \frac{\mu}{q} \sum_j \frac{1}{q - q_j} - \frac{1}{q} - \frac{2}{q + ia}, \quad \Re q > 0. \]  

(II.172)

The analytic continuation of this function onto the whole complex \( q \)-plane is used to obtain Eq.(II.149) for the second virial coefficient.

b) Kernel Properties

The kernel operator

\[ K^{(2)}(z) = \left( z - H_0^{(2)} \right)^{-1} \chi V_0(\chi), \]  

(II.173)
defined only for \( \Im q > 0 \), is clearly one dimensional with eigenvalue \( \eta(z) = V_0 Q_0(q) \), associated left eigenvector \( \langle \xi(z) \rangle = |\chi \rangle \) and right eigenvector

\[
|\zeta(z)\rangle = \frac{1}{Q_0(q)(z - H_0^{(2)})} |\chi\rangle.
\] (II.174)

Since it is only the condition that \( \langle \xi(z) | \zeta(z) \rangle = 1 \) that is required for normalization, the factor \( 1/Q_0(q) \) could be included in either right or left eigenvector. The integrand of Eq.(II.156) for the evaluation of the second virial coefficient, equivalently the trace of \( \mathcal{R}^{(2)}(z) \), is given in terms of kernel properties as

\[
\text{Tr}\mathcal{R}^{(2)}(z) = \frac{\eta(z)}{1 - \eta(z)} \langle \xi(z) | \frac{1}{z - H_0^{(2)}} | \zeta(z) \rangle
= \frac{V_0 Q_0(q)}{1 - V_0 Q_0(q)} \times \frac{-\partial Q_0(q)}{Q_0(q) \partial z} = \frac{\partial \ln[1 - V_0 Q_0(q)]}{\partial z}
= \frac{4 \mu^2 V_0 [q^2 + 3iaq - a^2]}{q^2(q + ia)[q(q + ia)^2 - 2\mu V_0(q + 2ia)]},
\] (II.175)

compare with the direct operator calculation of \( \text{Tr}\mathcal{R}^{(2)}(z) \). As previously mentioned this leads to Eq.(II.149) as an expression for the second virial coefficient in terms of \( w(y) \) functions.

c) Momentum Matrix Elements of \( \mathcal{R}^{(2)}(z) \)

The general momentum matrix element \( F(p, q, p') \), see Eq.(II.161), of \( q\mathcal{R}^{(2)}(z) \) but now for one dimension is given by

\[
F(p, q, p') = q \langle p | \mathcal{R}^{(2)}(z) | p' \rangle = \frac{\langle p | \chi \rangle 4 \mu^2 V_0 q (\chi | p')}{(q^2 - p^2)(1 - V_0 Q_0(q))(q^2 - p'^2)}
= \frac{\langle p | \chi \rangle 4 \mu^2 V_0 q^2 (q + ia)^2 (\chi | p')}{(q^2 - p^2)(q^2 - p'^2) \Pi_{j=1}^3(q - q_j)}
= \sum_{j=1}^7 \frac{\mu^2 V_0 \langle p | \chi \rangle g_j(p, p')(\chi | p')}{q - q_j}.
\] (II.176)
While the matrix element evaluation must be carried out with the restriction that \( \Im q > 0 \), as a function of \( q \), \( F(p, q, p') \) is considered as having been (trivially, considering its structure) extended via analytic continuation onto the whole complex \( q \)-plane. As written, the first three pole positions \( q_j \) are to be associated with the zeros of \( 1 - V_0 Q_0(q) \) while the remaining four “structural” poles are respectively at \( p, -p, p' \) and \( -p' \). The pole expansion indicated in the last line recognizes that each term has \( \mu^2 V_0 \langle p|\chi\rangle \langle\chi|p'\rangle \) as a common factor. Since all poles are first order, the factorization can easily be obtained by using Cauchy residue theory in the form

\[
F(p, q, p') = \frac{1}{2\pi i} \oint \frac{F(p, q', p')dq'}{q - q'}
\]

where \( q' \)-contour clockwise about \( q \). Deforming the contour to the circle at infinity crosses all other poles and leads to the factorization. For \( j = 1, 2, 3 \), the resultant weight factors are found to be

\[
g_j(p, p') = \frac{4q_j^2(q_j + ia)^2}{(q_j^2 - p^2)(q_j - q_k)(q_j - q_l)(q_j^2 - p'^2)}
\]

where \( q_k \) and \( q_l \) are the other two roots of \( 1 - V_0 Q_0(q) \) besides \( q_j \). For \( j = 4, \cdots, 7 \), the weight factors have the alternate form

\[
g_j(p, p') = \frac{2\Delta_j q_j(q_j + ia)^2}{(p^2 - p'^2)(q_j - q_k)(q_j - q_l)(q_j - q_3)}
\]

where \( \Delta_j = +1 \) for \( j = 4, 5 \) and \( -1 \) for \( j = 6, 7 \), this corresponding to whether it is \( \pm p \) or \( \pm p' \) that is the pole. It is noted that for \( j \geq 4 \), the \( p \) and \( p' \) dependence of \( g_j(p, p') \) does not factor, essentially because of the presence of \( (p^2 - p'^2) \) in the denominator.

For the correlated state poles, the contribution to \( q\text{Tr}\mathcal{R}^{(2)}(z) \) as expressed in the form of Eq.(II.166) has amplitude

\[
f_j = \mu^2 V_0 \int |\langle p|\chi\rangle|^2 g_j(p, p)dp = \mu \left( \frac{q_j + ia}{q_j - ia} \right)^3 \frac{q_j^2 - 3iaq_j - a^2}{q_j^2 + 3iaq_j - a^2}.
\]

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This somewhat lengthy evaluation inherently involves carrying out the integral by residue theory and simplifying the result. Some useful relations between the three roots $q_1$, $q_2$, $q_3$ of $1 - V_0 Q_0(q)$ are

$$q(q + ia)^2 - 2\mu V_0(q + 2ia) = (q - q_1)(q - q_2)(q - q_3) \quad (II.181)$$

$$3q_j^2 + 4ia q_j - a^2 - 2\mu V_0 = (q_j - q_k)(q_j - q_l) \quad (II.182)$$

$$q_1q_2 + q_2q_3 + q_3q_1 = -a^2 - 2\mu V_0 \quad (II.183)$$

$$q_1 + q_2 + q_3 = -2ia \text{ and } q_1q_2q_3 = 4ia\mu V_0. \quad (II.184)$$

For the structural contributions, it is necessary to combine the $g_4$ and $g_6$ terms and include the $(\chi|p')$ factor before carefully taking the limit $p' \to p$ so as to get a finite quantity that can be integrated over $p$. Combined with the analogous term from $g_5$ and $g_7$, a very lengthy computation results in

$$\sum_m \frac{x_m}{q - q_m} = \mu^2 V_0 \int \lim_{p' \to p} \sum_{j=4}^{7} \langle p|\chi \rangle \frac{g_j(p, p')}{q - q_j} (\chi|p') dp = -\frac{\mu}{q} - \frac{2\mu}{q + ia}$$

$$-4ia^3\mu^2 V_0 \sum_{j=1}^{3} \frac{(5q_j^2 + a^2)(q_j + 2ia)}{(q - q_j)q_j(q_j - ia)^3(q_j + ia)^2(q_j^2 + 3iaq_j - a^2)} \quad (II.185)$$

This has the form of Eq.(II.167), with poles at $q = 0$, $-ia$ and the three correlated state pole positions $q_j$. Combining all contributions gives the previously obtained result, Eq.(II.172). It follows that while the final result is quite simple and has a nice structure, the contributions to the second virial coefficient from the correlated state "energies" come not only from the poles of $\langle p|\mathcal{R}^{(2)}(z)|p' \rangle$ associated with these "energies", but also from the "structural pole" terms. Stated differently, the structural pole parts of $F(p, q, p')$, see Eq.(II.165), determine not only the contributions $w(0)$ and $w(ia\sqrt{2/\mu})$ to $B(T)$, which appear to be "structural" in nature, but also influence the magnitude of the contributions $w(-iq_j\sqrt{2/\mu})$ at the correlated
state momenta \( q_j, \ j = 1, \cdots, 3 \). The question remains as to whether there is a way of partitioning these terms so their contributions are more intuitively identified.

II-3.3 Normalizable Resonance States

The poles of the analytically continued momentum matrix elements of the operator \( \mathcal{R}^{(2)}(z) \) in the complex \( z \)-plane are usually associated with resonance phenomena in scattering theory. The normalizable resonance states characterized by the poles are called correlated states\(^{40} \) here because of their association with statistical pair correlations through the pair Ursell operator. Section II-3.3 is divided into two parts. In the first part the correlated states are explicitly identified and expressed in both position and momentum representation. The second part examines some aspects of analytic continuation for the purpose of contrasting normalizable resonance states with non-normalizable Gamow states.

a) Correlated States

It was noted in Section II-3.1 that in the pole expansion of the momentum representation \( F(p, q, p') \) of \( \mathcal{R}^{(2)}(z) \), certain of the expansion coefficients naturally factored into separate \( p \) and \( p' \) dependences, see Eq.(II.165). Such poles were there referred to as correlated state poles and the associated functions as the momentum representation of correlated states. For the one-dimensional Yamaguchi potential these functions have the form

\[
\langle p|\zeta_j \rangle = \frac{2\mu N_j}{q_j^2 - p^2} \langle p|x \rangle. \tag{II.186}
\]

The \( q_j \) are the three zeros of \( 1 - V_0Q_0(q) \) and \( N_j \) are appropriate normalization constants. There are three kinds of zeros that can arise depending on the
value of the dimensionless ratio \( \nu \equiv \mu V_0/a^2 \), see for example reference\(^{120}\).

For \( \nu < 0 \), there is one bound state with positive imaginary \( q_b = i\kappa_b \) while for positive \( \nu \) this becomes a complex momentum state with \( q_r = -k_r - i\kappa_r \). The other two \( q_j \) are organized in such a manner that the distribution of pole positions is symmetrically distributed about the imaginary axis. Such complex momenta are usually associated with resonances, especially if the \( q_j \) are in the fourth quadrant and lie close to the real axis.

The correlated states are square integrable functions so their normalizations can be determined by the usual Hilbert space inner product \( \langle \zeta_j|\zeta_j \rangle = 1 \). This is in contrast to the biorthonormality discussed in Section II-3.1. The normalization constants are found as follows. For a \( q_j \) associated with a bound or virtual state, the "energy" \( z_j = -\kappa_j^2/2\mu \) is real so that

\[
\frac{1}{|N_j|^2} = \frac{1}{(z_j - H_0^{(2)})^2} |\chi\rangle = \frac{\partial}{\partial z_j} \langle \chi \left| \frac{1}{z_j - H_0^{(2)}} \right| \chi \rangle = \frac{\mu}{\kappa_j} \frac{\partial Q_0(\pm i\kappa_j)}{\partial \kappa_j} = \frac{4\mu^2(\kappa_j^2 + 3a|\kappa_j| + a^2)}{|\kappa_j|^3(|\kappa_j| + a)^3}, \quad q_j = i\kappa_j \text{ imaginary, } (II.187)
\]

while for a resonance \( q_j \),

\[
\frac{1}{|N_j|^2} = \langle \chi \left| \frac{1}{(z_j^* - H_0^{(2)})(z_j - H_0^{(2)})} \right| \chi \rangle = \frac{1}{z_j - z_j^*} \left( \langle \chi \left| \frac{1}{z_j^* - H_0^{(2)}} \right| \chi \rangle - \langle \chi \left| \frac{1}{z_j - H_0^{(2)}} \right| \chi \rangle \right) = \frac{1}{z_j - z_j^*} [Q_0(q_j^*) - Q_0(-q_j)] = \frac{4\mu^2[\kappa_j k_j^2 + (\kappa_j + a)(\kappa_j^2 + 3a\kappa_j + a^2)]}{\kappa_j(k_j^2 + \kappa_j^2)[k_j^2 + (\kappa_j + a)^2]^2}, \quad q_j = k_j - i\kappa_j, \quad \kappa_j > 0. \quad (II.188)
\]
In these calculations it must be assured that the \( q \) parameter for which the free resolvent matrix element is identified as \( Q_0(q) \) necessarily lies in the upper half plane, which is the reason for the presence of the ± and \(| \) s that appear in the formulas. The final form for the "resonance state" normalization reduces to that for the "virtual state" normalization \((k_j = 0)\) even though the derivation of the former needs \( k_j \neq 0 \).

As properly normalizable functions, the correlated states can also be expressed in position representation. The transformation from momentum to position representation is via the usual Fourier transform, see Eq.(II.169). The resulting \( p \) integral can be carried out by contour integration, being careful to close the contour in a manner consistent with the vanishing of the integrand as \(|\Im p| \to \infty\). Just as all momentum representations of the correlated states have the same form, so does the position representation

\[
Z_j(x) = \frac{1}{\hbar^{1/2}} \int e^{i p x / \hbar} \langle p | \zeta_j \rangle dp
= \frac{2 \mu N_j}{(q_j^2 + a^2)} \left( \frac{2 \pi a^3}{\hbar} \right)^{1/2} \left[ \frac{e^{-a|x|/\hbar}}{a} - \frac{i e^{\pm i q_j x / \hbar}}{\pm q_j} \right],
\]

where the ± is chosen so that \( \Im(\pm q_j) > 0 \). Therefore even in position representation the correlated states have the standard inner product normalization

\[
\langle \zeta_j | \zeta_j \rangle = \int_{-\infty}^{\infty} |Z_j(x)|^2 dx = 1.
\]

b) Some Aspects of Analytic Continuation

The analytic properties of functions associated with the kernel and its eigenvectors and eigenvalues are discussed as functions of \( z \). It is emphasized that as an operator, see Eq.(II.173), the kernel involves the resolvent of the free hamiltonian and so is defined only for \( z \) off the positive real axis. Thus,
as an operator, its analytic continuation through the positive real axis is not defined. In order to carry out an analytic continuation it is necessary to express the kernel operator and its eigenvectors in some representation. Specifically the momentum and position representations are considered.

In momentum representation, the kernel operator becomes the kernel of the an integral equation, specifically

$$\langle p|K^{(2)}(z)|p'\rangle = \langle p \bigg| \frac{1}{z - H^{(2)}_0} \bigg| p' \rangle = \frac{4\mu a^3 V_0}{\pi(a^2 + p^2)(q^2 - p^2)(a^2 + p^2)},$$  

(II.191)

while its right eigenvector $$|\zeta(z)\rangle \equiv (z - H^{(2)}_0)^{-1}|\chi\rangle$$ [the $$Q_0(z)$$ factor of Eq.(II.174) is left out for simplicity] has the (normalized) momentum representation

$$\langle p|\zeta(z)\rangle = \left(\frac{2a^3}{\pi}\right)^{\frac{1}{2}} \frac{2\mu}{(q^2 - p^2)(a^2 + p^2)}.$$  

(II.192)

Consistent with the operator properties of $$K^{(2)}(z)$$, $$z$$ is restricted from being on the positive real axis, and for definiteness, $$q = u + iv$$ is that unique square root of $$2\mu z$$ with positive imaginary component ($$v > 0$$). The integral equation representation of the eigenvector equation $$K^{(2)}(z)|\zeta(z)\rangle = \eta(z)|\zeta(z)\rangle$$ is

$$\int \langle p|K^{(2)}(z)|p'\rangle\langle p'|\zeta(z)\rangle dp'$$

$$= \int \frac{4\mu a^3 V_0}{\pi(a^2 + p^2)(q^2 - p^2)(a^2 + p^2)} \left(\frac{2a^3}{\pi}\right)^{\frac{1}{2}} \frac{2\mu}{(q^2 - p^2)(a^2 + p^2)} dp'$$

$$= \langle p|\zeta(z)\rangle \int \frac{4\mu a^3 V_0}{\pi(a^2 + p^2)(q^2 - p^2)} dp'.$$

(II.193)

The integral over $$p'$$ gives for $$q = u + iv$$ with $$v > 0$$, the eigenvalue

$$\eta(z) = V_0Q_0(q) = \frac{2\mu V_0(u + iv + 2ia)}{(u + iv)(u + iv + i)^2}.$$  

(II.194)
As functions of $z$, both the integral kernel $\langle p | K^{(2)}(z) | p' \rangle$ and the eigenfunction $\langle p' | \zeta(z) \rangle$ have simple poles at $(\pm p)^2/2\mu$ as the only singularities, in particular neither have any branch points so analytic continuation gives nothing new. But the eigenvalue $\eta(z)$ has branch points at $z = 0$ and $z = \infty$ so as a function of $z$, it requires a two sheeted Riemann surface. Analytically continuing the kernel function, the eigenfunction and the eigenvalue into the lower half $q$-plane, explicitly following each function from $u + iv$ to $u - iv$, $u, v > 0$ for fixed $u$ gives

\[
\langle p | K^{(2)}((u - iv)^2) | p' \rangle = \frac{4\mu a^3 V_0}{\pi (a^2 + p^2)((u - iv)^2 - p^2)(a^2 + p^2)},
\]

\[
\langle p | \zeta((u - iv)^2) \rangle = \left(\frac{2a^3}{\pi}\right)^{\frac{1}{2}} \frac{2\mu}{(q^2 - p^2)(a^2 + p^2)},
\]

\[
\eta((u - iv)^2) = \frac{2\mu V_0(u - iv + 2ia)}{(u - iv)(u - iv + ia)^2}.
\]  (II.195)

Now it is possible to examine whether the eigenvector equation (II.174) is satisfied with this value of $q = u - iv$. Clearly all that has to be checked is the value of the $p'$ integral! This integral is now

\[
\int \frac{4\mu a^3 V_0}{\pi (a^2 + p^2)((u - iv)^2 - p^2)(a^2 + p^2)} dp' = \frac{2\mu V_0(-u + iv + 2ia)}{(-u + iv)(-u + iv + ia)^2}.
\]  (II.196)

On comparison, this is NOT $\eta((u - iv)^2)$ so the eigenfunction equation has changed its character! While the analytically continued eigenfunction still satisfies the eigenfunction equation with the analytically continued kernel function, the eigenvalue has jumped from what it would be if it was obtained by the same analytic continuation as was applied to the kernel and the eigenfunction. By direct comparison, and by the nature of the integral, the value of the integral (II.196) can be recognized as $V_0Q_0(-u + iv)$, whose argument in $Q_0$ has a positive imaginary part. Since resonance and virtual states are
classified by having $V_0Q_0(q) = 1$ with $q$ in the lower 1/2-plane, such an
eigenvalue can NOT arise by an integration of the form of Eq.(II.196), thus
not as an operator property, but only by analytic continuation to where the
operator equation is invalid.

In contrast, for $q$ in the upper 1/2-plane, the position representation of
the kernel is

$$
\langle x|K^{(2)}(z)|x' \rangle = \langle x \left| \frac{1}{z - H^{(2)}_0} \right| x' \rangle
$$

$$
= \left( \frac{4\pi \mu a}{\hbar q(q^2 + a^2)} \right)^\frac{1}{2} \left[ qe^{-a|x|/\hbar} - iae^{i|q|x|/\hbar} \right] e^{-a|x'|/\hbar}
$$

(II.197)

while its eigenvector (having non-zero eigenvalue) is

$$
\langle x|\zeta(z) \rangle = \langle x \left| \frac{1}{z - H^{(2)}_0} \right| \chi \rangle
$$

$$
= \frac{2\mu}{q(q^2 + a^2)} \left( \frac{2\pi a}{\hbar} \right)^\frac{1}{2} \left[ qe^{-a|x|/\hbar} - iae^{i|q|x|/\hbar} \right].
$$

(II.198)

Expressed in position representation the operator equation becomes

$$
\int \langle x|K^{(2)}(z)|x' \rangle \langle x'|\zeta(z) \rangle dx'
$$

$$
= \langle x|\zeta(z) \rangle \int \left( \frac{4\pi \mu V_0a}{\hbar q(q^2 + a^2)} \right) e^{-a|x'|/\hbar} \left[ qe^{-a|x|/\hbar} - iae^{i|q|x|/\hbar} \right] dx'.
$$

(II.199)

For $q$ having positive imaginary part, the integral can be evaluated to give the
eigenvalue $\eta(z) = V_0Q_0(q)$, which confirms the $K^{(2)}(z)$ eigenvector equation
in position representation.

Examination of the form of the kernel $\langle x|K^{(2)}(z)|x' \rangle$ in position represen-
tation, it is seen that its analytic continuation from $q = u + iv$ to $q = u - iv$
gives a function that diverges as $x \to \pm \infty$, so loses its compactness as an integral operator. Likewise, the position representation of the eigenvector $\langle x|\zeta(z) \rangle$ diverges in the same manner. This is the 1-dimensional analog of the Gamow state. Clearly the position integral (II.199) for the eigenfunction equation diverges for $q$ having a negative imaginary part.

It is thus seen that the analytic continuation (as a function of $z$ or $q$) of the momentum and position representations of the various quantities in the eigenfunction equation have drastically different behaviors. In position representation, both the kernel and the eigenfunction become divergent at large positions. In contrast, for the momentum representation, all quantities remain well behaved at all momenta. The correlated states have been identified through the analytic continuation of the momentum representation of the kernel eigenfunction to where the analytically continued eigenvalue $\eta(z)$ has the value 1, to give well behaved, square integrable functions. In position representation, the analogous functions are the Gamow states, but as functions diverging at large positions, they have very different properties. This emphasizes the importance of which representation is used to carry out the analytic continuation.

II-3.4 Discussion

It has been shown how a pole expansion of the momentum matrix elements of the difference $\mathcal{R}^{(2)}(z)$ between the resolvents of the interacting and free hamiltonians, and eventually the evaluation of its trace, leads to an expression for the second virial coefficient in the same form as found by Nussenzveig\textsuperscript{73}. In contrast, Nussenzveig based his derivation on the poles of the $S$-matrix for cutoff potentials. While intimately connected, it would
seem that the resolvents are closer to the basic properties of the hamiltonians and possibly easier to calculate than is the $S$-matrix. Indeed, many of the pole properties of the resolvents are determined by the kernel operator $K^{(2)}(z)$ defined in Eq.(II.92). The Yamaguchi potential\textsuperscript{111} has been used to provide an explicit example of this expansion, see Section II-3.2.

On the basis that the difference in resolvents of the relative interacting and free hamiltonians is a measure of the correlation between a pair of particles, all properties of this difference have been associated with the word “correlation”. While the difference in resolvents $R^{(2)}(z)$ is an operator and subject to the rules of functional analysis, in particular that it is a trace class operator (and consequently compact) for $z$ not on the spectrum of either hamiltonian, a matrix element of $R^{(2)}(z)$ is a function of $z$ and subject to analysis via analytic function theory. The latter can rapidly lead to properties that are unattainable by the usual application of functional analysis. It is the interplay between these two approaches and the recognition of their respective properties that is utilized in this chapter.

For definiteness, and simplicity since the free hamiltonian commutes with the momentum, the analytic function theory analysis is carried out using momentum matrix elements of $R^{(2)}(z)$. Note that entirely different properties would be obtained if the position matrix elements were analytically continued. The poles, which have been assumed to be the only singularities and of first order, of the function $F(p, q, p') = q(p|R^{(2)}(z)|p')$ analytically continued into the whole complex $q = \sqrt{2\mu z}$ plane are recognized as being of two types. There are immediately poles at $\pm$ the magnitudes $p$ and $p'$ of the momenta $p$ and $p'$ appearing in the matrix element which are associated with “structural” properties of $R^{(2)}(z)$, and other “correlated state” poles that are inherently determined by the (analytically continued) properties of
the resolvent of the interacting hamiltonian. The residue of a correlated state pole factors into separate momentum dependent functions $\zeta_j(p)$ which can be identified as particular analytically continued eigenvectors of the kernel $K^{(2)}(z)$, which being Hilbert-Schmidt, implies that the $\zeta_j(p)$ are square integrable and thus can be associated with abstract states $|\zeta_j\rangle$ of Hilbert space. They consequently have normalizable position representations $Z_j(r)$ as well as normalizable momentum representations $\zeta_j(p)$. It should be mentioned that there is no requirement that these correlated states be orthogonal as elements of Hilbert space. Returning to a functional analysis viewpoint, this has provided a means of partitioning the momentum matrix elements of $\mathcal{R}^{(2)}(z)$ into a sum of pole terms, each associated with a correlated state, and a further structural part.

Excluding those $q$ associated with bound states of the hamiltonian, $\mathcal{R}^{(2)}(z)$ is compact for $\Im q > 0$. Thus it has a discrete spectrum and set of eigenvectors, see Eq.(II.155), which are in one-one correspondence with those of $K^{(2)}(z)$. The momentum matrix element $F(p, q, p')$ thus constitutes the compact kernel for an integral equation, parameterized by $q$. It is this function which is analytically continued into the lower half of the complex $q$-plane, assumed for simplicity to be meromorphic and to retain its compactness except at its $q$ singularities. Under these assumptions, $F(p, q, p')$ has a pole expansion. Moreover, based on the compactness of $\mathcal{R}^{(2)}(z)$, the trace of $\mathcal{R}^{(2)}(z)$ can be obtained by a careful integration over $F(p, q, p')$ to have a pole expansion, see Eq.(II.166), whose positions include those of the correlated poles. It follows that the second virial coefficient is again a sum of contributions, one for each correlated state plus a number of contributions from the structural part of $F(p, q, p')$. As learned from the example in Section II-3.2, the structural pole terms can contribute after the trace to the residues of $\text{Tr}\mathcal{R}^{(2)}(z)$ at the
correlated state pole positions.

As special analytically continued eigenvectors of $K^{(2)}(z)$ with eigenvalue parameterized by the complex momentum $q_j$, they might be considered as solutions of an operator equation, see Eq.(II.157), that looks like the Schrödinger equation. For $q_j$ in the upper half $q$-plane, the eigenvector of $K^{(2)}(z_j)$ is identical to a bound state of the Hamiltonian and the Schrödinger equation interpretation is perfectly valid with $z_j = q_j^2/2\mu$ the (negative) bound state energy. It can also be recognized that no analytic continuation of the matrix elements of $K^{(2)}(z)$ need be made to get this result. But if the pole $q_j$ lies in the lower half $q$-plane, this pole is identified only through analytic continuation of the matrix elements of $K^{(2)}(z)$, equivalently, of $R^{(2)}(z)$, and the operator equation is false. Essentially the analytically continued eigenvalue $z_j$ now lies on the second (unphysical) sheet of the (energy) Riemann surface so cannot be attributed a physical meaning. Since the Schrödinger operator and indeed all of Hilbert space is defined only over a unified complex field without being split into a multisheeted Riemann surface, this formal operator equation for the correlated states is invalid. The Yamaguchi potential of Section II-3.2 is now used to explicitly show how Eq.(II.157) fails in that case.

We recall that the poles of the analytically continued momentum matrix element of $pR^{(2)}(z)$ are determined predominantly by $\eta(z) = 1$, which are identical to the poles $q_j$ of $Q(q)$, equivalently the roots of $1 - V_0 Q_0(q)$. Except for a single bound state which can exist if $V_0 < 0$, the $q_j$ lie in the lower half $q$-plane. For such a $q_j$, equation (II.157) appears to imply that the corresponding $z_j$ is an eigenvalue of $H^{(2)}$. This is indeed incorrect! From the form, Eq.(II.174), for $|\zeta(z)\rangle$ and the momentum representation of the
Schrödinger equation,

\[
\langle p| (H_0^{(2)} + V)|\zeta_j\rangle = \left[ \frac{p^2}{2\mu} \frac{2\mu}{Q_0(q_j)(q_j^2 - p^2)} \langle p|\chi\rangle + \langle p|\chi\rangle V_0(\chi|\zeta_j) \right] \\
= \frac{q_j^2}{2\mu} \langle p|\zeta_j\rangle + \left[ \frac{-1}{Q_0(q_j)} + V_0(\chi|\zeta_j) \right] \langle p|\chi\rangle.
\]

(II.200)

Provided \(V_0Q_0(q_j)(\chi|\zeta_j) = 1\), the term in square brackets vanishes and the Schrödinger equation is satisfied. But the evaluation of the inner product \(\langle \chi|\zeta_j \rangle\) for \(q_j\) in the lower half plane gives

\[
Q_0(q_j)\langle \chi|\zeta_j \rangle = \langle \chi \left| \frac{1}{z_j - H_0^{(2)}} \right| \chi \rangle = Q_0^{-1}(q_j) \\
= \frac{2a^3}{\pi} \int \frac{2\mu dp}{(p^2 + a^2)(q_j^2 - p^2)} = \frac{2\mu(q_j^2 - 2ia)}{q_j(q_j - ia)^2} \\
= Q_0(-q_j) \neq Q_0(q_j).
\]

(II.201)

Note that the evaluation of the integral by the method of residues can be used by closing the contour either above or below the real axis. But whichever is used, care must be exercised as to which poles are to contribute to the integral. Essentially \(q_j\) is a root of \(V_0Q_0(q) = 1\) while \(V_0Q_0(-q_j) \neq 1\). Thus Eq.(II.200) is not the Schrödinger equation and \(z_j = q_j^2/2\mu\) with \(q_j\) in the lower half plane is not an eigenvalue of \(H^{(2)}\). In making these identifications it is necessary to identify \(Q_0(q)\) as that function of \(q\) which is the analytic continuation of the function obtained by evaluating the matrix element \(\langle \chi|(z - H_0^{(2)})^{-1}|\chi\rangle\) for \(q\) in the upper \(\frac{1}{2}\)-plane, and not by evaluating the matrix element for arbitrary \(q\). Stated differently, analytic continuation and matrix element evaluation do not commute!

The correlated state poles \(q_j\) in the lower half of the momentum plane correspond to \(z_j\) energies in the second sheet associated with resonance and
virtual state phenomena. There is no unique definition of resonance state. A resonance is usually associated with a pole of the $S$-matrix, a pole in the Jost function, a pole of the resolvent, a bump in a scattering cross section, or a rapid increase in the scattering amplitude or phase shift. It has been known that these associations are not always consistent with each other.

The square integrable functions, called correlated states in the present chapter, are associated with these poles and thus associated with resonance and virtual states of the pair of interacting particles. Whereas these states are square integrable and their position representations $Z_j(r)$ vanish for $|r| \to \infty$, the conventional treatment of resonance and virtual states treat resonance states as diverging exponentially as $|r| \to \infty$. There is a large literature on resonance state theory that follows this approach. From the theory of Fredholm determinants and the Lippmann-Schwinger equation it has been argued that resonance states in the momentum representation are $L^2$ functions while their position representations have divergent behaviour at infinity. It seems to the author that these arguments appear to be applying the properties of the kernel operator $K^{(2)}(z)$ beyond its domain of definition. Both the Schrödinger operator and the Lippmann-Schwinger kernel are defined on Hilbert space which is a vector space over the complex field. For resonance states whose energies are on the second Riemann sheet, neither the Schrödinger operator nor the Lippmann-Schwinger kernel are correctly defined, they have a meaning only in terms of the analytic continuation of their matrix elements. Consequently the physical boundary conditions of the Schrödinger and Lippmann-Schwinger equations, such as regularity at the origin and pure outgoing asymptotic behaviour at large distances may not be required.

As indicated earlier, the present work differs from most treatments of
resonances by analytically continuing the momentum matrix elements of the difference of the resolvents, in contrast to analytically continuing the position representation of the same quantity. Thus entirely different properties are obtained. Analytically continuing position matrix elements leads to non-normalizable wavefunctions, and for the resonance momenta, the Gamow states. Again, the evaluation of matrix elements and analytic continuation do not commute! There seems to be an advantage to using momentum matrix elements. More often, treatments involve the analytic continuation of scattering wavefunctions. But a scattering wavefunction is a solution of the Schrödinger equation with energy associated with the initial (incoming) momentum, so the analytic continuation is of the “physical” momentum. In contrast, the analytic continuation considered here is for the momentum “parameter” in the resolvent, so that neither the “physical” momentum nor position play a role in the analytic continuation. Thus the present approach selects out only particular representations of the resolvent operators rather than modifying physical quantities. Ghirardi et al.\textsuperscript{119} discuss how the pole positions of the analytically continued matrix elements of the resolvent depend on the basis set used for calculating the matrix elements. One of their conclusions is that the eigenstates of $H_0^{(2)}$ play a unique role in the study of the resolvent for $H^{(2)}$, specifically the analytic properties are then determined essentially by the off-shell $T$-matrix. But Ghirardi et al. restrict their basis elements to be square integrable functions of the $H_0^{(2)}$ eigenvalues which are also, from an analytic function viewpoint, entire functions. Calculating a trace with such functions would appear to be an extra complication. Using the “improper” momentum functions simplifies the trace calculation for evaluation the second virial coefficient, but appears to add the complexity of introducing “structural” pole terms.
The method of analytic continuation first introduced by Romo for normalizing resonance states is conceptually different from the analytic continuation implemented here. The resonance states in that work are the Gamow states. In order to define a “norm”, Romo analytically continues the resonance states to the first Riemann sheet, normalizing them there as if they were properly defined there, then taken (continued) back to the second sheet with the first sheet norm. This is not the same as the analytic continuation of the momentum representation of eigenvectors and matrices used here.
Part III

Quantum Kinetic Theory of Reactive Moderately Dense Gases
Chapter III-1
Introduction to Part III

Gas kinetic theory attempts to explain macroscopic observations\textsuperscript{123,124} in terms of microscopic properties of the atoms and/or molecules based on classical or quantum mechanics. Typical macroscopic observations deal with $N(\sim 10^{20})$ particles over an volume much larger than the size of the individual molecules, and over a time period large compared to the time scale of the individual molecular dynamics. An ab-initio description of the time dependence of such macroscopic observations from the quantum Liouville equation\textsuperscript{2} is practically impossible not only because of the conceptual difficulty with the meaning of measurement\textsuperscript{125,126,127,128,129}, but also due to the number of degrees of freedom. The kinetic theory approach simplifies the $N$ particle problem dramatically by looking at the behaviour of one typical particle under the influence of all the other particles.

The most successful kinetic theory has been based on the Boltzmann equation\textsuperscript{130,131,16,132,133,134,135,136}. Specifically this has been related to the hydrodynamic equations and has given rise to molecular expressions for the transport coefficients\textsuperscript{137,16}. Various attempts have been made to understand the Boltzmann equation from the $N$-body Liouville equation\textsuperscript{2}, or utilizing the BBGKY hierarchy\textsuperscript{21,22}. A first principles "derivation" of the Boltzmann equation from the Liouville equation has been achieved by Bogoliubov\textsuperscript{21}, and independently Green\textsuperscript{61}. Their classic work paves the way for other developments\textsuperscript{138,139,140,141,142,133,143,132}, in particular to provide suitable kinetic descriptions for polyatomic gases, dense gases, rarefied gases and plasmas.

The Wang Chang-Uhlenbeck-de Boer equation\textsuperscript{59} was the first attempt to generalize the Boltzmann equation, to account for the internal degrees
of freedom of a polyatomic gases. It was not generally realized until 1957
that polyatomic gases can only be treated properly by a quantum mechani-
cal method due the fact that the internal energy levels of such molecules are,
in general, degenerate\textsuperscript{144}. Subsequent work by Waldmann\textsuperscript{60} and, indepen-
dently, by Snider\textsuperscript{26} led to a quantum kinetic equation, the Waldmann-Snider
equation, which is still the basis for the kinetic theory of polyatomic gases.
Snider's derivation starts from the well-known BBGKY hierarchy, while a dif-
ferent approach starting from the generalized master equation has been given
by Tít\textsuperscript{145} and by Andersen and Oppenheim\textsuperscript{146}. Most of the developments in
this field, including various applications\textsuperscript{147,148,149}, such as to the Senftleben-
Beenakker effect\textsuperscript{150,151}, have been recently summarized in two monographs
by McCourt, Beenakker, Köhler and Kusčer\textsuperscript{132}.

The kinetic theory of dense gases is, by itself, a very diverse field. There
are several lines of development.

Starting with Enskog\textsuperscript{152}, there is need to take into account the non local
collision correction due to the spatial separation of the two colliding frag-
ments. Enskog showed how this affects the transport coefficients by using
hard spheres. Bogoliubov\textsuperscript{21}, and independently Green\textsuperscript{61}, have also consid-
ered this effect while formulating their kinetic theories. Snider and Curtiss\textsuperscript{62}
have developed Bogoliubov and Green's formulas to work out detailed trans-
port expressions. Enskog\textsuperscript{152}, using the hard sphere model, also treated the
effect a third particle has on binary collisions and the consequent effect on
the transport coefficients. A similar treatment for general (soft) potentials
was provided by Hoffman and Curtiss\textsuperscript{153}. Rainwater and co-workers\textsuperscript{154,155}
have numerically implemented the theories of Snider and Curtiss, of Hoff-
man and Curtiss, and of the bound state effect, as prescribed by Stogryn
and Hirschfelder\textsuperscript{156}, by using realistic potentials and found that a combi-
nation of the theories gives a very successful explanation for experimental transport coefficient data.

Another aspect of dense gas kinetic theory is the possibility of the formation and reaction of stable molecules\textsuperscript{156,157} due to strong attractive potentials. Olmsted and Curtiss\textsuperscript{17} discussed the influence on the pair particle distribution functions by the presence of bound states from the BBGKY hierarchy point of view. Eu\textsuperscript{18} has considered a gas mixture with two fragment rearrangement collisions. A three-body collision operator with bound state effects has also been constructed by McLennan\textsuperscript{19} in terms of Green-Kubo formalism\textsuperscript{50}. Klimontovich \textit{et al.}\textsuperscript{20} has formulated a reactive fluid theory at the three-body level. A kinetic theory of a dimer and monomer mixture has been treated by Lowry and Snider\textsuperscript{23,24} with a novel counting procedure and a reactive Boltzmann ansatz. Hoffman, Kouri and coworkers\textsuperscript{27,28} formulated a rigorous reactive quantum fluid theory in terms of the BKLT scattering theory\textsuperscript{9}. Their theory reduces to that of Lowry and Snider\textsuperscript{23} at the appropriate level of approximation.

A systematic theory of dense gases was initiated by Bogoliubov\textsuperscript{21}. The essential assumptions of the theory are the Bogoliubov's well-known dense gas hypotheses. It is assumed that there are three relevant time scales — collision time, mean free time and hydrodynamic relaxation time. For times long compared to the collision time, it is assumed that the higher order distribution functions are functionals of the singlet distribution function

\[
f^{(n)}(x^{n},t) = f^{(n)}(x^{n}|f^{(1)}(x_{1},t)). \tag{III.1}
\]

Moreover, it is assumed that these functionals are expandable as series in the density. The consequence of these assumptions has been examined by Choh and Uhlenbeck\textsuperscript{158}. Cohen\textsuperscript{159} and coworkers\textsuperscript{160,161} elaborated on Bogoliubov's
idea and provided detailed boundary conditions for evaluating the collisions and estimating transport coefficients. In particular, the resulting generalized Boltzmann equation can be expressed as

\[
\frac{\partial f^{(1)}}{\partial t} + \mathbf{v} \cdot \frac{\partial f^{(1)}}{\partial \mathbf{r}} = J(f^{(1)f^{(1)}}) + K(f^{(1)f^{(1)}f^{(1)}}) + L(f^{(1)f^{(1)}f^{(1)}f^{(1)}}) + \cdots,
\]

where \(J, K,\) and \(L\) respectively designate binary, ternary and quaternary collision terms. Divergences of the density expansions have been found in calculating transport coefficients using hard spheres and discs\(^{163,164,160}\). A resummation or renormalization procedure has been introduced by Kawasaki and Oppenheim\(^{165}\), and others\(^{166,160,167,168}\) to eliminate the divergences and a novel density dependence of the transport coefficients, namely an \(n^2 \ln n\) term, has been discovered\(^{165}\). Despite the difficulties, this line of development has contributed much to the modern understanding of dense gas kinetic theory. It is noted that Bogoliubov's assumption of complete weakening of the initial correlations is one particular boundary condition for dense gas evolution and successive collisions are required to include higher ordered corrections. Various different approaches have been proposed by various authors\(^{169,170,171,172,173,175}\) to partially retain the initial correlations.

While the conventional method depends on the evaluation of collision integrals for the transport coefficients, there are two other distinct kinetic theory techniques that have been developed: Firstly, the time-correlation function formalism\(^{176,177,140,178,179,180,181}\) leads to expressions for the transport coefficients. Secondly the double (real and imaginary) time Green's function method\(^{182,183,184,185,186,187,188}\) provides another elegant formulation of kinetic equations\(^{186}\) and transport theory\(^{184}\), and describes various collective motions of the many-body system as a whole. This method has been very successful.
in solving liquid helium\textsuperscript{189} and condensed matter\textsuperscript{190} problems. Both methods have become an indispensable part of modern kinetic theory.

Of immediate concern for Part III is a renormalized quantum Boltzmann equation proposed by Snider\textsuperscript{52}

\begin{equation}
\frac{\partial (\rho_{f1} + \rho_{c1})}{\partial t} = \mathcal{L}_1^{(1)} (\rho_{f1} + \rho_{c1}) + \text{Tr}_2 \mathcal{V}_{12} \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^1,
\end{equation}

where the contribution of pair correlations to the singlet density operator has been explicitly accounted for through a renormalized singlet $\rho_{f1} + \rho_{c1}$. The solution to this equation has been pursued on and off by Snider and coworkers for the last few years. The present goal is to generalize the renormalized quantum Boltzmann equation (III.3) to a set of coupled quantum kinetic equations appropriate for a reactive moderately dense gas system including free particles, pair correlations and bound pairs, and eventually to solve the set of equations for the transport coefficients. This is presented in Part III of this thesis.

Part III consists of four chapters. Chapter III-2 is devoted to the formulation of three kinetic equations, one for each of the renormalized singlet, pair correlation and bound pair for a reactive moderately dense gas system. The quantum kinetic equation for the renormalized singlet is now appropriately called a generalized Boltzmann equation since it contains reactive three fragment collision operators. Statistical operators appropriate for the reactive moderately dense gas system are given in the spirit of the Lowry-Snider\textsuperscript{23} counting (see also Section I-3.1). The essential ingredient is that the singlet operator has contributions both from the pair correlation and from the bound pair. The dynamic evolution of each species is described by free motion and collisions with free fragments. The structure of the kinetic equations arrived in Chapter I-3 for arbitrary clusters is adopted in the present treatment while
the two-Liouville space notation and conceptual arguments are left out for simplicity. It is noted that the notation in Part III is consistent with Refs. (52) and (23). In particular, the Liouville operators $\mathcal{L}^{(n)}$ are defined as

$$\mathcal{L}^{(n)} = \sum_{i} \mathcal{L}^{(1)}_{i} + \sum_{1 \leq i < j \leq n} \mathcal{V}_{ij},$$

(III.4)

with $\mathcal{L}^{(1)}_{i}$ and $\mathcal{V}_{ij}$ being given in terms of hamiltonian $H^{(1)}_{i}$ and potential $V_{ij}$

$$\mathcal{L}^{(1)}_{i} A = \frac{1}{\hbar} \left( H^{(1)}_{i} A - A H^{(1)}_{i} \right)$$

(III.5)

and

$$\mathcal{V}_{ij} A = \frac{1}{\hbar} \left( V_{ij} A - A V_{ij} \right).$$

(III.6)

$H^{(n)}$ is the $n$-particle hamiltonian

$$H^{(n)} = \sum_{i} H^{(1)}_{i} + \sum_{1 \leq i < j \leq n} V_{ij}.$$  

(III.7)

The difficulty of incorporating a correlated pair as a collision partner, which motivated the work of Part II, is bypassed by introducing the concept of interacting pairs through an exact chain rule relation\cite{42,24}. The interacting pairs provide a suitable domain of applicability for the Møller superoperators of Section I-2.3 and are intimately related to the pair correlations, particularly in the pair particle space. The molecular picture has been emphasized throughout Chapter III-2. The method of coupled kinetic equations provides a practical scheme for systematically including higher ordered correlations and arbitrary bound states.

The macroscopic properties of the three kinetic equations formulated in Chapter III-2 are discussed in Chapter III-3 to enhance the understanding of a reactive moderately dense gas system, and to provide the basis for the practical solution to the three coupled kinetic equations. The hydrodynamic
equations for each of the three kinetic equations are first derived in density operator form\textsuperscript{123,58,191}. The collision operators in the three kinetic equations are then restricted to non-reactive binary collisions in order to simplify the presentation. Within the non-reactive binary collision approximation, a modified equation for the pair correlations (called the modified pair correlation equation) is proposed. The Wigner\textsuperscript{192} phase space representation of quantum mechanical density operators and collision superoperators is utilized to allow a simultaneous description of the momentum and position dependences of the density operators, thus separating the macroscopic properties from the microscopic. In particular, the local equilibrium form of the various density operators, which is central to the Chapman-Enskog method\textsuperscript{131,16,132,133}, is discussed in detail. Various macroscopic variables, such as number densities, stream velocities, kinetic and potential energies, heat fluxes and pressure tensors, are expressed in terms of the Wigner representation. Two solution schemes, Scheme I, to solve the renormalized quantum Boltzmann equation\textsuperscript{52} together with the modified pair correlation equation for molecules without bound states, and Scheme II, to solve the three kinetic equations for a moderately dense gas with bound states, are introduced while presenting the macroscopic variables.

The Chapman-Enskog\textsuperscript{131,16,132,133} solutions and transport coefficients according Schemes I and II are obtained in Chapter III-4. In such a method the distinctions between local equilibrium and non-equilibrium, and between macroscopic and microscopic properties are first required. These are aided by linearization about local equilibrium of the collision superoperators and the three kinetic equations. The local inhomogeneity is responsible for the non-equilibrium. A set of common macroscopic variables $v_0$ and $T$ for all species at local equilibrium is used in linearizing the kinetic equations. The collision
non-locality$^{152,193,194}$ of two arbitrary colliding fragments is estimated by a gradient expansion retaining only up to linear in gradient terms. The bound state density operator is assumed to be diagonal in the internal state energy in order to simplify the presentation, as well as the structure of the solutions and transport coefficients.

For Scheme I, the renormalized Boltzmann equation and the modified pair correlation equation are solved separately, since to first order in gradient, the renormalized Boltzmann equation is essentially decoupled from the modified pair correlation equation. With the pair correlation operator being assumed to be in complete equilibrium with the free, the time derivatives in the renormalized Boltzmann equation are eliminated by the three hydrodynamic equations, namely the equation of continuity, equation of motion and equation of energy balance. This results in equations that are linear in the gradients. Unlike in the standard Chapman-Enskog method$^{131,16,132,133}$, the potential energy, as well as the kinetic energy, is needed for energy conservation. The potential energy is involved due to non-local collisions which give rise to the interconversion of kinetic energy and potential energy. The Fredholm alternative$^{42,195}$ is used to guarantee the existence and uniqueness of the solution of the renormalized Boltzmann equation. The transport coefficients are estimated to lowest order in a Sonine expansion. There are contributions to the transport coefficients from free motion, pair correlations and collisional transfer.

For Scheme II, the generalized Boltzmann equation, the bound pair equation and the modified pair correlation equation are solved as for a binary gas mixture, with one component being the renormalized particle 1 and the other the bound pair. According to the Chapman-Enskog procedure, the density operators are treated as functionals of the three hydrodynamic vari-
ables, namely the number densities, velocity and temperature with their time derivatives eliminated by use of the Euler equations. The total energy, including the kinetic energies of the renormalized particle 1 and the bound pair, as well as the potential energy of an interacting pair, are used for the determination of the time rate of change of the temperature. Two energy transfer mechanisms, namely the energy transfers between kinetic energy and potential, and between "kinetic" and internal energy, are appropriately treated for total energy conservation. The latter is crucial for establishing the conditions which allows the Fredholm alternative to insure the existence and uniqueness of the Chapman-Enskog solution. Only the monomer-monomer collisional non-locality associated with the generalized Boltzmann equation is included. It is considered that it would be inconsistent at this order of the density expansion to include monomer-dimer and dimer-dimer non local collisions, which are proportional to the monomer-dimer and dimer-dimer correlations respectively at equilibrium. The solution for the generalized Boltzmann equation and the bound pair equation is estimated using the lowest order Sonine polynomials\textsuperscript{16,131} and Wang Chang-Uhlenbeck polynomials\textsuperscript{196}. Uniqueness of the first order solution is guaranteed by the requirement of being orthogonal to the five right invariants. The transport coefficients are calculated in the same manner as that in Scheme I with additional diffusional contributions to the heat flux, and bound pair contributions to all macroscopic quantities.
Chapter III-2
Kinetic Equations of Reactive Moderately Dense Gases

In this chapter, a set of kinetic equations appropriate for a reactive moderately dense gas system is discussed. The purpose of such a treatment is to enhance the understanding of a reactive moderately dense gas system and to provide a sound basis for further development in the subsequent two chapters, where solutions and transport coefficients are found for a limited set of kinetic processes. The quantum kinetic theory of reactive moderately dense gases is a virtually untackled problem, which is technically demanding and conceptually complicated. There are three major aspects to be handled appropriately in such a kinetic theory as briefly introduced in the following three paragraphs.

The first aspect is the role of the fundamental properties of quantum mechanics. In comparison to classical mechanical treatment, the quantum mechanical treatment makes a kinetic theory complicated in the following ways: i) Non-commutation of quantum mechanical operators, for instance the non-commutation of position and momentum operators, requires that the classical distribution functions be replaced by statistical density operators and that the various operator relations are treated properly. ii) Internal states, such as vibration and rotation, for polyatomic molecules result in an off-diagonal density matrix which makes a kinetic description very complicated. The presence of internal states is assumed in this thesis but such a presence is not explicitly emphasized, particularly when solving the kinetic equations in the succeeding two chapters. iii) Quantum mechanical exchange symmetry of indistinguishable particles requires the system wave function to be either symmetric or antisymmetric to the exchange of a pair of particles.
However this effect is not important except for very dense gases at very low temperature, which is not the case in the present treatment. Thus one ignores the exchange effects and assumes that the reactive moderately dense gas system obeys Boltzmann statistics.

The second aspect is the role of those reactive collisions that cause formation and break-up of bound states. There are two issues regarding this aspect: i) A formal kinetic theory of a reactive gas system requires a multi-channel quantum scattering theory capable of appropriately handling the non-orthogonality of different channel spaces. One method of rigorously treating such a non-orthogonality problem is to formulate the kinetic theory in terms of a two-Liouville space quantum scattering theory. This was attempted in Part I. Such a theory requires the conceptual distinction of four different spaces and two types of channels, thus complicating any kinetic description dramatically. Since the emphasis in Part III is not on the channel non-orthogonality problem, the asymptotic orthogonality of rearrangement channel spaces and asymptotic completeness are assumed throughout this part. The distinction between channel space and asymptotic channel space is not explicitly stressed in Part III. ii) Conceptual problems arise as whether the theory formulated in terms of a molecular picture or an atomic picture. The atomic picture treats the presence of bound states as a perturbation to the atomic density operators or distribution functions, and therefore restrains the full role of bound states in the kinetic description. In contrast, the molecular picture treats atoms and bound states on an equal footing. Such a treatment requires a consistent partition of the total $N$ particles into monomers and bound pairs, which partitioning is not unique.

The last aspect, also the least understood, is the non-ideality due to statistical correlations between the particles. A few words are needed to
specify the scope of the discussion of the correlations. In general a correlation is the measurement of the influence of one physical observable on another. Correlations can be i) the influence between states of the same physical object at different times, so called time correlations; ii) between states of different physical objects at the same time; iii) non-locality of a density operator in a particular representation. There are a few points regarding the notation to be specified: Firstly the role of time correlations in kinetic theory is not an explicit object of this thesis. Secondly the pair particle bound states are obviously special cases of correlations. Due to the distinct spectral property of bound states, bound pairs are treated separately and will not be referred as correlations in this thesis. Thirdly, correlations induced by the non-locality of the density operator is not explicitly discussed until the next chapter. Since correlations become important as the density of the gas increases, the presence of pair correlations and pair particle bound states for a reactive moderately dense gas system are essential to the consideration in Part III. Instead of using the assumption of completely weakening initial correlations and treating correlations only as an after effects of a collision, it seems to be more reasonable to assume the persistent existence of statistical correlations and to take care of the dynamical processes of creation and decay of pair correlations through collisions. Thus a separate kinetic equation for pair correlations is introduced to handle both this formation and decay as well as their dynamical evolution.

This chapter is divided into four sections. A set of statistical operators appropriate for the description of a reactive moderately dense gas system is derived from a molecular picture in Section III-2.1. The derivation is analogous to the Lowry-Snider method for the partition into monomers and dimers but also takes into account the additional presence of pair correla-
tions. The singlet frees, bound pairs and correlated pairs are treated on an equal footing. The resulting structure of the reduced density operators is the same as that of Lowry and Snider, and that of Part I for a reactive gas mixture. A major characteristic of those density operators is that the full singlet density operator describes not only free particles but also has contributions from correlated pairs and bound pairs. Such a singlet density operator may be considered as a renormalized singlet density operator and gives rise to the full second virial corrections to the equation of state at equilibrium. Statistically it is reasonable that the density operator is systematically renormalized for a dense gas system in the sense that renormalization is required in order to give the proper macroscopic expectation values for the moderately dense gas system. In this way the singlet density operator has a substructure.

The structure of the density operators appropriate for the description of various dynamic processes is discussed in Section III-2.2. Dynamically it is necessary that only the undressed density operators be used in various dynamical processes because the dynamical processes are microscopic in origin. From a scattering theory point of view the pair correlation operators do not provide a proper domain for a scattering and/or Møller superoperator, thus the usual Møller superoperators and transition superoperators can not be directly applied to the pair correlation operators. In order to formulate kinetic theory in terms of few-body collision processes, an exact chain rule relation is utilized to introduce interacting pairs. The interacting pairs provide a suitable domain for the Møller superoperators and are intimately related to the pair correlations, particularly in the pair particle space.

Section III-2.3 is devoted to a discussion of three coupled kinetic equations. The first equation is for the bound pairs (dimers) and is "derived" in a way similar to what as was done for the bound clusters in Part I. Projection
superoperators are used not for the reason of channel non-orthogonality but due to the ambiguity in the transition operators in three- and more particle scattering theory as noticed by Faddeev\textsuperscript{5}. The scattering channels are modified according to the chain rule so as to include interacting pairs in the three and more particle spaces. The second kinetic equation is for $\rho_{f1} + \rho_{c1}$, the singlet without the bound pair part. Such a division seems natural because it gives rise to a density corrected (renormalized) quantum Boltzmann equation\textsuperscript{52} when the bound states are neglected and because a correlated pair can easily be converted into two free particles in the moderately dense gas. In an effort to treat the pair correlations on an equal footing to the free and bound states, the last kinetic equation is devoted to the correlated pairs. Since technically the pair correlations can not be handled directly in terms of the usual operators of scattering theory, an indirect treatment through the chain rule and interacting pairs is introduced. The resulting equation is consistent with equilibrium. All kinetic equations are such that they incorporate the interplay between the statistical macroscopic and dynamical microscopic descriptions. Finally some general discussion is given in Section III-2.4.

III-2.1 Statistical Density Operators

In Part I reduced density operators $\rho^{(n)}$ are derived from a two-Liouville space scattering theory for an $N$-particle gaseous system with the possibility of formation of all kinds of clusters, such as monomers, dimers, trimers etc. The resulting reduced density operators are similar to those of Lowry and Snider on limiting the clusters to monomers and dimers, but the description is in terms of a two-Liouville space scattering theory, which is necessary for sorting out the channel non-orthogonality problem. Since the explicit treat-
Part of the channel non-orthogonality problem is not an object of present concern, the difference between a channel and an asymptotic channel is not emphasized in the present discussion. The results of two-Liouville space theory, such as asymptotic orthogonality, are used whenever they are needed without reintroducing the complicated notation and concepts. The new feature in this section is the presence of pair correlations. Section III-2.1 is separated into two subsections. First, statistical correlations of arbitrary order are introduced in a conventional manner. Then a set of reduced density operators, including the roles of singlet free, pair correlations and bound pairs, are “derived” using the Lowry-Snider partition method.

a) Correlations

Particles are correlated in a moderately dense gas. It is well known that the correlations give rise to virial corrections to the equation of state at equilibrium as shown in Section II-2.1. In general correlations measure the influence that the state of one particle has on the state of another particle in the system. The pair particle correlations in a moderately dense gas system is defined through

$$\rho_{c12} \equiv \rho_{12}^{(2)} - \rho_{1}^{(1)} \rho_{2}^{(1)}, \quad (III.8)$$

The correlation $\rho_{c12}$ vanishes whenever the states of two particles become independent of each other $\rho_{12}^{(2)} \rightarrow \rho_{f1}\rho_{f2}$.

The singlet $\rho_{1}^{(1)}$ in Eq. (III.8) has a substructure

$$\rho_{1}^{(1)} = \rho_{f1} + \rho_{c1}. \quad (III.9)$$

Here $\rho_{c1}$ is given by

$$\rho_{c1} \equiv \text{Tr}_{2}\rho_{c12}. \quad (III.10)$$
The substructure in the singlet is essential to the discussion in Part III. Such a substructure implies that the singlet density operator is a density corrected singlet, equivalently a renormalized singlet density operator. The influence of pair correlations, together with those of the bound states, on kinetic equations and transport coefficients is the subject of the rest of this thesis.

Conventionally higher-order correlations are defined as the following\textsuperscript{141,159}:

\begin{align*}
\rho^{(2)} &= \rho_{1}^{(1)} \rho_{2}^{(1)} + \rho_{c12} \\
\rho^{(3)} &= \rho_{1}^{(1)} \rho_{2}^{(1)} \rho_{3}^{(1)} + \rho_{c123} \\
&+ \rho_{1}^{(1)} \rho_{c23} + \rho_{2}^{(1)} \rho_{c13} + \rho_{3}^{(1)} \rho_{c12} \\
\rho^{(4)} &= \rho_{1}^{(1)} \rho_{2}^{(1)} \rho_{3}^{(1)} \rho_{4}^{(1)} \\
&+ \rho_{1}^{(1)} \rho_{2}^{(1)} \rho_{c34} + \rho_{1}^{(1)} \rho_{3}^{(1)} \rho_{c24} \\
&+ \rho_{1}^{(1)} \rho_{4}^{(1)} \rho_{c23} + \rho_{2}^{(1)} \rho_{3}^{(1)} \rho_{c14} \\
&+ \rho_{2}^{(1)} \rho_{4}^{(1)} \rho_{c13} + \rho_{3}^{(1)} \rho_{4}^{(1)} \rho_{c12} \\
&+ \rho_{c12} \rho_{c34} + \rho_{c13} \rho_{c24} \\
&+ \rho_{c14} \rho_{c23} + \rho_{1}^{(1)} \rho_{c234} \\
&+ \rho_{2}^{(1)} \rho_{c134} + \rho_{3}^{(1)} \rho_{c124} \\
&+ \rho_{4}^{(1)} \rho_{c123} + \rho_{c1234} \\
\end{align*}

These correlations are proportional to the Ursell operators\textsuperscript{64} (see Section II-2.1) at equilibrium

\[ \rho_{c1...n}^{eq} \propto U^{(n)}. \] (III.14)

The density operators \( \rho^{(n)} \) factorize into products of independent free singlet
density operators whenever the correlations vanish

\[ \lim_{\rho_c \to 0} \rho_1^{(n)} \to \prod_{i=1}^{n} \rho_{fi}. \quad (III.15) \]

b) Bound States and Correlations

This thesis is interested in reactive moderately dense gases. For such a system, there are two modifications to the aforementioned density operators. First concerns the presence of bound states due to the strong attractive interactions between particles. A two-Liouville space reactive gas theory has been formulated in Part I for arbitrary clusters. Here for simplicity, only the bound pairs (dimers) \( \rho_{bij} \) are assumed to exist. The generalization to include arbitrary clusters is similar to the procedure followed in Part I. The second modification is to limit the discussion to pair-particle correlations, which is of prime importance for a moderately dense gas system. Higher-order correlations become more important as the density of the system increases.

The kinetic theory including higher-order correlations and bound states is expected to be complicated. However the structure presented in this thesis gives an indication of how to approach higher-order correlations together with the presence of various bound states (see the discussion in Section III-2.4).

The derivation of density operators in a molecular picture can be accomplished in the same way as the Lowry-Snider counting\(^{23}\) presented in Section I-3.1. A state \( \rho_{M,D,C}^{(N)} \), characterized by \( M \) monomers, \( D \) dimers and \( C \) correlated pairs, is assumed to be given by

\[
\rho_{M,D,C}^{(N)} = g(N, M, D, C)^{-1} M^{-M} (2D)^{-D} (2C)^{-C} \times \sum_{(\alpha, \beta, \gamma) \in \alpha} \prod_{\{j,k\} \in \beta} \rho_{bjk} \prod_{\{l,m\} \in \gamma} \rho_{clm}, \quad (III.16)
\]
where $\alpha$ is the list of particles in the set \{1, 2, $\cdots$, N\} which are monomers, $\beta$ is the list of pairs of particles which are bound pairs (dimers) and $\gamma$ is the list of pairs of particles which are correlated pairs.

$$g(N, M, D, C) = \frac{N!}{M!D!2^D C!2^C}$$  \hspace{1cm} (III.17)

is the number of possible ways of partitioning the $N$ particles into $M$ monomers, $D$ dimers and $C$ correlated pairs. By going through a similar procedure as that in Section I-3.1 one can end up with an expression for the reduced density operators $\rho^{(n)}(1 \cdots n)$, in the hydrodynamic limit,

$$\rho^{(n)}(1 \cdots n) = \sum_{(\alpha, \beta, \gamma) \in \alpha} \prod_{(i, j) \in \beta} \rho_{ijk} \prod_{(i, m) \in \gamma} \rho_{cim},$$  \hspace{1cm} (III.18)

where $\alpha$, $\beta$ and $\gamma$ have similar interpretation as in Eq. (III.16) but limited to the set of particles \{1 $\cdots$ n\}.

The density $n_b$ of bound particles and the density $n_c$ of correlated particles follow from the corresponding density operators $\rho_{b12}$ and $\rho_{c12}$ according to

$$\text{Tr}_{12}(\delta_1 + \delta_2)\rho_{c12} = 2n_c,$$  \hspace{1cm} (III.19)

and

$$\text{Tr}_{12}(\delta_1 + \delta_2)\rho_{b12} = 2n_b,$$  \hspace{1cm} (III.20)

where $\delta_1 = \delta(r - r_1)$. $r$ denotes the macroscopic position variable at which the particle is to be observed, while $r_i$ is the position operator for particle $i$.

The use of two delta functions $\delta_1 + \delta_2$ in Eqs.(III.19) and (III.20) reflects the atomic picture view of density operator $\rho_{c12}$ and $\rho_{b12}$ and results in a factor of 2 for the densities $n_c$ and $n_b$.

The singlet density operator has components, similar to that in Section I-3.1 and in the density corrected Boltzmann equation$^{52}$

$$\rho^{(1)} = \rho_{f1} + \rho_{b1} + \rho_{c1}$$

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\[ = \rho_{f1} + \text{Tr}_2 \rho_{b12} + \text{Tr}_2 \rho_{c12}. \]  
\quad (III.21)

The trace over the position of particle 1 gives the number density of free particles

\[ \text{Tr}_1 \delta_1 \rho_{f1} = n_f. \]  
\quad (III.22)

Thus the number density of the full singlet \( \rho^{(1)} \) is

\[ n = \text{Tr}_1 \delta_1 \rho^{(1)} = n_f + n_b + n_c. \]  
\quad (III.23)

It is noted that \( \delta_1 \) is a physical observable which asks if a particle is at macroscopic position \( \mathbf{r} \) and counts physical states \( \rho_{f1} \), \( \rho_{b1} \) and \( \rho_{c1} \) on an equal footing. In contrast to Eqs. (III.19) and (III.20), Eq. (III.23) gives the molecular picture density of the gas system. The difference between molecular and atomic pictures arises when physical observations are treated in a different manner.

First a few terms in expression (III.18) are listed explicitly as follow

\[ \rho^{(1)} = \rho_{f1} + \rho_{b1} + \rho_{c1} \]  
\quad (III.24)

\[ \rho^{(2)} = \rho^{(1)}_1 \rho^{(1)}_2 + \rho_{b12} + \rho_{c12} \]  
\quad (III.25)

\[ \rho^{(3)} = \rho^{(1)}_1 \rho^{(1)}_2 \rho^{(1)}_3 + \rho^{(1)}_1 (\rho_{b23} + \rho_{c23}) + \rho^{(1)}_2 (\rho_{b13} + \rho_{c13}) + \rho^{(1)}_3 (\rho_{b12} + \rho_{c12}) \]  
\quad (III.26)

\[ \rho^{(4)} = \rho^{(1)}_1 \rho^{(1)}_2 \rho^{(1)}_3 \rho^{(1)}_4 + \rho^{(1)}_1 \rho^{(1)}_2 (\rho_{b34} + \rho_{c34}) + \rho^{(1)}_1 \rho^{(1)}_3 (\rho_{b24} + \rho_{c24}) + \rho^{(1)}_1 \rho^{(1)}_4 (\rho_{b23} + \rho_{c23}) + \rho^{(1)}_2 \rho^{(1)}_3 (\rho_{b14} + \rho_{c14}) + \rho^{(1)}_2 \rho^{(1)}_4 (\rho_{b13} + \rho_{c13}) + \rho^{(1)}_3 \rho^{(1)}_4 (\rho_{b12} + \rho_{c12}) + (\rho_{b12} + \rho_{c12})(\rho_{b34} + \rho_{c34}) + (\rho_{b13} + \rho_{c13})(\rho_{b24} + \rho_{c24}) + (\rho_{b14} + \rho_{c14})(\rho_{b23} + \rho_{c23}) \]  
\quad (III.27)
This set of density operators can be alternatively derived by introducing bound pairs into the equations of Ref. (52) containing pair correlations. Since different methods end up with the same structure for the reduced density operators, this set of reduced density operators is considered to have the correct structure and be appropriate for the kinetic description of a reactive moderately dense gases.

III-2.2 Density Operators for Dynamical Processes

Conventionally kinetic equations involve the microscopic dynamical processes described by the classical or quantum mechanical scattering theory. In
such a microscopic dynamical process it is necessary to deal with an isolated set of a few particles. For this purpose, a modification of the previously defined density operators is needed. This modification has been called the "exorcism of ghosts" by Lowry and Snider\textsuperscript{23}

$$\left[\rho^{(n)}\right]_{\text{iso}} = \sum_{(\alpha, \beta, \gamma) \in \alpha} \prod_{(i,j) \in \beta} \rho_{ij} \prod_{(l,m) \in \gamma} \rho_{lm}. \quad (\text{III.29})$$

Here $\rho_i^{(1)}$, which can inherently involve other particles in the system, through the presence of $\rho_{c1}$ and $\rho_{b1}$, that are not in the set of $\{1, \ldots, n\}$, are replaced by $\rho_{fi}$. The subscript $\text{iso}$ stands for "isolated" ($n$ particles). The density operators in Eq.(III.29) involve explicitly all $n$ particles and no others. The first a few terms in Eq.(III.29) are

$$\left[\rho^{(1)}\right]_{\text{iso}} = \rho f_1 \quad (\text{III.30})$$

$$\left[\rho^{(2)}\right]_{\text{iso}} = \rho f_1 \rho f_2 + \rho b_{12} + \rho c_{12} \quad (\text{III.31})$$

$$\left[\rho^{(3)}\right]_{\text{iso}} = \rho f_1 \rho f_2 \rho f_3 + \rho f_1 (\rho b_{23} + \rho c_{23})$$
$$+ \rho f_2 (\rho b_{13} + \rho c_{13}) + \rho f_3 (\rho b_{12} + \rho c_{12}) \quad (\text{III.32})$$

$$\left[\rho^{(4)}\right]_{\text{iso}} = \rho f_1 \rho f_2 \rho f_3 \rho f_4 + \rho f_1 \rho f_2 (\rho b_{34} + \rho c_{34})$$
$$+ \rho f_1 \rho f_3 (\rho b_{24} + \rho c_{24}) + \rho f_1 \rho f_4 (\rho b_{23} + \rho c_{23})$$
$$+ \rho f_2 \rho f_3 (\rho b_{14} + \rho c_{14}) + \rho f_2 \rho f_4 (\rho b_{13} + \rho c_{13})$$
$$+ \rho f_3 \rho f_4 (\rho b_{12} + \rho c_{12}) + (\rho b_{12} + \rho c_{12})(\rho b_{34} + \rho c_{34})$$
$$+ (\rho b_{13} + \rho c_{13})(\rho b_{24} + \rho c_{24}) + (\rho b_{14} + \rho c_{14})(\rho b_{23} + \rho c_{23})$$
$$\ldots \ldots \quad (\text{III.33})$$

This set of reduced density operators has a structure similar to that of $\rho^{(n)}$ and is good for a kinetic description of a set of $n$ particles isolated from
the rest of the gas, but is not in a form convenient for a detailed dynamical
description of the precollision state. The problem is due to the pair corre­
lations. Specifically, the correlation operator $\rho_{cij}$ is neither the eigenstate of
the full two particle Liouville operator $L_{ij}^{(2)}$, nor the eigenstate of the two
particle kinetic superoperator $K_{ij}^{(2)}$.

Consequently the time evolution involving the full evolution superoper­
ator $e^{-iL_{ij}^{(2)}t} \rho_{cij}$ and the streaming superoperator $e^{-iK_{ij}^{(2)}t} \rho_{cij}$ vanishes in the
time limit of $t \to \pm \infty$.

$$
\lim_{t \to \pm \infty} e^{-iL_{ij}^{(2)}t} \rho_{cij} \to 0, \quad (\text{III.34})
$$
and

$$
\lim_{t \to \pm \infty} e^{-iK_{ij}^{(2)}t} \rho_{cij} \to 0. \quad (\text{III.35})
$$
As a result, operator $\rho_{cij}$ is not appropriate for a Møller superoperator and/or
transition superoperator, which are frequently used in kinetic theory for the
description of dynamic processes. In order for a kinetic theory description
in terms of conventional collision dynamics, one needs either to create a
new hamiltonian, which has $\rho_{cij}$ as eigenstate, or to modify the form of the
density operators $\rho^{(n)}$. The rest of this section looks for a set of reduced
density operators which have the correct structure from a statistical point of
view and are convenient for few-body dynamical operations.

Quantum mechanically, few-body time evolution is governed by the quan­
tum Liouville equation

$$
i \frac{\partial [\rho^{(n)}]_{\text{coll}}(t)}{\partial t} = L^{(n)}[\rho^{(n)}]_{\text{coll}}(t)
= \frac{1}{\hbar} [\hat{H}^{(n)}, [\rho^{(n)}]_{\text{coll}}]. \quad (\text{III.36})
$$
A formal solution of the Liouville equation (III.36) is

$$
[\rho^{(n)}]_{\text{coll}}(t) = e^{-iL^{(n)}(t-t_0)}[\rho^{(n)}]_{\text{coll}}(t_0). \quad (\text{III.37})
$$
From the quantum mechanical scattering theory point of view Eq. (III.36) has an exact solution under the scattering boundary condition
\[
\lim_{t \to -\infty} ||[\rho^{(n)}]_{\text{coll}}(t) - [\rho^{(n)}]_{\text{asy}}(t)|| = 0, \tag{III.38}
\]
where subscript \text{asy} stands for "asymptotic". \([\rho^{(n)}]_{\text{asy}}\) is given by
\[
[\rho^{(n)}]_{\text{asy}} = \lim_{t \to -\infty} [\rho^{(n)}]_{\text{iso}}(t)
= \sum_{(\alpha,\beta) \in \alpha} \prod_{i \in \alpha} \rho_{fi} \prod_{\{j,k\} \in \beta} \rho_{bjk}. \tag{III.39}
\]
Here under the time limit necessarily only the asymptotically stable fragments are important. The stable fragments furnish various asymptotic channels as described in a two-Liouville space scattering theory of Part I, while for simplicity the notation of Part I is not used. Explicitly the first few terms of the density operators in Eq.(III.39) are
\[
[\rho^{(1)}]_{\text{asy}} = \rho_{f1}, \tag{III.40}
\]
\[
[\rho^{(2)}]_{\text{asy}} = \rho_{f1}\rho_{f2} + \rho_{b12}, \tag{III.41}
\]
\[
[\rho^{(3)}]_{\text{asy}} = \rho_{f1}\rho_{f2}\rho_{f3} + \rho_{f1}\rho_{b23}
+ \rho_{f2}\rho_{b13} + \rho_{f3}\rho_{b12}, \tag{III.42}
\]
\[
[\rho^{(4)}]_{\text{asy}} = \rho_{f1}\rho_{f2}\rho_{f3}\rho_{f4} + \rho_{f1}\rho_{f2}\rho_{b34}
+ \rho_{f1}\rho_{f3}\rho_{b24} + \rho_{f1}\rho_{f4}\rho_{b23}
+ \rho_{f2}\rho_{f3}\rho_{b14} + \rho_{f2}\rho_{f4}\rho_{b13}
+ \rho_{f3}\rho_{f4}\rho_{b12} + \rho_{b12}\rho_{b34}
+ \rho_{b13}\rho_{b24} + \rho_{b14}\rho_{b23}. \tag{III.43}
\]
where \([\rho^{(1)}]_{asy}\) is the correct asymptotic form for a single particle but is hardly an asymptotic state for collisions. \([\rho^{(2)}]_{asy}\) has an extra term \(\rho_{b12}\) from the scattering point of view.

The solution of the Liouville equation (III.36) for an isolated set of \(n\) particles under the boundary condition of Eq. (III.38) is given either in terms of a Møller superoperator \(\Omega^{(n)}\), or in terms of channel Møller superoperators \(\Omega_{(\alpha,\beta)}\)

\[
[\rho^{(n)}]_{coll}(t) = e^{-i\mathcal{L}^{(n)}t} \Omega^{(n)}[\rho^{(n)}]_{asy} = \sum_{(\alpha,\beta)} \Omega_{(\alpha,\beta)} e^{-i\mathcal{L}_{(\alpha,\beta)}t} \prod_{i \in \alpha} \rho_{f_i} \prod_{(j,k) \in \beta} \rho_{b_{jk}}, \quad (III.44)
\]

where the (asymptotic) channel Liouville operators \(\mathcal{L}_{\alpha,\beta}\) are given by

\[
\mathcal{L}_{(\alpha,\beta)} \equiv \sum_{i \in \alpha} \mathcal{L}^{(1)}_i + \sum_{j,k \in \beta} \mathcal{L}^{(2)}_{j,k}. \quad (III.45)
\]

The channel Møller superoperators \(\Omega_{(\alpha,\beta)}\) are defined as

\[
\Omega_{(\alpha,\beta)} \equiv \lim_{t \to -\infty} e^{i\mathcal{L}^{(n)}t} e^{-i\mathcal{L}_{(\alpha,\beta)}t}. \quad (III.46)
\]

An alternative expression for the solution Eq. (III.44) is possible through an exact relation

\[
\Omega_{(\alpha,\beta)} = \Omega_{(\alpha',\beta',\gamma')} \Omega_{(\alpha',\beta',\gamma'),(\alpha,\beta)}. \quad (III.47)
\]

This is usually called Kato’ chain rule\(^{42}\) but was independently rediscovered by Snider and Lowry\(^{24}\) in a three-body transition superoperator form. The Møller superoperators are defined in a similar way as before

\[
\Omega_{(\alpha',\beta',\gamma')} \equiv \lim_{t \to -\infty} e^{i\mathcal{L}^{(n)}t} e^{-i\mathcal{L}_{(\alpha',\beta',\gamma')}t} \quad (III.48)
\]

\[
\Omega_{(\alpha',\beta',\gamma'),(\alpha,\beta)} \equiv \lim_{t \to -\infty} e^{i\mathcal{L}_{(\alpha',\beta',\gamma')}t} e^{-i\mathcal{L}_{(\alpha,\beta)}t}. \quad (III.49)
\]
The new set of channel states introduced by the Møller operator $\Omega_{(\alpha', \beta', \gamma'), (\alpha, \beta)}$ are characterized by $(\alpha', \beta', \gamma')$ and are usually called the secondary asymptotic channel states in quantum scattering theory\textsuperscript{197}. The first two indices $\alpha'$ and $\beta'$ list the free particles and pairs of particles which are bound pairs respectively. In contrast to the previous definition for $\gamma$, the third index $\gamma'$ is a list of pairs of particles which are interacting. The secondary asymptotic channel Liouville operators $\mathcal{L}_{(\alpha', \beta', \gamma')}$ are given by

$$\mathcal{L}_{(\alpha', \beta', \gamma')} \equiv \sum_{i \in \alpha'} \mathcal{L}_{i}^{(1)} + \sum_{j,k \in \beta'} \mathcal{L}_{j,k}^{(2)} + \sum_{l,m \in \gamma'} \mathcal{L}_{l,m}^{(2)}.$$  \hfill (III.50)

The states in secondary asymptotic channels involve not only stable fragments but can also include interacting wave packets of subsystems, the latter will be restricted to two-particle subsystems and called interacting pairs in this work.

The following example is used to illustrate the use of the chain rule. In the isolated three-particle dynamics the chain rule gives

$$3 \Omega_{f_1, f_2, f_3; \rho_{f_1} \rho_{f_2} \rho_{f_3}} = \Omega_{p_{12}, f_3; \rho_{p_{12}} \rho_{f_1} \rho_{f_2} \rho_{f_3}}$$
$$+ \Omega_{p_{13}, f_2; \rho_{p_{13}} \rho_{f_{12}} \rho_{f_2} \rho_{f_3}}$$
$$+ \Omega_{p_{23}, f_1; \rho_{p_{23}} \rho_{f_{12}} \rho_{f_3} \rho_{f_3}}$$ \hfill (III.51)

$$= \Omega_{p_{12}, f_3; \rho_{p_{12}} \rho_{f_3}}$$
$$+ \Omega_{p_{13}, f_2; \rho_{p_{13}} \rho_{f_2}}$$
$$+ \Omega_{p_{23}, f_1; \rho_{p_{23}} \rho_{f_1}},$$ \hfill (III.52)

where for example

$$\rho_{p_{12}} \rho_{f_3} = \Omega_{p_{12}, f_3; \rho_{p_{12}} \rho_{f_1} \rho_{f_2} \rho_{f_3}},$$ \hfill (III.53)

are the states of a secondary asymptotic channel. The factor of three in Eq. (III.51) is due to the fact that there are three different but equally
probable ways for fulfilling the chain rule relation Eq. (111.47) in the three particle space. Following Bencze and Chandler, one assumes the secondary asymptotic channel spaces are complete and furnish the $n$-particle scattering subspace $\mathcal{S}_n^{(n)}$ (see Section I-2.2)

$$
\sum_{(\alpha', \beta', \gamma')} Q_{(\alpha', \beta', \gamma')}^{(n)} = \delta_{n\infty}, \quad (III.54)
$$

where the projection superoperator $Q_{(\alpha', \beta', \gamma')}^{(n)}$ is

$$
Q_{(\alpha', \beta', \gamma')}^{(n)} = \Omega^{(-)}_{(\alpha', \beta', \gamma')} \Omega^{(-\dagger)}_{(\alpha', \beta', \gamma')}, \quad (III.55)
$$

defined in terms of Møller superoperator

$$
\Omega^{(-)}_{(\alpha', \beta', \gamma')} \equiv \lim_{t \to +\infty} e^{i\mathcal{L}^{(n)}(t)} e^{-i\mathcal{L}^{(n)}(\alpha', \beta', \gamma')t}. \quad (III.56)
$$

Eqs. (111.44) and (111.51) suggest the reduced density operator $\rho^{(3)}$ can be written in terms of secondary asymptotic channels as

$$
\rho^{(3)}_{2nd-asy} = -2\rho_{f1}\rho_{f2}\rho_{f3} + \rho_{f1}(\rho_{b23} + \rho_{p23}) + \rho_{f2}(\rho_{b13} + \rho_{p13}) + \rho_{f3}(\rho_{b12} + \rho_{p12}). \quad (III.57)
$$

As for the structure of expression (III.57), it has three basic building blocks: the free, the bound pair and the interacting pair. This structure is analogous to the structure of statistical density operators $\rho^{(3)}$ of Eq.(III.26). It is argued in the following that the interacting pairs are intimately related to the pair correlations.

The interacting pair density operator $\rho_{pij}$ is different from the statistical operator $\rho^{(2)}$ in general, but it is equivalent to $\rho^{(2)}$ excluding the bound states in the pair-particle space (pps)

$$
\rho_{pij} \big|_{pps} = \rho^{(2)}_{ij} \big|_{pps} - \rho_{bij}
= \rho_{ciij} + \rho_{fj} \rho_{fj}. \quad (III.58)
$$
By extending the above relation to the three-particle space, it is reasonable to rewrite Eq. (III.57) as

\[
\begin{align*}
[\rho^{(3)}]_{2nd-asy} & \simeq \rho_{f1}\rho_{f2}\rho_{f3} + \rho_{f1}(\rho_{b23} + \rho_{c23}) \\
& \quad + \rho_{f2}(\rho_{b13} + \rho_{c13}) + \rho_{f3}(\rho_{b12} + \rho_{c12}).
\end{align*}
\tag{III.59}
\]

This expression has exactly the same structure as Eq. (III.32), which resembles the true statistical operator \(\rho^{(3)}\) of Eq. (III.26). Therefore expression (III.57) is the form we look for. The solution to the isolated three-body collision is then written in terms of secondary channel states, Eq. (III.57) as

\[
[\rho^{(3)}]_{coll} = -2\Omega_{f1,f3,p13}p_{f1}p_{f2}p_{f3}p_{p13}p_{p12}p_{p13}p_{p14}p_{p12}p_{p13}p_{p14}p_{p12}.
\tag{III.60}
\]

Similarly the expression for \([\rho^{(4)}]_{coll}\) is

\[
[\rho^{(4)}]_{coll} = -2\Omega_{f1,f2,f3,f4}p_{f1}p_{f2}p_{f3}p_{f4}p_{p12}p_{p13}p_{p14}p_{p12}p_{p13}p_{p14}p_{p12}p_{p13}p_{p14}p_{p12}.
\tag{III.61}
\]

This form for \([\rho^{(n)}]_{coll}\) can be generalized to an arbitrary number of particles \(n\) by systematically introducing possible interacting pairs to the right side of Eq. (III.39) and subtracting appropriate terms involving \(\rho_{fs}\).
III-2.3 Kinetic Equations

In this section three coupled kinetic equations for the description of the time evolution of a reactive moderately dense gas are obtained. The first kinetic equation is for bound pair $p_{b12}$. As the bound pairs are treated as a distinct species in the gaseous system, a separate equation for the bound pairs is easily justified. The second kinetic equation is an equation for $p_{f1} + p_{c1}$. Statistically pair correlations describe the non-ideality and are responsible for the second virial coefficient at equilibrium. Dynamically two free particles may become correlated due to potential interactions and a correlated pair may be destroyed by a third particle as time progress. These are well described in two or more particle space. But there is no clear separation between a particle which is free and a particle which is correlated to another particle in a single particle space. For these reasons one does not look for separate equations for the free singlet but treats only the combination of the free singlet with the pair correlation contribution to the singlet. The last kinetic equation is for the pair correlations. In order to determine the pair correlations uniquely, either a functional relation or a separate equation for the pair correlations is needed. Since the pair correlations are treated on an equal footing with the bound pairs and free singlets, a separate equation for the pair correlations is appropriate.

This section is divided into four subsections. In the first subsection one specifies the set of kinetic processes which are important for the present description. Only a small set of kinetic processes are selected in order to make the presentation more lucid. In the subsequent three subsections the three kinetic equations are presented one after another.
Kinetic Processes

To simplify the presentation the treatment is restricted to consider at most three fragment collisions, therefore at most six particles. Since an interacting pair is produced from a genuine two-particle collision, thus only two-fragment collisions are to be considered if one of the collision partners is an interacting pair. The simultaneous presence of two interacting pairs, which is equivalent to a four-fragment collision, is not treated. The selected collision processes are thus

\[ M + M \leftrightarrow M + M \quad (III.62) \]
\[ M + M + M \leftrightarrow M + M + M \quad (III.63) \]
\[ M + M + M \leftrightarrow M + D \quad (III.64) \]
\[ M + D \leftrightarrow M + D \quad (III.65) \]
\[ M + D \leftrightarrow M + P \quad (III.66) \]
\[ M + P \leftrightarrow M + P \quad (III.67) \]
\[ M + M + D \leftrightarrow D + D \quad (III.68) \]
\[ D + D \leftrightarrow D + D \quad (III.69) \]
\[ P + D \leftrightarrow P + D \quad (III.70) \]
\[ P + D \leftrightarrow D + D \quad (III.71) \]
\[ M + D + D \leftrightarrow M + D + D \quad (III.72) \]

and

\[ D + D + D \leftrightarrow D + D + D, \quad (III.73) \]

where \( M \) stands for a monomer, \( D \) for a dimer and \( P \) for an interacting pair. In addition to being simple, the above selection has the physical justification that in a moderately dense gas with short range potential interactions,
the possibility of four and more fragment collisions are extremely low and consequently can be ignored.

With the above selection, the density operators appropriate for a collision process are explicitly as follows:

\[
[rho^{(2)}]_{coll} = \Omega_{f1,f1} \rho_{f1} \rho_{f2}, \quad (\text{III}.74)
\]

\[
[rho^{(3)}]_{coll} = -2\Omega_{f1,f1} \rho_{f1} \rho_{f2} \rho_{f3} + \Omega_{p12,f3} \rho_{p12} \rho_{f3} + \Omega_{p13,f2} \rho_{p13} \rho_{f2} + \Omega_{p23,f1} \rho_{p23} \rho_{f1} + \Omega_{b12,f3} \rho_{b12} \rho_{f3} + \Omega_{b13,f2} \rho_{b13} \rho_{f2} + \Omega_{b23,f1} \rho_{b23} \rho_{f1}, \quad (\text{III}.75)
\]

\[
[rho^{(4)}]_{coll} = \Omega_{b12,b34} \rho_{b12} \rho_{b34} + \Omega_{b13,b24} \rho_{b13} \rho_{b24} + \Omega_{b14,b23} \rho_{b14} \rho_{b23} + \Omega_{b12,b34} \rho_{b12} \rho_{b34} + \Omega_{b13,b24} \rho_{b13} \rho_{b24} + \Omega_{b14,b23} \rho_{b14} \rho_{b23} + \Omega_{p12,b34} \rho_{p12} \rho_{b34} + \Omega_{p13,b24} \rho_{p13} \rho_{b24} + \Omega_{p14,b23} \rho_{p14} \rho_{b23}, \quad (\text{III}.76)
\]

\[
 rho^{(5)}_{coll} = \Omega_{f1,b23,b45} \rho_{f1} \rho_{b23} \rho_{b45} + \Omega_{f1,b24,b35} \rho_{f1} \rho_{b24} \rho_{b35} + \Omega_{f1,b25,b34} \rho_{f1} \rho_{b25} \rho_{b34} + \Omega_{f2,b13,b45} \rho_{f2} \rho_{b13} \rho_{b45} + \Omega_{f2,b14,b35} \rho_{f2} \rho_{b14} \rho_{b35} + \Omega_{f2,b15,b34} \rho_{f2} \rho_{b15} \rho_{b34} + \Omega_{f3,b12,b45} \rho_{f3} \rho_{b12} \rho_{b45} + \Omega_{f3,b14,b25} \rho_{f3} \rho_{b14} \rho_{b25} + \Omega_{f3,b15,b24} \rho_{f3} \rho_{b15} \rho_{b24} + \Omega_{f4,b12,b35} \rho_{f4} \rho_{b12} \rho_{b35} + \Omega_{f4,b13,b25} \rho_{f4} \rho_{b13} \rho_{b25} + \Omega_{f4,b15,b23} \rho_{f4} \rho_{b15} \rho_{b23} + \Omega_{f5,b12,b34} \rho_{f5} \rho_{b12} \rho_{b34} + \Omega_{f5,b13,b24} \rho_{f5} \rho_{b13} \rho_{b24} + \Omega_{f5,b14,b23} \rho_{f5} \rho_{b14} \rho_{b23}, \quad (\text{III}.77)
\]

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The above set of expressions is written briefly as

\[ \rho^{(n)}_{\text{coll}} = \sum_{(\alpha, \beta, \gamma)} \Omega_{(\alpha, \beta, \gamma)} \prod_{i \in \alpha} \rho_i^{(1)} \prod_{(j, k) \in \beta} \rho_{jk} \prod_{(i, m) \in \gamma} \rho_{im} \]

\[ \equiv \Omega_{2_{\text{nd-asym}}}^{(n)} \left[ \rho^{(n)} \right]_{2_{\text{nd-asym}}} \]  

(III.79)

This is the desired form for the formulation of kinetic equations in terms of collisions.

\[ b) \text{ Kinetic Equation for Bound Pairs} \]

It was noted by Lowry and Snider that it is inappropriate to derive a kinetic equation for bound pairs in the molecular picture by closing the second BBGKY equation\textsuperscript{22,21} at the \( \rho^{(3)} \) term. A multispecies collision ansatz was used to close the kinetic equation. Such a method was used later by Klimontovich and coworkers\textsuperscript{57}. The BBGKY equations are derived using an atomic picture without the existence of different species. The whole set of BBGKY equations are considered to be equivalent to the Liouville equation, and thus
exact. However, the individual BBGKY equations (except for the last one) are not closed. As long as one is only interested in deriving kinetic equations for the low order clusters from a molecular picture, it is not necessary to use the BBGKY hierarchy. A rigorous argument for formulating kinetic equations in terms of two-Liouville space scattering theory was presented in Chapter Three of Part I. It is impossible to reproduce that argument here without employing the two-Liouville space notation and various related concepts. Here the basic form of kinetic equations of Part I is adopted for bound pairs and present the equations within the current simplified notation.

The kinetic equation for the bound pairs is

\[
\frac{i}{\hbar} \frac{\partial \rho_{b12}}{\partial t} = L_{12}^{(2)} \rho_{b12} + \sum_n \sum_{(\alpha, \beta, \gamma | b12)} \text{Tr}_{3, \ldots, n} Q_{(\alpha, \beta, \gamma | b12)}^{(n)} \psi_{(\alpha, \beta, \gamma | b12)}^{(n)} \left[ \rho^{(n)} \right]_{\text{coll}},
\]

(III.80)

where \((\alpha, \beta, \gamma | b12)\) denotes those secondary asymptotic channels that have bound pair \((b12)\) as a subchannel. The conditional channel potential superoperator \(\psi_{(\alpha, \beta, \gamma | b12)}^{(n)}\) is

\[
\psi_{(\alpha, \beta, \gamma | b12)}^{(n)} = L^{(n)} - L_{(\alpha, \beta, \gamma | b12)},
\]

(III.81)

with \(L_{(\alpha, \beta, \gamma | b12)}\) being the same as defined in Eq. (III.50) but restricted to the secondary asymptotic channel that has bound pair \((b12)\) as a subchannel. The conditional projection superoperator \(Q_{(\alpha, \beta, \gamma | b12)}^{(n)}\), as defined in Eq. (III.55), ensures that the states after the final operator state interaction \(\psi_{(\alpha, \beta, \gamma | b12)}^{(n)}\) will evolve into the designed secondary asymptotic channel \((\alpha, \beta, \gamma | b12)\).

Define a transition superoperator analogous to that of Lowry and Snider

\[
\psi_{(\alpha, \beta, \gamma | b12)}^{(n)} = \psi_{(\alpha, \beta, \gamma | b12)}^{(n)} \gamma_{2nd-asy}^{(n)}.
\]

(III.82)
With this transition superoperator Eq. (III.80) can then be written as

\[ i \frac{\partial \rho_{b12}}{\partial t} = \mathcal{L}_{12}^{(2)} \rho_{b12} + \sum_n \sum_{(\alpha, \beta, \gamma|\mathfrak{b}_{12})} \text{Tr}_{2,\cdots,n} Q_{(\alpha, \beta, \gamma|\mathfrak{b}_{12})}^{(n)} \mathcal{T}_{(\alpha, \beta, \gamma|\mathfrak{b}_{12})} \left[ \rho^{(n)} \right]_{2nd-asy}. \]  

(III.83)

This equation is in terms of secondary asymptotic channel states of Eq. (III.79) and describes the various kinetic processes of Eqs. (III.62-III.73).

\textbf{c) Kinetic Equation for the Renormalized Singlet}

In this subsection one looks for a kinetic equation for \( \rho_{f1} + \rho_{c1} \), the singlet density operator without the bound-pair part. This equation is the same as the density corrected (renormalized) quantum Boltzmann equation proposed by Snider\textsuperscript{52} for a binary collision approximation. From a dynamical point of view the separation into whether particle 1 is a free singlet state \( \rho_{f1} \) or part of a correlated state as \( \rho_{c1} \) is not clear because of the chain rule relation. Thus it is appropriate to keep \( \rho_{f1} \) and \( \rho_{c1} \) together. Using the same argument as in the last subsection, the form of the monomer equation of Part I is adopted and rewritten in the current simplified notation

\[ i \frac{\partial (\rho_{f1} + \rho_{c1})}{\partial t} = \mathcal{L}_{1}^{(1)} (\rho_{f1} + \rho_{c1}) + \sum_n \sum_{(\alpha, \beta, \gamma|f1/p1)} \text{Tr}_{2,\cdots,n} Q_{(\alpha, \beta, \gamma|f1/p1)}^{(n)} \mathcal{V}_{(\alpha, \beta, \gamma|f1/p1)}^{(n)} \left[ \rho_{\text{coll}}^{(n)} \right], \]  

(III.84)

where \( (\alpha, \beta, \gamma|f1/p1) \) denotes those secondary asymptotic channels that either contain particle 1 as a free singlet or in interaction with another particle. The projection superoperator \( Q_{(\alpha, \beta, \gamma|f1/p1)}^{(n)} \) selects out the appropriate channel states which are relevant to the time evolution of \( (\alpha, \beta, \gamma|f1/p1) \). In terms of a transition superoperator and the secondary asymptotic channel
states, Eq. (III.84) can be written as

\[ \frac{i \partial (\rho f_1 + \rho e_1)}{\partial t} = \mathcal{L}_1^{(1)} (\rho f_1 + \rho e_1) 
+ \sum_n \sum_{(\alpha, \beta, \gamma) (f_1/p_1)} \text{Tr}_{2, \ldots, n} Q^{(n)}_{(\alpha, \beta, \gamma) (f_1/p_1)} T^{(n)}_{(\alpha, \beta, \gamma) (f_1/p_1)} \left[ \rho^{(n)} \right]_{2n-asy} \quad (\text{III.85)} \]

This equation is analogous to the renormalized Boltzmann equation\textsuperscript{52}, but has one more aspect that it includes various three-fragment collisions and employs the secondary asymptotic channel concept. It will be called the generalized Boltzmann equation in this work.

**d) Kinetic Equation for Pair Correlations**

As has been noticed in Section III-2.2, pair correlations do not admit a direct scattering theory description, thus the equation for pair correlations is more complicated. From Eq. (III.25), the definition of the pair correlations

\[ \rho_{e12} = \rho_{12}^{(2)} - \rho_{12}^{(1)} - \rho_{12}^{(1)} \rho_{2}^{(1)} \]

it appears possible to "derive" the pair correlation equation through

\[ i \frac{\partial \rho_{e12}}{\partial t} = i \frac{\partial \left( \rho_{12}^{(2)} - \rho_{12}^{(1)} - \rho_{12}^{(1)} \rho_{2}^{(1)} \right)}{\partial t}. \quad (\text{III.86)} \]

There are two difficulties in carrying out such a procedure. The first difficulty is that it needs an equation for \( \rho^{(2)} \), which is an indefinite task from the collision theory point of view. The second difficulty, similar to a problem noted by Balescu\textsuperscript{198}, is that the quantities in Eq. (III.25) are not consistently normalized for an \( N \)-particle finite system because the relation between \( \rho^{(2)} \) and \( \rho^{(1)} \) implies

\[ \text{Tr}_{12} (\rho_{12} + \rho_{e12}) = -N. \quad (\text{III.87)} \]
This difficulty is due to the fact that Eq. (III.25) deals simultaneously with quantities of different orders in density. For this reason an alternate derivation of a pair correlation equation is needed. According to Eq. (III.58), one has

\[ i \frac{\partial \rho_{12}}{\partial t} = i \frac{\partial (\rho_{p12} - \rho_{f1} \rho_{f2})}{\partial t}. \]

(III.96)

An equation for interacting pairs is thus needed first and it can be easily written down in the same manner as that for the bound pair equation (III.80), using the multispecies scattering ansatz

\[ i \frac{\partial \rho_{p12}}{\partial t} = \mathcal{L}^{(2)}_{12} \rho_{p12} + \sum_{n} \sum_{(\alpha, \beta, \gamma | p12)} \text{Tr}_{3, \cdots, n} Q_{(\alpha, \beta, \gamma | p12)}^{(n)} \left( \mathcal{L}^{(n)} - \mathcal{L}_{(\alpha, \beta, \gamma | p12)}^{(n)} \right) \left[ \rho^{(n)} \right]_{\text{coll}} = \mathcal{L}^{(2)}_{12} \rho_{p12}. \]

* A consistent normalization can be found by using the Lowry-Snider counting as follows

\[ \rho_{\text{normed}}^{(n)} = \rho_{f1}^{(1)} \text{normed} + \rho_{p12}^{(1)} + \rho_{e12} - \frac{1}{M}\rho_{f1}\rho_{f1} - \frac{2}{D}\rho_{b1}\rho_{b1} - \frac{2}{C}\rho_{c1}\rho_{c1}. \]

(III.88)

where

\[ \rho_{f1}^{(1)} \text{normed} = \rho_{f1} + \rho_{b1} + \rho_{c1}. \]

(III.89)

All quantities in Eq. (III.88) and Eq. (III.89) are consistently normalized

\[ M = \text{Tr}_{i} \rho_{f1}, \]

(III.90)

\[ 2D = \text{Tr}_{i} \rho_{b1}^{(1)} = \text{Tr}_{ij} \rho_{bij}, \]

(III.91)

\[ 2C = \text{Tr}_{i} \rho_{c1}^{(1)} = \text{Tr}_{ij} \rho_{cij}, \]

(III.92)

\[ N = M + 2D + 2C, \]

(III.93)

\[ \rho_{\text{normed}}^{(n)} = \frac{N!}{(N-n)!} \text{Tr}_{n+1, \cdots, N} \rho^{(N)}, \]

(III.94)

and

\[ \text{Tr}_{1, \cdots, n} \rho_{\text{normed}}^{(n)} = N(N-1) \cdots (N-n+1). \]

(III.95)

A kinetic equation for pair correlations according to the exact relation of Eq. (III.88) is possible but appears very complicated to handle, and for a large system, the correlation terms are negligible.
where \((\alpha, \beta, \gamma | p12)\) denoted those secondary asymptotic channels that have interacting pair \((p12)\) as a subchannel.

The desired kinetic equation for pair correlations according to Eq. (III.96) is, in terms transition superoperators and secondary asymptotic channel states

\[
\frac{\partial \rho_{12}}{\partial t} = \mathcal{L}_{12}^{(2)} \rho_{c12} + \mathcal{V}_{12} \rho_{f1} \rho_{f2} + \sum_{n} \sum_{(\alpha, \beta, \gamma | p12)} \text{Tr}_{3, \ldots, n} Q_{(\alpha, \beta, \gamma | p12)}^{(n)} T_{(\alpha, \beta, \gamma | p12)}^{(n)} \left[ \rho^{(n)} \right]_{2nd-asym}.
\]

This equation describes the dynamics of pair correlations in terms of scattering processes involving the interacting pairs. The last three terms in Eq. (III.98) are written in transition superoperator form separately in order to keep track the origins of the different contributions. An attempt to merge the last three terms in Eq. (III.98) results in some ambiguity because there is no appropriate hamiltonian for a correlated pair, and moreover, in three- or more particle space the potential interactions appearing in the transition (super-) operators are not sufficient to uniquely discriminate between the various final states (see the discussion in Section III-2.4).

One important property of Eq. (III.98) is that the Ursell operator \(U_{12}^{(2)}\) is
an equilibrium solution of this equation

\[ \rho_{c12}^{eq} \propto e^{-\beta H_{12}^{(2)}} - e^{-\beta K_{12}^{(2)}}. \]  

(III.99)

III-2.4 Discussion

Three coupled kinetic equations, Eqs. (III.83), (III.85) and (III.98), are presented for the purpose of describing the time evolution of a reactive moderately dense gas system. The structure of a kinetic equation as proposed in Part I has been adopted for formulating the three equations without reproducing the detailed formalism because that requires a two-Liouville space scattering theory notation. The first equation is for bound pairs and is analogous to that of Lowry and Snider\textsuperscript{23}, but allows more collision processes and utilizes the secondary asymptotic concept. The second equation is for \( \rho_f + \rho_c \) and is called the generalized Boltzmann equation. Such an equation is analogous to the density corrected Boltzmann equation (renormalized Boltzmann equation) of Snider\textsuperscript{52} in the binary collision approximation. The last equation is for the pair correlations. One has managed to "derive" a pair-correlation equation involving quantum scattering theory with the help of introducing an interacting pair state. Such a method allows a dynamical description for the creation and decay of pair correlations in terms of few-body collisions. The Bogolubov\textsuperscript{21} treatment of a dense gas system requires a complete initial weakening of correlations. That treatment provides one particular boundary condition for solving the dense gas problem and demands successive collisions to generate their own correlations. In contrast, here one treats the free singlet, bound pairs and correlated pairs on an equal footing and does not require the complete weakening of correlations. In this manner a separate equation is needed to determine the (pair) correlations.
The scheme is clear in that, if other correlations are introduced, e.g. those between monomers and dimers, then an extra equation for these correlations will be also required.

The dimer number density $n_b$ is of order $n_2^2$ from an atomic picture point of view. This has led to perturbational treatments\textsuperscript{17,19} for the bound pairs. In such a treatment, the kinetic equation involving the collisional contribution of bound states is derived by closing the second BBGKY equation\textsuperscript{22,21} at the $\rho^{(3)}$ term. In contrast, the number densities $n_f$ and $n_b$ are of the same order from a molecular picture point of view, that follows from treating the bound pairs as a distinct species. From the molecular picture point of view the density operator $\rho^{(n)}$ involves subterms of different orders in the number density. Therefore it is inappropriate to derive kinetic equations by closing the BBGKY hierarchy at a particular level. The multispecies collision ansatz of Lowry and Snider\textsuperscript{23} is appropriate to account for the various dynamical processes. Kinetic equations for arbitrary clusters were rigorously derived in Part I by incorporating the multispecies collision ansatz within a two-Liouville space scattering theory. The structure of that set of kinetic equations is adopted in the present chapter without reproducing the detailed two-Liouville space scattering theory argument.

The existence of correlated pairs and bound pairs results in the full singlet density operator having a substructure [see Eq.(III.24)]. Such a substructure accounts for the density corrections to the equation of state at equilibrium. Therefore the full singlet density operator can be considered to be a renormalized singlet density operator. A kinetic equation for the full singlet density operator is a (density) renormalized Boltzmann equation. However, The renormalized Boltzmann equation cannot be closed and it necessarily couples to other kinetic equations, one for each kind of substructure except for the
free singlet. This set of kinetic equations provides a reasonable description to the reactive moderately dense gas system. A systematic generalization to higher order correlations is possible, through the introduction of more kinetic equations and keeping higher order collisions. Such a program will lead to higher order corrections to the equation of state and to transport coefficients. As indicated in Part II, since the grand partition function expansion of the equation of state is well-defined from the point of view of Faddeev's analysis, it suggests that the density expansion for transport coefficients may be well-defined. However even at the three-body collision level, the individual terms in a particular binary collision expansion can be divergent. Faddeev's analysis, or alternatively the BKLT method is indispensable for taking care of the detailed evaluation of higher order collisions.

The renormalized density operators are a concise statistical concept, but they complicate the dynamical description of a kinetic process. In a dynamical process such as the collision of two objects, it is necessary that the involved fragments are naked, that is, not correlated or bound to any other particle, because the dynamical processes involve isolated microscopic few-body quantum mechanics. In contrast, the renormalized statistical density operators give rise to macroscopic predictions with a free singlet dressed by correlated pairs and/or bound pairs. This apparent contradiction in statistical and dynamical descriptions is resolved by the systematic scheme of exorcizing ghosts [see Eq. (III.29)], a method introduced by Lowry and Snider. It is with this interplay between statistical macroscopic and dynamical microscopic descriptions that the introduced set of kinetic equations allows a derivation of the hydrodynamic equations and evaluation of macroscopic transport coefficients, such as the viscosity and thermal conductivity, from microscopic atomic and molecular properties for a reactive moderately dense
gas system (see the following chapters).

In kinetic theory the dynamical processes are usually formulated in terms of few-body quantum mechanics, specifically few-particle scattering theory. However the dynamics of pair correlations does not admit a direct time-dependent scattering theory description as indicated in Eqs. (III.34) and (III.35). To overcome this difficulty, the chain rule\textsuperscript{42,24} has been used to introduce the concepts of secondary asymptotic channels and interacting pairs. By identifying the relation between an interacting pair and a correlated pair in the pair particle space [see Eq.(III.58)], a scattering theory description of the dynamics of pair correlations is achieved. The secondary asymptotic channels, expressed in terms of a two-potential formalism, is a very powerful method for solving various difficult problems and has been widely used in quantum scattering theory\textsuperscript{197}, for example, multichannel coulomb potential scattering. The orthogonality and completeness of various secondary asymptotic channel states has been assumed.

It is noted that a transition superoperator $T^{(n)}$ for a bound pair channel, say (b12)\textsubscript{3}, may coincide with that for an interacting pair channel, say (p12)\textsubscript{3}. Such a lack of uniqueness reflects the fact that three- and more particle transition operators do not in general give rise to unique processes. Stated differently, the potential terms in a transition operator do not determine the final scattering states in a unique channel. A similar problem is that the homogeneous three-body Lippmann-Schwinger equation\textsuperscript{6} for bound states admits scattering state solutions. The Faddeev analysis is needed to split the various transition operator. For this reason, projection superoperators $Q^{(n)}$ (see the discussion in Section I-2.4) are used to ensure appropriate final states.

The set of kinetic processes are limited to at most three fragment colli-
sions. The interacting pairs, equivalently the correlated pair, are allowed to take part in a binary collision with another stable partner [see Eqs.(III.62-III.73)]. Four fragment collisions are neglected because they include three-body correlations as scattering subsystems, which are not retained in the present treatment. A systematic generalization to include higher order collisions is straightforward within the present scheme of description, but it seems to be inappropriate to pursue the generalization without simultaneously introducing higher order correlations. It is believed that the choice made in this thesis is appropriate for the kinetic theory of a reactive moderately dense gas system.


Chapter III-3

Macroscopic Properties

The purpose of this chapter is to study the macroscopic properties of the three kinetic equations "derived" in Chapter III-2. This is to aid in the understanding of a reactive moderately dense gas system and to provide the basis for obtaining a practical solution to the equations. Three coupled quantum kinetic equations were discussed in Section III-2.3, namely the generalized Boltzmann equation

\[
\frac{i}{\hbar} \frac{\partial (\rho f_1 + \rho c_1)}{\partial t} = \mathcal{L}_1^{(1)} (\rho f_1 + \rho c_1) + \sum_n \sum_{(\alpha, \beta, \gamma) f_1/p_1} \text{Tr}_2 \cdots n Q^{(n)}_{(\alpha, \beta, \gamma) f_1/p_1} T^{(n)}_{(\alpha, \beta, \gamma) f_1/p_1} [\rho^{(n)}]_{2nd-asy},
\]

(III.100)

the bound pair equation

\[
\frac{i}{\hbar} \frac{\partial \rho_{b12}}{\partial t} = \mathcal{L}_2^{(2)} \rho_{b12} + \sum_n \sum_{(\alpha, \beta, \gamma) b12} \text{Tr}_3 \cdots n Q^{(n)}_{(\alpha, \beta, \gamma) b12} T^{(n)}_{(\alpha, \beta, \gamma) b12} [\rho^{(n)}]_{2nd-asy},
\]

(III.101)

and the equation for the pair correlations

\[
\frac{i}{\hbar} \frac{\partial \rho_{c12}}{\partial t} = \mathcal{L}_2^{(2)} \rho_{c12} + \mathcal{V}_{12} \rho_{f1} \rho_{f2} + \sum_n \sum_{(\alpha, \beta, \gamma) p12} \text{Tr}_3 \cdots n Q^{(n)}_{(\alpha, \beta, \gamma) p12} T^{(n)}_{(\alpha, \beta, \gamma) p12} [\rho^{(n)}]_{2nd-asy} \rho_{f1} \rho_{f2}
\]

(III.102)
(see Section III-2.3 for explanations of the notation). The central quantities are the free singlet density operator $\rho_{f1}$, the pair correlation operator $\rho_{c12}$ and the bound pair density operator $\rho_{b12}$. These are to be used to give expectation values for the macroscopic physical observables, such as mass, velocity and energy for the gas mixture as a whole. The time evolution of the three operators, equivalently the macroscopic physical observables, depend on the microscopic dynamical processes, such as free motion and collisions. The collision processes involve few-body quantum scattering theory and have been discussed in detail while formulating the kinetic equations in Chapter III.2. In contrast, it is the connection with macroscopic properties that is to be elaborated in this chapter.

The objective is to solve the three kinetic equations within the philosophy of the Chapman-Enskog\textsuperscript{131,16,133,132} method, by treating the free, bound and pair correlation as a multicomponent gas mixture. In such a method, what is first required is a perturbation expansion of the density operator about local thermodynamic equilibrium, the latter being characterized by the three local variables, number density $n(r,t)$, stream velocity $v_0(r,t)$ and temperature $T(r,t)$. In the Chapman-Enskog method the perturbations are considered to be functionals of the three local variables with their time dependence determined through the time dependence of the three local variables. This philosophy of solving the kinetic equations is implemented in this and the following chapter to solve the three kinetic equations for the non-ideal gas mixture.

While solving the three kinetic equations using the Chapman-Enskog procedure it is necessary to simultaneously keep track of both the position and momentum dependences of the various density operators. The phase space representation\textsuperscript{199,200}, in particular the Wigner function\textsuperscript{192} is very convenient
for this purpose. In the Wigner form the center of mass motion of a molecule
is expressed in terms of position and momentum variables, while the rela-
tive motion or internal states of a molecule remains expressed in operator
form. In terms of the Wigner functions, the local equilibria are assumed to
be Maxwellian for the velocity distribution and of Boltzmann distribution
form for the relative motion operators. The non-equilibrium effects, in par-
ticular the perturbations, are assumed to be linear in the various gradients
associated with the gas' inhomogeneity. This presents the Wigner functions
in a form appropriate for solving the three kinetic equations, see Chapter
III-4.

This chapter is divided into six sections. The equations of change for the
number densities, stream velocities and energy densities for each of the three
kinetic equations are derived in Section III-3.1 by using operator methods.
The derivation is restricted to non-reactive collisions, as is the remainder of
this thesis, in order to simplify the presentation, specifically, to eliminate
various number density productions which could couple with the equations
of motion, and energy. The further simplification of the kinetic equations
(III.100), (III.101) and (III.102) are presented in Section III-3.2. In particu-
lar, the main concern here is whether the new scheme for solving the coupled
equations works and provides well behaved transport coefficients, rather than
higher order collision corrections. The Wignerization of the density operators
and the phase space representation of the non-reactive binary collision terms
are given in Section III-3.3 and their local equilibrium forms discussed in Sec-
tion III-3.4. In particular, the pair correlation operator $f_{c12}$ requires special
care since it contributes to both the pair correlation equation and the gen-
eralized Boltzmann equation. The description required in the two cases are
very different. Specifically, in the pair correlation equation a molecular pic-
ture for the pair correlation operator is required, whereas in the generalized Boltzmann equation, an atomic description is necessary. The difference between the two descriptions gives rise to delocalization effects\textsuperscript{201}, which are to first order, linear in the gradients. Macroscopic variables for the gas mixture as a whole are discussed in Section III-3.5, which does not simply reproduce the results of Section III-3.1. There are a couple of new aspects. Firstly, in Section III-3.1 the equations of change are derived from the individual kinetic equations with different sets of parameters, such as $n_i$ and $v_i$. The influence of one species on another in the hydrodynamic equations occurs through collisional coupling. Such a treatment of the gas mixture is not appropriate for using the Chapman-Enskog method of solving kinetic equations due to the presence of local inhomogeneities, whereas the description in Section III-3.5 provides a unified picture for a fluid of free, pair correlation and bound pair particles. Secondly, the separation between the local and non-local, equilibrium and non-equilibrium, homogenous and inhomogeneous contributions to macroscopic variables is achieved in Wigner representation through gradient expansions. The difference between local hydrodynamic variables $n_i$, $v_i$ and $T_i$ (where $i$ stands for $f$, $c$ and $b$) is associated with the inhomogeneity of the gas mixture and causes transport of mass, momentum and energy. It is noted that for the convenience of solving the kinetic equations, the density operator $\rho_b$ for the bound pairs is normalized to the number density $n_b$ of bound pairs in this and the next chapter, whereas in Chapter III-2, it was normalized to the number density $n_b$ of bound particles. A general discussion is given in Section III-3.6.
III-3.1 Equations of Change

In this section general expressions are obtained for the equations of change. The equations of change are important not only because they govern the time dependences of the macroscopic quantities but also because they are needed for solving kinetic equations in the Chapman Enskog method\textsuperscript{131}. The equations of change for each of the kinetic equations (III.100), (III.101) and (III.102) are derived in this section. In case there are no bound pairs, the generalized Boltzmann equation (III.100), at the binary collision approximation, reduces to the renormalized Boltzmann equation of Snider\textsuperscript{52}

\[
 i \frac{\partial (\rho_{f1} + \rho_{c1})}{\partial t} = L_1^{(1)}(\rho_{f1} + \rho_{c1}) + \text{Tr}_2 V_{12} \Omega_{12} \rho_{f1} \rho_{f2} \Omega_{12}^\dagger. \tag{III.103}
\]

The detailed solution of the renormalized Boltzmann equation (III.103), and of a modified pair correlation equation [see Eq. (III.161)] is pursued before solving the three coupled equations. Such a solution is useful for exploring the methodologies and technicalities required for solving the three equations. For this reason the equations of change for the renormalized Boltzmann equation (III.103) and the various related hydrodynamic variables\textsuperscript{52}, are reviewed in the second subsection.

a) Equations of Change for the Generalized Boltzmann Equation

A single-particle observable for particle 1 is denoted by $\psi_1$. The expectation value of physical observable $\psi_1$ is determined by the renormalized singlet density operator

\[
 \rho_1 = \rho_{f1} + \rho_{c1} \tag{III.104}
\]
according to
\( \langle \psi_1 \rangle_1 = \langle \psi_1 \rangle_f + \langle \psi_1 \rangle_c. \)  \hspace{1cm} (III.105)

Here \( \langle \psi_1 \rangle_f \) is defined as
\( \langle \psi_1 \rangle_f = \text{Tr}_1 \psi_1 \rho_f \) \hspace{1cm} (III.106)

and \( \langle \psi_1 \rangle_c \) is
\( \langle \psi_1 \rangle_c = \text{Tr}_1 \psi_1 \rho_c. \) \hspace{1cm} (III.107)

The most important physical observables are the number density \( n_1 \), stream velocity \( \mathbf{v}_1 \) and kinetic energy \( \varepsilon^K_1 \) which are discussed as follows. Firstly, the physical observable for the number density \( n_1 \) for the free and correlated particles is the Dirac delta function \( \psi_1 = \delta_1 = \delta(\mathbf{r} - \mathbf{r}_1) \) (see Section III-2.1), so that
\[ n_1 = \langle \delta_1 \rangle_f + \langle \delta_1 \rangle_c. \] \hspace{1cm} (III.108)

Secondly, the stream velocity \( \mathbf{v}_1 \) is given by
\[ \mathbf{v}_1 \equiv \frac{1}{n_1} \text{Tr}_1 \left[ \frac{1}{2m_1} (\mathbf{p}_1 \delta_1 + \delta_1 \mathbf{p}_1) \rho_1. \right. \] \hspace{1cm} (III.109)

Finally, the kinetic energy per particle is given by
\[ \varepsilon^K_1 \equiv \frac{1}{n_1} \text{Tr}_1 \left[ \frac{1}{8m_1} (\mathbf{p}_1^2 \delta_1 + 2 \mathbf{p}_1 \cdot \delta_1 \mathbf{p}_1 + \delta_1 \mathbf{p}_1^2) - \frac{1}{2} m_1 \mathbf{v}_1^2 \delta_1 \right] \rho_1. \] \hspace{1cm} (III.110)

Equations of change for a particle observable is obtained from the generalized Boltzmann equation (III.100) according to
\[ \frac{\partial \langle \psi_1 \rangle_1}{\partial t} = \frac{\partial \langle \psi_1 \rangle_1}{\partial t} = \frac{1}{i\hbar} ([\psi_1, H^{(1)}],_1 \] \[ + \frac{1}{n} \sum \sum \text{Tr}_{1,...,n} \psi_1 Q^{(n)}_{(\alpha,\beta,\gamma)(f1/p1)} T(\alpha,\beta,\gamma)(f1/p1) \left[ \rho^{(n)} \right]_{2nd-asy}. \] \hspace{1cm} (III.111)
In case physical observable $\psi_1$ is time independent, the second term on the left hand side of Eq. (III.111) vanishes. While this operator approach is used here to derive equations of change for the number density $n_1$, stream velocity $v_1$ and kinetic energy $\varepsilon^K_1$, in later sections it will be more appropriate to use the (equivalent) phase space expressions for the various fluid dynamic quantities. These are developed in Section III-3.5. The equations of change are of course independent of the detailed method of how the various quantities are to be expressed. The equation of continuity is

$$\frac{\partial n_1}{\partial t} = -\nabla \cdot (n_1 v_1) + \sigma_{n_1} \tag{III.112}$$

$$= -\nabla \cdot (n_f v_f + n_c v_c) + \sigma_{n_1} \tag{III.113}$$

where the second equality is understandable from Eq. (III.105), and the number density production $\sigma_{n_1}$ from reactive collisions is

$$\sigma_{n_1} = \frac{1}{i} \sum_n \sum_{(\alpha, \beta, \gamma|1/p_1)} \text{Tr}_{1\cdots n} \delta_1 \mathcal{O}^{(n)}_{(\alpha, \beta, \gamma|1/p_1)} \mathcal{T}_{(\alpha, \beta, \gamma|1/p_1)} \left[ \rho^{(n)} \right]_{2nd\text{-asy}}. \tag{III.114}$$

In the absence of reactive collisions, the number density $n_1$ is the density of a conserved quantity and the number density production vanishes ($\sigma_{n_1} = 0$). For simplicity, only non-reactive collisions are considered from now on.

The equation of motion is

$$n_1 m_1 \frac{\partial v_1}{\partial t} + n_1 m_1 v_1 \cdot \nabla v_1 + \nabla \cdot \mathbf{P}_1^K = \frac{1}{i\hbar} \sum_n \sum_{(\alpha, \beta|1/p_1)} \text{Tr}_{1\cdots n} \frac{1}{2} \left[ (p_1 \delta_1 + \delta_1 p_1), V_{(\alpha, \beta|1/p_1)} \right] - \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd\text{-asy}} \tag{III.115}$$

where $m_1$ is the mass of a single particle and $\mathbf{P}_1^K$ is the kinetic pressure tensor defined as

$$\mathbf{P}_1^K = \frac{1}{4 m_1} (\delta_1 p_1 + p_1 \delta_1 p_1 + (p_1 \delta_1 p_1)^\dagger + p_1 p_1 \delta_1) - n_1 m_1 v_1 v_1. \tag{III.116}$$

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The projection superoperator $Q_{(\alpha, \beta, \gamma, f_1/p_1)}^{(n)}$ is no longer needed for non-reactive collisions, but a superscript $nr$ on the pre-collision density operators is needed to indicate that only non-reactive secondary asymptotic channels are to be considered.

The kinetic energy equation of change, considering only non-reactive collisions, is

$$\frac{\partial n_1 \varepsilon_1^K}{\partial t} = -\nabla \cdot (n_1 v_1 \varepsilon_1^K + q_1^K) - P_1^K : \nabla v_1$$

$$+ \frac{1}{i\hbar} \sum \sum_{(\alpha, \beta, \gamma, f_1/p_1)} \text{Tr}_{1,,,n} \left[ \left( \frac{1}{8m_1} (p_1^2 \delta_1 + 2p_1 \cdot \delta_1 p_1 + \delta_1 p_1^2 - \frac{1}{2} (m_1 v_1^2 \delta_1 - v_1 \cdot p_1 \delta_1 - v_1 \cdot \delta_1 p_1) \right), V_{(\alpha, \beta, \gamma, f_1/p_1)} \right]$$

$$Q^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy}^{nr},$$

where the kinetic heat flux is

$$q_1^K = \text{Tr}_1 \left\{ \left( \frac{p_1}{m_1} - v_1 \right) \left( \frac{p_1 - m_1 v_1}{2m_1} \right)^2 \delta_1 \right\} \rho_1.$$

Here $\{ \}$ designates appropriately operator-symmetrized quantities. The rate of change of kinetic energy has contributions from three types of non-reactive collisions, and energy conservation is quite complicated at this stage. A detailed discussion of this matter is given in Section III-3.5 for the case of non-reactive binary collisions. The energy equation simplifies further if the generalized Boltzmann equation is restricted to the renormalized Boltzmann equation by ignoring the presence of bound pairs and considering only binary collisions.
b) Equations of Change for the Renormalized Boltzmann Equation

The renormalized Boltzmann equation\(^{52}\) (III.103) serves not just simply as a limiting case of the generalized Boltzmann equation (III.100), instead it represents a different kinetic system (see Section III-3.5). Its solution is presented in Section III-4.2, which provides most of the technicalities and methodologies needed for solving the three coupled kinetic equations (see Section III-4.4). The equations of change for the renormalized Boltzmann equation have been discussed in Ref. (52) and are summarized for convenience as follows: the equation of continuity

\[
\frac{\partial n_1}{\partial t} = -\nabla \cdot (n_1 \mathbf{v}_1); \tag{III.119}
\]

the equation of motion

\[
n_1 m_1 \frac{\partial \mathbf{v}_1}{\partial t} + n_1 m_1 \mathbf{v}_1 \cdot \nabla \mathbf{v}_1 = -\nabla \cdot \mathbf{P}_1, \tag{III.120}
\]

and the kinetic energy equation

\[
\frac{\partial n_1 \varepsilon_1^K}{\partial t} = -\nabla \cdot (n_1 \mathbf{v}_1 \varepsilon_1^K + \mathbf{q}_1^K + \mathbf{q}_{\text{coll}}) - \mathbf{P}_1 : \nabla \mathbf{v}_1 + \sigma^K, \tag{III.121}
\]

where the collisional heat flux is

\[
\mathbf{q}_{\text{coll}} = -\frac{1}{8m_1 \text{Tr}_{12}} \int_1 \nu \left\{ \delta \left[ \mathbf{r} \cdot \frac{\mathbf{r}_1 + \mathbf{r}_2}{2} - \frac{\nu}{2} (\mathbf{r}_1 - \mathbf{r}_2) \right] \right. \\
\times \left. (\mathbf{p}_1 + \mathbf{p}_2 - 2m_1 \mathbf{v}_1) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} \right\}_s \Omega^{(2)} \left[ \rho^{(2)} \right]_{asy} \tag{III.122}
\]

and the kinetic energy production results from the collisional transfer of energy

\[
\sigma^K = -\frac{1}{8m_1 \text{Tr}_{12}} \left\{ (\delta_1 + \delta_2)(\mathbf{p}_1 - \mathbf{p}_2) \cdot \frac{\partial V_{12}}{\partial \mathbf{r}_1} \\
+ \frac{\partial V_{12}}{\partial \mathbf{r}_1} : (\mathbf{p}_1 - \mathbf{p}_2) \right\}_s \Omega^{(2)} \left[ \rho^{(2)} \right]_{asy}. \tag{III.123}
\]
The pressure tensor $P_1 = P^K_1 + P_{\text{coll}}$ has a collisional contribution $P_{\text{coll}}$

$$P_{\text{coll}} = -\frac{1}{4} \text{Tr}_{12}(r_1 - r_2) \nabla_1 V_{12}$$

$$\times \int_{-1}^{1} \delta \left( \frac{r_1 + r_2}{2} + \frac{V}{2} (r_1 - r_2) - r \right) d\nu \Omega^{(2)} \left[ \rho^{(2)} \right]_{asy}. \quad (III.124)$$

The transpose $P^t_1$ of the pressure tensor $P_1$ enters to couple the convective energy to the "internal" kinetic energy per particle $\varepsilon^K_1$, heat flux contributions arise from "kinetic" $q^K_1$ and "collisional" $q_{\text{coll}}$ motion and finally there is a "production" term $\sigma^K$ which involves the transfer between kinetic and potential energy. While the equations of continuity and motion are consistent with the conservation of the number of particles and total momentum in the absence of bound pairs, the presence of the production term in the kinetic energy implies that the total kinetic energy is not conserved because of the possible conversion to potential energy due to the non-locality of the collisions. Thus it is necessary to look at the equation of change for the potential energy per particle $\varepsilon^V_1$

$$n_1 \varepsilon^V_1 = \frac{1}{4} \text{Tr}_{12} (\delta_1 + \delta_2) V_{12} \rho^{(2)}_{12}. \quad (III.125)$$

In Ref. (52) this was obtained in a manner consistent with pair particle interactions and shown to be of the form

$$\frac{\partial n_1 \varepsilon^V_1}{\partial t} = -\nabla \cdot (n_1 v_1 \varepsilon^V_1 + q^V_1) - \sigma^K, \quad (III.126)$$

where

$$q^V_1 = \frac{1}{4m_1} \text{Tr}_{12} [(p_1 - m_1 v_1) \delta_1 + \delta_1 (p_1 - m_1 v_1)] V_{12} \Omega^{(2)} \rho^{(2)}_{12}. \quad (III.127)$$

The productions of potential and kinetic energy exactly cancel and there is the added heat flux contribution $q^V_1$ associated with conductive potential.
energy flow. Obviously equations (III.119), (III.120) and (III.121) are special cases of Eqs. (III.112), (III.115) and (III.117) respectively.

c) Equations of Change for the Bound Pairs

The density operator $\rho_b$ contains information associated with both the center of mass and relative motion of the bound pair. In general a bound pair observable is denoted as $\psi_b$, and has the average value

$$\langle \psi_b \rangle_b = \text{Tr}_{12} \psi_{b12} \rho_{b12}$$  \hspace{1cm} (III.128)

The number density $n_b$ and stream velocity $v_b$ are associated with the center of mass position of the bound pair only and defined as follows:

$$n_b = \langle \delta_b \rangle_b$$  \hspace{1cm} (III.129)

and

$$v_b \equiv \frac{1}{n_b} \text{Tr}_b \frac{1}{2m_b} (p_b \delta_b + \delta_b p_b) \rho_b.$$  \hspace{1cm} (III.130)

Here the Dirac delta function

$$\delta_b = \delta(b - R)$$  \hspace{1cm} (III.131)

places the center of mass position $R$ of the bound pair at the macroscopic position $r$. $p_b$ is the center of mass momentum of the bound pair, and $m_b$ is the bound pair mass. The kinetic energy per molecule $\epsilon^K_b$ of the bound pairs is defined as

$$\epsilon^K_b \equiv \frac{1}{n_b} \text{Tr}_{12} \left[ \frac{1}{8m_b} (p_b^2 \delta_b + 2p_b \cdot \delta_b p_b + \delta_b p_b^2) \right. \right.$$  

$$

\left. - \frac{1}{2} m_b v_b^2 \delta_b + H_{\text{int}} \delta_b \right] \rho_b, \hspace{1cm} (III.132)

$$

where $H_{\text{int}}$ is the internal state hamiltonian of a bound pair.
For simplicity, only non-reactive collisions are considered here, thus the equation of change for the bound pairs is

\[
\frac{\partial (\psi_{b12})}{\partial t} - \left( \frac{\partial \psi_{b12}}{\partial t} \right)_b = \frac{1}{i \hbar} \{ [\psi_b, H_{12}^{(2)}] \}_b \\
+ \frac{1}{i \hbar} \sum_n \sum_{(\alpha, \beta, \gamma; b12)} \text{Tr}_{1, \ldots, n} \left[ \psi_{b12}, V_{(\alpha, \beta, \gamma; b12)} \right] - \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy}^{nr}.
\]

(III.133)

The equation of continuity is given by

\[
\frac{\partial n_b}{\partial t} = -\nabla \cdot (n_b \mathbf{v}_b),
\]

which is of conservative form since the collisions are non-reactive.

The equation of motion is

\[
n_b m_b \frac{\partial \mathbf{v}_b}{\partial t} + n_b m_b \mathbf{v}_b \cdot \nabla \mathbf{v}_b + \nabla \cdot \mathbf{P}_b^K = \frac{1}{i \hbar} \sum_n \sum_{(\alpha, \beta, \gamma; b12)} \text{Tr}_{1, \ldots, n} \left[ (p_b \delta_b + \delta_b p_b), V_{(\alpha, \beta, \gamma; b12)} \right] - \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy}^{nr}
\]

(III.135)

where \( \mathbf{P}_b^K \) is the pressure tensor

\[
\mathbf{P}_b^K = \frac{1}{4m_b} (\delta_b \mathbf{p}_b \mathbf{p}_1 + \mathbf{p}_b \delta_b \mathbf{p}_b + (\mathbf{p}_b \delta_b \mathbf{p}_b)^t + \mathbf{p}_b \mathbf{p}_b \delta_b)_{b} - n_b m_b \mathbf{v}_b \mathbf{v}_b.
\]

(III.136)

The total momentum of the bound pairs in the gas mixture is not conserved due to possible monomer-dimer collisions.

The kinetic energy equation of change is

\[
\frac{\partial n_b \varepsilon_b^K}{\partial t} = -\nabla \cdot (n_b \mathbf{v}_b \varepsilon_b^K + q^K) - \mathbf{P}_b^K : \nabla \mathbf{v}_b \\
+ \frac{1}{i \hbar} \sum_n \sum_{(\alpha, \beta, \gamma; b12)} \text{Tr}_{1, \ldots, n} \left[ \left( \frac{1}{8m_b} (p_b^2 \delta_b + 2 \mathbf{p}_b \cdot \delta_b \mathbf{p}_b + \delta_b \mathbf{p}_b^2) \\
- \frac{1}{2} (m_b \mathbf{v}_b^2 \delta_b - \mathbf{v}_b \cdot \mathbf{p}_b \delta_b - \mathbf{v}_b \cdot \delta_b \mathbf{p}_b) + H_{\text{int}} \delta_b \right), V_{(\alpha, \beta, \gamma; b12)} \right] - \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy}^{nr}
\]

(III.137)
where the kinetic heat flux is

\[ q^K_b = \text{Tr}_b \left\{ \left( \frac{p_b}{m_b} - v_b \right) \left[ \frac{(p_b - m_b v_b)^2}{2m_b} \delta_b + H_{\text{int}} \delta_b \right] \right\} \rho_b. \quad (III.138) \]

The bound pair kinetic energy is not conserved due to various collisional energy transfer mechanisms, such as the conversion between kinetic and potential energies, between monomer and bound pair kinetic energies and between pair correlation and bound pair energies. Details of the energy balance are discussed in Sections III-3.5.

d) Equations of Change for the Pair Correlations

To talk about an equation for the pair correlations inherently means that the pair correlations are treated on an equal footing with the two other species. This molecular picture treatment suggests that the combined mass \( m_c \) of the two correlated particles is appropriately placed at the center of mass position \( \mathbf{R} \) and the relative motion (labelled as \( \text{rel} \)) of the two correlated particles is viewed as the internal motion of the "molecule". In general a physical observable for a pair correlation is denoted as \( \psi_c \), and the expectation value of \( \psi_c \) is

\[ \langle \psi_c \rangle_c = \text{Tr}_{12} \psi_{c12} \rho_{c12} \quad (III.139) \]

The number density \( n_c \) and stream velocity \( \mathbf{v}_c \) of the pair correlations are, as macroscopic quantities, associated with the center of mass position \( \mathbf{R} \) and given in terms of the delta function \( \delta_c = \delta(\mathbf{r} - \mathbf{R}) \)

\[ n_c = \langle \delta_c \rangle_c \quad (III.140) \]

and

\[ \mathbf{v}_c = \frac{1}{n_c} \text{Tr}_c \frac{1}{2m_c} (\mathbf{p}_c \delta_c + \delta_c \mathbf{p}_c) \rho_c, \quad (III.141) \]

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where \( \mathbf{p}_c \) is the center of mass momentum of the pair correlation. The correlation energy for the pair correlation \( \varepsilon_{\text{corr}} \) is

\[
\varepsilon_{\text{corr}} = \frac{1}{n_c} \text{Tr}_c \left( \frac{1}{8m_c} (\mathbf{p}_c^2 \delta_c + 2\mathbf{p}_c \cdot \delta_c \mathbf{p}_c + \delta_c \mathbf{p}_c^2) - \frac{1}{2} m_c v_c^2 \delta_c + H_{\text{rel}} \delta_c \right) \rho_c,
\]

where \( H_{\text{rel}} \) is the relative energy operator of the pair correlation.

\[
H_{\text{rel}} = \frac{\mathbf{p}_{\text{op}}}{m_1} + V,
\]

with \( \mathbf{p}_{\text{op}} \) being the relative momentum operator of the pair of particles and \( V = V_{12} \) being the pair particle interaction potential. The general equation of change according to Eq. (III.102) for pair correlations is

\[
\frac{\partial \langle \psi_{c12} \rangle_c}{\partial t} - \langle \frac{\partial \psi_{c12}}{\partial t} \rangle_c = \frac{1}{i\hbar} \left( [\psi_{c12}, H_{12}^{(2)}] - \right)_{c}
\]

\[
+ \frac{1}{i\hbar} \text{Tr}_{12}[\psi_{c12}, V_{12}] - \rho_{f1} \rho_{f2}
\]

\[
+ \frac{1}{i\hbar} \sum_n \sum_{(\alpha, \beta, \gamma | p_{12}} \text{Tr}_{1, \ldots, n}[\psi_{c12}, V_{(\alpha, \beta, \gamma | p_{12})}] - \Omega^{(n)} \left[ \rho^{(n)} \right]^{nr}_{2nd-asy}
\]

\[
\cdot \sum_{(\alpha, \beta, \gamma | p_{12}} \text{Tr}_{1, \ldots, n}[\psi_{c12}, V_{(\alpha, \beta, \gamma | p_{12})}] - \Omega^{(n)} \left[ \rho^{(n)} \right]^{nr}_{2nd-asy} \rho_{f2}
\]

\[
\cdot \sum_{(\alpha, \beta, \gamma | p_{12}} \text{Tr}_{1, \ldots, n}[\psi_{c12}, V_{(\alpha, \beta, \gamma | p_{12})}] - \Omega^{(n)} \left[ \rho^{(n)} \right]^{nr}_{2nd-asy} \rho_{f1}, (III.144)
\]

where the second term on the left-hand-side of Eq. (III.144) vanishes for time independent observables as does the second term on the right-hand-side for observables that are independent of the relative motion. The last two collision terms involve essentially four fragments from the atomic picture point of view. Due to the present restriction to non-reactive collisions, these are, thus dropped from further consideration. The first collision term with the restriction to non-reactive collisions involves three initial fragments.
The equation of continuity is

\[ \frac{\partial n_c}{\partial t} = -\nabla \cdot (n_c v_c), \quad (III.145) \]

where the number density for the pair correlations is a collisional invariant for truly non-reactive collisions. However, such a restriction is not very reasonable for pair correlations. A different treatment for the pair correlation is introduced in Section III-3.2 (see also Section III-4.2). The equation of motion is

\[ n_c m_c \frac{\partial v_c}{\partial t} + n_c m_c v_c \cdot \nabla v_c + \nabla \cdot P^K_c = \frac{1}{i\hbar} \sum_n \sum_{(\alpha,\beta,\gamma|p12)} \text{Tr}_{1,\ldots,n} \left[ (p_c \delta_c + \delta_c p_c), V_{(\alpha,\beta,\gamma|p12)} \right] \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy}, \quad (III.146) \]

where \( P^K_c \) is the pressure tensor defined as

\[ P^K_c \equiv \frac{1}{4m_c} \langle \delta_c p_c p_1 + p_c \delta_c p_c + (p_c \delta_c p_c)^t + p_c p_c \delta_c \rangle_c - n_c m_c v_c v_c. \quad (III.147) \]

The collision term in Eq. (III.146) involves interacting pairs. The correlation energy equation is

\[ \frac{\partial n_c \varepsilon_{corr}}{\partial t} = -\nabla \cdot (n_c v_c \varepsilon_{corr} + q^K_c) - P^K_c \cdot \nabla v_c \]

\[ + \frac{1}{i\hbar} \text{Tr}_{12}[H_{rel} \delta_c, V_{12}] - \rho_{f1} \rho_{f2} \]

\[ + \frac{1}{i\hbar} \sum_n \sum_{(\alpha,\beta,\gamma|p12)} \text{Tr}_{1,\ldots,n} \left[ \left( \frac{1}{8m_c} (p_c^2 \delta_c + 2p_c \cdot \delta_c p_c + \delta_c p_c) \right) \right] \]

\[ + H_{rel} \delta_c - \frac{1}{2} (m_c v_c^2 \delta_c - v_c \cdot p_c \delta_c - v_c \cdot \delta_c p_c) \right), V_{(\alpha,\beta,\gamma|p12)} \right] \]

\[ \times \Omega^{(n)} \left[ \rho^{(n)} \right]_{2nd-asy} \quad (III.148) \]

where the pair correlation heat flux is

\[ q^K_c = \text{Tr}_{12} \left\{ \left( \frac{p_c}{m_c} - v_c \right) \left[ \frac{(p_c - m_c v_c)^2}{2m_c} \delta_c + H_{rel} \delta_c \right] \right\} \rho_{c12}. \quad (III.149) \]
Upon restricting the treatment to non-reactive collisions, only those secondary asymptotic channels that contain the interacting pair as a subchannel are considered, thus the collision term in Eq. (III.148) essentially involves three fragments. An attempt to classify various collisional energy transfers is possible but not physically meaningful because the present non-reactive collision constraint is not physically reasonable for the pair correlations. It is due to the fact that the neglected reactive two fragment collisions might occur with a higher probability than do the non-reactive collisions involving an interacting pair. This problem is resolved in the next section by introducing a modified equation for the pair correlations and the associated equations of change are discussed in Section III-4.2.

### III-3.2 Binary Collision Approximation

A full solution to the coupled quantum kinetic equations (III.100), (III.101) and (III.102), including all collision processes prescribed in Section III-2.3, is not feasible at present since it involves reactive collisions and three fragment collisions. The equations of change for such a system are very lengthy [see for example Ref. (58)], thus their solution and transport processes are very cumbersome to describe. The primary interest is to explore the properties of the coupled kinetic equations for *moderately dense* systems. To this end the treatment is restricted to only the most important collision processes, which in kinetic theory are the non-reactive binary collisions:

\[
M + M \leftrightarrow M + M, \quad (III.150)
\]
\[
M + D \leftrightarrow M + D, \quad (III.151)
\]

and

\[
D + D \leftrightarrow D + D. \quad (III.152)
\]
In the non-reactive binary collision approximation, the generalized Boltzmann equation (III.100) simplifies to

\[ i \frac{\partial (\rho_{f1} + \rho_{c1})}{\partial t} = \mathcal{L}_1^{(1)} (\rho_{f1} + \rho_{c1}) + \sum_i \text{Tr}_i T^{(1,i)} \rho_{f1} \rho_i \]

\[ \equiv \mathcal{L}_1^{(1)} (\rho_{f1} + \rho_{c1}) + \sum_i \text{Tr}_i \mathcal{V}_{1,i} \Omega_{1,i} \rho_{f1} \rho_i, \quad (\text{III.153}) \]

where \( i = 1, b \) denotes the other collision partner, which is either a monomer labelled as 1 or a bound-pair labelled as \( b \). The potential superoperators \( \mathcal{V}_{1,1} \) and \( \mathcal{V}_{1,b} \) are given by

\[ \mathcal{V}_{1,1} = \mathcal{V}_{12} \quad (\text{III.154}) \]

and

\[ \mathcal{V}_{1,b} = \mathcal{V}_{12} + \mathcal{V}_{13}. \quad (\text{III.155}) \]

\( \text{Tr}_i \) denotes the trace over all variables in fragment \( i \). Similarly the bound pair equation (III.101) can be written as

\[ i \frac{\partial \rho_{b12}}{\partial t} = \mathcal{L}_{12}^{(2)} \rho_{b12} + \sum_i \text{Tr}_i T^{(b,i)} \rho_{b12} \rho_i \]

\[ \equiv \mathcal{L}_{12}^{(2)} \rho_{b12} + \sum_i \text{Tr}_i \mathcal{V}_{b,i} \Omega_{b,i} \rho_{b12} \rho_i, \quad (\text{III.156}) \]

where potential superoperator \( \mathcal{V}_{b,1} \) and \( \mathcal{V}_{b,b} \) are given by

\[ \mathcal{V}_{b,1} = \mathcal{V}_{13} + \mathcal{V}_{23} \quad (\text{III.157}) \]

and

\[ \mathcal{V}_{b,b} = \mathcal{V}_{13} + \mathcal{V}_{23} + \mathcal{V}_{14} + \mathcal{V}_{24}. \quad (\text{III.158}) \]

Note the dual usages of the symbol “1”. it means particle 1 in \( \rho_{f1} \), and means a monomer in \( \mathcal{V}_{1,1}, \mathcal{V}_{1,b} \) and \( \mathcal{V}_{b,1} \). The second usage is understandable from the explicit definitions of Eqs. (III.154), (III.155) and (III.157).
In the non-reactive binary collision approximation, Eqs. (III.150-III.152), the equation for the pair correlations is decoupled from the generalized Boltzmann equation and the bound-pair equation. This decoupling is valid since coupling to pair correlations arises only from higher order collision processes. From the atomic picture point of view, the correlations are of order \( n_j^2 \) in number density. By ignoring the collision terms which are third order in particle density, the resulting equation for the pair correlations is

\[
 i \frac{\partial \rho_{c12}}{\partial t} = L_{12}^{(2)} \rho_{c12} + \nu_{12} \rho_{f1} \rho_{f2}.
\]  

(III.159)

This equation is correct at equilibrium. However, this equation has no relaxation term, which is unreasonable from the kinetic theory point of view, so can cause divergent transport coefficients. For this reason the (three-fragment) non-reactive collision terms and/or two fragment reactive collision terms for the pair correlation equation (III.102) can not be totally neglected. It is now assumed that the collision terms act to drive the pair correlations to their local homogeneous equilibrium form at their center of mass motion, as determined by the local density \( n_f \), temperature \( T_f \) and mean velocity \( \mathbf{v}_f \) of the free particle density operator. At equilibrium, the relative motion is described by Ursell operator\(^{64}\)

\[
 \rho_{c12}^e \propto U(T_f),
\]  

(III.160)

For small deviations from equilibrium, the collision term is modeled as a linear decay rate

\[
 i \frac{\partial \rho_{c12}}{\partial t} = L_{12}^{(2)} \rho_{c12} + \nu_{12} \rho_{f1} \rho_{f2} + i \frac{\rho_{c12}^e - \rho_{c12}}{\tau}.
\]  

(III.161)

This equation is called the modified pair correlation equation and is used in the rest of this thesis to determine the state of the pair correlations when the gas is out of equilibrium.
III-3.3 Wignerization

The Chapman-Enskog\textsuperscript{131,16,132} theory of gas transport properties is standardly described in classical phase space, and based on the idea that the gas is locally close to equilibrium with a local number density $n$, temperature $T$ and stream velocity $v_0$, each of which is a function of the macroscopic position $r$ and time $t$. For free (monatomic) particles, the local equilibrium distribution is a Maxwellian centred at the local stream momentum $mv_0(r,t)$. This mix of momentum and position dependence is most easily described for a quantum system, by using a phase space (Wigner function\textsuperscript{192}) representation of the density operator\textsuperscript{179}.

The phase space function $A(r,p,t)$ associated with an operator $A(t)$ is obtained by the Fourier transform\textsuperscript{202,203}

$$A(r,p,t) = \frac{1}{\pi} \int dq e^{iqr/\hbar} < p + \frac{1}{2} q | A(t) | p - \frac{1}{2} q >$$

$$= \text{Tr} \Delta(r,p) A(t),$$

(III.162)

where the trace Tr is over the translational states and the operator\textsuperscript{202} $\Delta$ is defined by

$$\Delta(r,p) = \frac{1}{\pi} \int dq e^{iqr/\hbar} | p - \frac{1}{2} q > < p + \frac{1}{2} q |$$

$$= \frac{1}{\pi} \int dR e^{iRr/\hbar} | r + \frac{1}{2} R > < r - \frac{1}{2} R |$$

(III.163)

in both momentum and position representations. The inverse transformation

$$A(t) = \frac{1}{\pi} \int dpdr \Delta(r,p) A(r,p,t)$$

(III.164)

enables the quantum operator to be obtained from the phase space function. It is also useful to know that

$$\text{Tr} AB = \frac{1}{\pi} \int dpdr [\text{Tr} A \Delta(r,p)][\text{Tr} \Delta(r,p) B]$$

(III.165)
as well as the trace properties

\[ \int \int \Delta(r, p)drdp = 1; \quad \text{Tr}\Delta(r, p) = h^{-3}; \]

\[ \text{Tr}\Delta(r, p)\Delta(r', p') = \delta(r - r')\delta(p - p')/h^3 \]  

(III.166)

and the relation between individual particle and center of mass - relative phase space representations

\[ \Delta_1(r_1, p_1)\Delta_2(r_2, p_2) = \Delta_{CM}\left(\frac{r_1 + r_2}{2}, \frac{p_1 + p_2}{2}\right)\Delta_{rel}(r_2 - r_1, \frac{p_2 - p_1}{2}). \]  

(III.167)

It is noted that the quantum property of the non-commutation of the position and momentum operators is reflected in the properties of the phase space representation.

As the full singlet density operator \( \rho^{(1)} \) involves \( \rho_{f1}, \rho_{c1} \) and \( \rho_{b1} \)

\[ \rho^{(1)}_1 = \rho_{f1} + \text{Tr}\rho_{c12} + \text{Tr}\rho_{b12}, \]  

(III.168)

the Wigner form for each of \( \rho_{f1}, \rho_{c12} \) and \( \rho_{b12} \) is discussed in turn.

The Wigner function \( f_{f1}(t) \) associated with the density operator \( \rho_{f1}(t) \) is given by

\[ f_{f1}(r, p_1, t) = h^{-3}\int dq e^{iq\cdot r/h} < p_1 + \frac{1}{2}q | \rho_{f1}(t) | p_1 - \frac{1}{2}q > \]

\[ = \text{Tr}\Delta(r, p_1)\rho_{f1}(t), \]  

(III.169)

where \( r \) is the macroscopic position and \( p_1 \) is momentum of particle 1.

For the bound pair density operator \( \rho_{b12} \) a separation between the center of mass variable and relative motion is first required. The center of mass dependence is then expressed in Wigner representation, whereas the relative motion is left as a density operator

\[ f_{b12}(R, P, t) = h^{-3}\int dQ e^{iQ\cdot R/h} < \frac{1}{2}Q | \rho_{b12}(t) | \frac{1}{2}Q > \]

\[ = \text{Tr}_{CM}\Delta_{CM}(R, P)\rho_{b12}(t). \]  

(III.170)
In analogy to the case for the bound pair, after the separation between the center of mass and relative motion, the Wigner representation of the center of mass variable of the pair correlation operator gives

\[ f_{c12}(R, P, t) = \hbar^{-3} \int dQ e^{iQ \cdot R / \hbar} < P + \frac{1}{2} Q | \rho_{c12}(t) | P - \frac{1}{2} Q > = \text{Tr}_{CM} \Delta_{CM}(R, P) \rho_{c12}(t). \] (III.171)

For kinetic theory, however, both the molecular picture and atomic picture descriptions of a pair correlation is required, thus involving more complications than for a bound pair. The macroscopic position \( r \) can be placed either at the center of mass position \( R \) or at \( r_1 \), the position particle 1, depending on emphasizing the molecular or atomic picture. Basically, for discussing the modified pair correlation equation (III.161), it is appropriate to view the correlated pair as a "molecule" and place the macroscopic position at the center of mass of the "molecule", while for evaluating the generalized quantum Boltzmann equation (III.153), it is important to emphasize the particle 1 point of view. The latter leads to a delocalization to the pair correlation Wigner function \( f_{c12} \) which can be important in non-equilibrium situations, see Section III-3.4.

In order to Wignerize the kinetic equations (III.153), (III.156) and (III.161), the collision term \( T^{(i,j)} \rho_i \rho_j \) needs to be written in phase space representation. The Weyl correspondence of the collision term of two particles of equal mass has been given by Thomas and Snider\textsuperscript{193}. Here the general phase space representation

\[ J^{(i,j)}(r_i, p_i) = -\frac{i}{\hbar^3} \int dq e^{iq \cdot r_i / \hbar} < p_i + \frac{1}{2} q | T^{(i,j)} \rho_i \rho_j | p_i - \frac{1}{2} q > \] (III.172)

of the collision term, for two fragments having arbitrary masses \( m_i \) and \( m_j \) is presented. After some manipulation, which is similar to that in Ref. (193),
\( J^{(i,j)}(r_i, p_i) \) can be written as

\[
J^{(i,j)}(r_i, p_i) = -\frac{i}{\hbar^3} \left( \frac{m_i + m_j}{m_i} \right)^3 2^6 T^{\text{int}(j)} \int \int \int \int e^{-\frac{i}{\hbar} (\mathbf{k} \cdot \mathbf{x} - q \cdot y)} \times T^{(i,j)}(\beta q \mathbf{k} \kappa) f_i(r_i + \frac{y}{2} - \frac{m_j}{m_i + m_j} \mathbf{x}, p_i + \beta - k, t) \\
	imes f_j(r_i + \frac{y}{2} + \frac{m_i}{m_i + m_j} \mathbf{x}, p_j - \beta + k, t) dk d\mathbf{k} d\beta dq dy dx, \quad (\text{III.173})
\]

where \( T^{\text{int}(j)} \) denotes the trace over all the internal states of fragment \( j \), and the superoperator \( T^{(i,j)}(\beta q \mathbf{k} \kappa) \) is defined by

\[
\hbar T^{(i,j)}(\beta q \mathbf{k} \kappa) f_i(r_i + \frac{y}{2} - \frac{m_j}{m_i + m_j} \mathbf{x}, p_i + \beta - k, t) \times f_j(r_i + \frac{y}{2} + \frac{m_i}{m_i + m_j} \mathbf{x}, p_j - \beta + k, t) = (\beta + \frac{2m_j}{m_i + m_j} q |V_{ij} \Omega_{ij}| k + \kappa) \\
\times (k - \kappa |\Omega_{ij}^\dagger| \beta - \frac{2m_j}{m_i + m_j} q) - (\beta + \frac{2m_j}{m_i + m_j} q |\Omega_{ij}| k + \kappa) \\
\times f_i(r_i + \frac{y}{2} - \frac{m_j}{m_i + m_j} \mathbf{x}, p_i + \beta - k, t) f_j(r_i + \frac{y}{2} + \frac{m_i}{m_i + m_j} \mathbf{x}, p_j - \beta + k, t) \times (k - \kappa |\Omega_{ij}^\dagger| V_{ij} \beta - \frac{2m_j}{m_i + m_j} q). \quad (\text{III.174})
\]

The interpretation of the various quantities is similar to that of Thomas and Snider\(^{193}\). The position vector \( \frac{1}{2} y \) is the difference between the center of mass of the colliding pair and the position of fragment \( i \), while \( x \) measures the role of the distance between the fragments when they collide, the non-locality of the collision. \( \beta \) is the relative momentum of the colliding pair after collision, while \( k \) is the average relative momentum before the collision [average in the sense that a matrix element \( \langle p' | A | p'' \rangle \) of an operator \( A \) has two momenta \( p' \) and \( p'' \) and it is the average \( \frac{1}{2}(p' + p'') \) of these]; \( q \) is a measure of the off-diagonality in the total momentum of the pair density.
matrix (before collision); and \( \kappa \) measures the relative contribution to this from the two different fragments. The center of mass momentum does not appear in the matrix elements since \( V_{i,j} \) and \( \Omega_{i,j} \) are independent of the center of mass motion. For the case of \( m_i = m_j \), Eqs. (III.173) and (III.174) reduce to Eqs. (12) and (13) of Ref. (193).

Various expressions in this section are exact and can be inverted by Eq. (III.164). When solving the three kinetic equations of Section III-3.3 by the Chapman-Enskog method, a local equilibrium form for the density operators is assumed and the delocalizations in \( f_{c12} \) and \( J^{(i,j)} \) can be approximated by gradient expansions. These are carried out in detail in Sections III-3.4 and III-4.1 respectively.

### III-3.4 Localization

In order to eventually solve the three kinetic equations of Section III-3.2 within the principles of the Chapman-Enskog method, the distinctions between local and non-local, equilibrium and non-equilibrium, and between homogeneous and inhomogeneous are first required and considered now in the Wigner function representation. The Wigner forms of the various density operators are specified in this section. The delocalization of the pair correlation operator from the atomic picture point of view gives rise to non-locality and is expanded in powers of the position gradient. Only the terms that are constant and linear in the gradient are kept in this expansion. This section is divided into three subsections, dealing respectively with the free, the bound pair and the pair correlation.
a) Localization of $f_f$

The local equilibrium (inhomogeneous) Wigner function for the free particles (equivalent to the density operator $\rho^{\ell}_f$) is Maxwellian

$$f_f^\ell(r, p_1, t) = \frac{n_f}{(2\pi m_1 k T_f)^{3/2}} e^{-\frac{(p_1 - m_1 v_f)^2}{2m_1 k T_f}}, \quad (III.175)$$

with free particle density $n_f(r, t)$, free particle stream velocity $v_f(r, t)$ and free particle temperature $T_f(r, t)$. The word inhomogeneous has been used because the gas stream velocity $v_0$ and temperature $T$ of the gas mixture as a whole would be appropriate for a local equilibrium and homogeneous gas mixture, but these can differ from $v_f$ and $T_f$. The position and time dependence of these local parameters are to be understood in the following even when they are not explicitly expressed, and it is noted that $f_f^\ell$ depends on $r$ and $t$ only through these local parameters. For purposes of the Chapman Enskog expansion, deviations of $f_f$ from local equilibrium are associated with linear gradients in $v_f$, $T_f$ and $n_f$, specifically written as

$$f_f(r, p_1, t) = f_f^\ell(r, p_1, t)(1 + \phi_1), \quad (III.176)$$

with the perturbation $\phi_1$ linear in the gradients (see Sections III-4.3 and III-4.4).

b) Localization of $f_b$

The local equilibrium (inhomogeneous) Wigner function for the bound pair is Maxwellian in the center of mass momentum $p_b$ and of Boltzmann form for the relative (internal state) motion operator, with center of mass of the bound pair being located at the macroscopic position $r$

$$f_b^\ell(r, p_b, t) = \frac{n_b}{(2\pi m_b k T_b)^{3/2}} q_b e^{-\frac{(p_b - m_b v_b)^2}{2m_b k T_b}} e^{-H_{int}/k T_b}. \quad (III.177)$$
Here the internal state partition function $q_b$ is

$$q_b = \text{Tr}_{\text{int}} e^{-H_{\text{int}}/kT_b}.$$  \hspace{1cm} (III.178)

The local bound pair quantities, such as the number density $n_b(r,t)$, stream velocity $v_b(r,t)$ and temperature $T_b(r,t)$, are functions of the macroscopic position $r$ and time $t$. The local equilibrium form $f_{b12}^{le}$ depends on $r$ and $t$ only through $n_b, v_b$ and $T_b$. The non-equilibrium part of $f_{b12}$ is assumed to be linear in the gradients of $v_b$, $T_b$ and various number densities ($n_f, n_c$, and $n_b$), denoted as $f_{b}^{le} \phi_b$,

$$f_{b12}(r,p_b,t) = f_{b12}^{le}(r,p_b,t)(1 + \phi_b).$$  \hspace{1cm} (III.179)

A detailed form of $\phi_b$ is given in Section III-4.4.

c) Localization of $f_c$

At equilibrium the pair correlations are governed by the Ursell\textsuperscript{64} operator

$$U(T) \equiv e^{-H_{rel}/kT} - e^{-K_{rel}/kT}$$  \hspace{1cm} (III.180)

involving the relative free motion and total Hamiltonians $K_{rel} \equiv \frac{p_{rel}^2}{m}$ and $H_{rel} = K_{rel} + V$, times a Maxwellian for the center of mass motion. At local equilibrium, the hydrodynamic variables of correlation density $n_c(R,t)$, temperature $T_c(R,t)$ and mean velocity $v_c(R,t)$ are to be localized at the position $R$ of the center of mass of the pair, so the local equilibrium state is most conveniently written in terms of a Wigner function for the center of mass motion and an operator for relative motion, thus in the molecular picture

$$f_{c}^{le}(R,P,t) = \frac{n_c}{\text{Tr}_{rel}U(T_c)} \frac{e^{-(P-2m_1v_c)^2/4m_1kT_c}}{(4\pi m_1kT_c)^{3/2}} U(T_c).$$  \hspace{1cm} (III.181)
Of prime importance for the generalized Boltzmann equation (III.153) and the renormalized Boltzmann equation (III.103) is the pair correlation contribution \( f^{le}_{cl} \), in the atomic picture, to the renormalized local equilibrium singlet Wigner function \( f^*_1 \)

\[
f^{le}_{cl}(r, p_1, t) \equiv \Tr_{12} \Delta_1(r, p_1) \rho^{le}_{cl2}
= 8 \int dr_{21} dp_{21} \Tr_{rel} \Delta_{rel}(r_{21}, p_{21}) f^{le}_{cl2}(r + \frac{1}{2} r_{21}, 2p_1 + 2p_{21}, t)
\approx f^{th}_{cl} + f^{lc}_{cl},
\]

(III.182)

involving an expansion of the center of mass position dependence about \( r \) in powers of the relative position \( r_{21} \). The notation \( f^{th}_{cl} \) denotes the localized contribution calculated as if the center of mass of the pair correlation were at \( r \), the position of particle 1. Thus the values of \( n_c, v_c \) and \( T_c \) are to be associated with the macroscopic position \( r \) of particle 1, with

\[
f^{th}_{cl}(r, p_1, t) = \frac{n_c \Lambda_r^3}{\hbar^3 \Tr_{rel} U(T_c)} \int dq e^{-(q + p_1 - m_1 v_c)^2/4m_1 kT_c} < q |U(T_c)| q >,
\]

(III.183)

where \( \Lambda_r \equiv \hbar/(\pi m_1 kT_c)^{1/2} \) is the relative motion thermal deBroglie wavelength and \( q \) is a relative momentum. It is convenient to recognize that the exponential factor in Eq.(III.183) is that associated with the center of mass motion since \( 2(p_1 + p_{op}) = P_{op} \) is the center of mass momentum operator associated with particle 1 having momentum \( p_1 \) and relative momentum (operator) \( p_{op} \). On introducing the notation \( K_{CM} \equiv (P_{op} - 2m_1 v_c)^2/4m_1 = (p_1 + p_{op} - m_1 v_c)^2/m_1 \), the integration over relative momentum can be written as a trace. With the notation \( \Tr_r \) to emphasize that the trace over relative motion is to be carried out keeping the momentum of particle 1 fixed, Eq.(III.183) can be rewritten as

\[
f^{th}_{cl}(r, p_1, t) = \frac{n_c \Lambda_r^3}{\hbar^3 \Tr_{rel} U(T_c)} \Tr_r e^{-K_{CM}/kT_c U(T_c)}.
\]

(III.184)
The delocalized contribution $f^{lc}_{c1}$ is the center of mass correction to $f^{th}_{c1}$, formally obtained by expanding the position dependence of $n_c$, $v_c$ and $T_c$ about the position $r$ that appears as a parameter in $f_{c1}$, retaining only first order gradient terms, compare the treatment of Baerwinkel et al\textsuperscript{194} and of Thomas et al\textsuperscript{193} for obtaining the phase space representation of the corresponding collision integral. This is labelled $I_c$ for “local center of mass correction factor” since it is associated with the fact that the center of mass of the pair correlation is displaced from the macroscopic position $r$, this implying a common gradient contribution $\frac{1}{2}r_{op} \cdot \nabla$ acting on all the local parameters, where $r_{op}$ is the relative position operator (particle 2 minus particle 1) and $\nabla \equiv \partial / \partial r$ is the gradient with respect to the macroscopic position. This center of mass correction term is thus

$$f^{lc}_{c1}(r, p_1, t) = \nabla \cdot \frac{n_c \Lambda_r}{4h^3 \Tr_{rel}U(T_c)} \Tr r e^{-K_{CM}/kT_c} \left[ r_{op}, U(T_c) \right]_+$$

$$= F^c_{cn} \cdot \nabla \ln n_c + F^c_{cv} \cdot \nabla v_c + F^c_{cT} \cdot \nabla \ln T_c \quad (\text{III.185})$$

where $[ , ]_+$ denotes an anticommutator,

$$F^c_{cn} = \frac{n_c \Lambda_r}{2h^3 \Tr_{rel}U(T_c)} \Tr r e^{-K_{CM}/kT_c} \left[ r_{op}, U(T_c) \right]_+ , \quad (\text{III.186})$$

$$F^c_{cv} = \frac{n_c \Lambda_r}{2kT_c h^3 \Tr_{rel}U(T_c)} \Tr (p_1 + p_{op} - m_1 v_c) e^{-K_{CM}/kT_c} \left[ r_{op}, U(T_c) \right]_+ , \quad (\text{III.187})$$

and

$$F^c_{cT} = \frac{n_c \Lambda_r}{4h^3 \Tr_{rel}U(T_c)} \Tr r e^{-K_{CM}/kT_c} \left[ r_{op}, \left( \frac{K_{CM}}{kT_c} - 3 \right) U(T_c) + T_c U_{T_c} \right]_+ , \quad (\text{III.188})$$

using the definition $U_T \equiv \partial U / \partial T$ for the temperature derivative of $U$.

Parallel to the treatment of $f_f$, for the purpose of making a Chapman Enskog expansion, deviations of $f_{c12}$ from local equilibrium are associated
with linear gradients in \( v_c \) and \( T_c \) so that

\[
f_{c12}(R, P, t) = f'_{c12}(R, P, t)(1 + \phi_c), \tag{III.189}
\]

with the perturbation \( \phi_c \) linear in the gradients (see Section III-4.2).

There remains one more term to be specified. That is the local homogeneous equilibrium form for the pair correlations as they arise in Eqs. (III.160) and (III.161). This depends on the density, temperature and mean velocity of the free particle density operator,

\[
f^\varepsilon_{c12}(R, P, t) = \text{Tr} \Delta(R, P) \rho^\varepsilon_{c12}(t)
\]

\[
= \frac{n_f^2 \Lambda_2(T_f)}{(4\pi m_1 k T_f)^{3/2}} e^{-\frac{(P - 2m_1 v_f)^2}{4m_1 k T_f} U(T_f)}, \tag{III.190}
\]

with \( n_f, v_f \) and \( T_f \) all evaluated at the center of mass position \( R \) and time \( t \), including the temperature dependence of the relative motion Ursell operator\(^{64}\). Such a form is appropriate if the pair correlations are in local homogeneous equilibrium with the free singlets. In terms of the spectrum of the pair hamiltonian, at equilibrium both a pair of free particles and a pair of correlated particles are represented by the same absolutely continuous spectrum. In contrast, the bound pairs are represented by the singular spectrum\(^{65,35}\). Consequently the pair correlations are inherently more intimately related to the free singlets than to the bound pair. In true local homogeneous equilibrium, all differences between the velocities \( v_f, v_c, \) and \( v_b \), and between the temperatures \( T_f, T_c, \) and \( T_b \) vanish (see Section III-4.4).

### III-3.5 Macroscopic Variables

The purpose of a quantum kinetic theory is to predict and describe, from quantum mechanical first principles, the time dependence of those macro-
scopic variables which are experimentally measurable. Central to the macroscopic description of a moderately dense gas mixture is the presence of the three species, free singlets, pair correlations, and bound pairs. The time evolution of the three species is given by the three coupled kinetic equations (III.100 -III.102), which lead to the equations of change for various macroscopic quantities as presented in Section III-3.1. Those macroscopic variables are defined in terms of quantum operators. It is useful to have their equivalent phase space expressions for the purpose of solving the quantum kinetic equations. These are provided in this section based on the various results of the previous four sections.

As seen in the last few sections, the pair correlations can be treated from either a molecular picture or an atomic picture. To formulate kinetic equations, in particular dynamical processes, it is necessary to view the pair correlations as a distinct species. In contrast, to describe the macroscopic properties, it is appropriate to treat the pair correlations as a correction to the free singlet, because in most experiments the pair correlations are not measured as a separate species. For this reason, in calculating macroscopic variables, the pair correlation is combined with the free, forming a renormalized “particle” 1 with a density operator of \( \rho_1 = \rho_{f1} + \rho_{c1} \). A full macroscopic description of the gas mixture is then determined by the pair of density operators \( \rho_1 \) and \( \rho_{b12} \) together with a potential energy contribution from \( \rho_{c12} \). Similar to the reasons discussed in Section III-3.2, in this section only non-reactive binary collisions are assumed to be of importance.

It follows from Eqs.(III.168), (III.175) and (III.184) that the total (molecular) number density of the gas mixture, at the macroscopic position \( r \) and time \( t \), is

\[
n(r, t) = n_1(r, t) + n_5(r, t). \tag{III.191}
\]
Here $n_1$ would be the number density of the system if the bound pairs were absent

$$n_1(r, t) \equiv \int dp_1 f_1(r, p_1, t)$$

$$= \int dp_1 f_{f_1}^{le}(1 + \phi_1) + 8 \int\int dp_1 dr_{21} dp_{21} T_{rel}$$

$$\times \Delta_{rel}(r_{21}, p_{21}) f_{c12}^{le}(r + \frac{1}{2} r_{21}, 2p_1 + 2p_{21}, t)(1 + \phi_c)$$

$$= n_f(r, t) + n_c(r, t), \quad (III.192)$$

with the “Chapman Enskog” constraint, auxiliary condition, that the perturbation from local equilibrium does not contribute to any local equilibrium hydrodynamic variables, in particular

$$\int dp_1 f_{f_1}^{le}(r, p_1, t) \phi_1 + \int dP Tr_{rel} f_{c12}^{le}(r, P, t) \phi_c = 0. \quad (III.193)$$

The bound pair number density $n_b(r, t)$ is

$$n_b(r, t) = \int dp_b f_b(r, p_b, t)$$

$$= \int dp_b Tr_{int} f_{b12}^{le}(1 + \phi_b), \quad (III.194)$$

with constraint, that the perturbation from local equilibrium does not contribute to the number density of bound pairs

$$\int Tr_{int} f_{b12}^{le}(r, p_b, t) \phi_b dp_b = 0. \quad (III.195)$$

It is also useful to define the total mass density $\rho$ of the gas mixture as

$$\rho(r, t) = \rho_1(r, t) + \rho_b(r, t)$$

$$= m_1 n_1(r, t) + m_b n_b(r, t). \quad (III.196)$$

The mass average velocity (stream velocity) of the gas mixture is the average velocity of the renormalized particle 1 and the bound pair,

$$v_0(r, t) \equiv \frac{1}{\rho} (\rho_1 v_1 + \rho_b v_b), \quad (III.197)$$

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subject to the auxiliary condition that the perturbations do not contribute to the total local equilibrium momentum of the gas mixture

\[ \int dp_1 p_1 f_{1e}^\phi \phi_1 + Tr_{rel} \int P f_{cl2}^{1e}(r, P, t)\phi_c dP + Tr_{int} \int p_b f_{b12}^{le} \phi_b dp_b = 0, \]  
(III.198)

and where

\[ \phi_1 \mathbf{v}_1(r, t) = \int dp_1 p_1 f_1(r, p_1, t) \]
\[ = n_f m_1 v_f + n_c m_1 v_c \]  
(III.199)

and

\[ \phi_b \mathbf{v}_b = \int dp_b Tr_{int} p_b f_{b12}. \]  
(III.200)

Clearly, if the gas mixture was in internal equilibrium it would have a common convective motion, so that \( v_f = v_c = v_b = v_0 \). Thus any difference in these velocities is associated with non-equilibrium processes driven by the inhomogeneities of the gas.

The diffusion velocity for the renormalized particle 1 is

\[ \mathbf{V}_1(r, t) = \frac{1}{n_1} \int dp_1 \frac{p_1 - m_1 v_0}{m_1} f_1(r, p_1, t) \]
\[ = \frac{n_f}{n_1} (v_f - v_0) + \frac{n_c}{n_1} (v_c - v_0) \]
\[ + \frac{1}{n_1} \int dp_1 \frac{p_1 - m_1 v_0}{m_1} f_{1e}^\phi \phi_1 \]
\[ + \frac{1}{n_1} Tr_{rel} \int \frac{P - 2p_{op} - 2m_1 v_0}{2m_1} f_{cl2}^{1e}(r, P, t)\phi_c dP. \]  
(III.201)

The diffusion velocity for the bound pairs is

\[ \mathbf{V}_b(r, t) = \frac{1}{n_b} \int dp_b Tr_{int} \frac{p_b - m_b v_0}{m_b} f_{b12}(r, p_b, t) \]
\[ = (v_b - v_0) + \frac{1}{n_b} \int dp_b Tr_{int} \frac{p_b - m_b v_0}{m_b} f_{b12}^{le} \phi_b. \]  
(III.202)
Expressions (III.201) and (III.202) are subject to the constraint of Eq. (III.198), which implies that
\[ \varrho_1 \mathbf{V}_1 + \varrho_b \mathbf{V}_b = 0. \] (III.203)

The diffusion velocities depend on the gradients of the renormalized number density \( n_1 \) and bound pair number density \( n_b \), of the renormalized hydrostatic pressure \( P_1 \) and bound pair hydrostatic pressure \( P_b^K \), and of the local equilibrium temperature \( T \) (see Section III-4.4 for detail). An important aspect is that in the moderately dense gas mixture, it is the renormalized quantities, rather than the properties of the free singlet that enters into the various macroscopic processes such as diffusion (see Section III-4.4).

Ignoring for the moment the possible contribution from the perturbations, the local equilibrium kinetic energy density is
\[ n_e^{K, le}(r, t) \equiv n_1 \epsilon_1^{K, le}(r, t) + n_b \epsilon_b^{K, le}(r, t) \] (III.204)

where
\[
n_1 \epsilon_1^{K, le}(r, t) = \int dp_1 \frac{(p_1 - m_1 v_0)^2}{2m_1} f_1^{le}(r, p_1, t) + \\
= n_f \left[ \frac{3}{2} kT_f + \frac{m_1}{2} (v_f - v_0)^2 \right] \\
+ n_c \left[ \frac{3}{4} kT_c + \frac{m_1}{2} (v_c - v_0)^2 \right] \\
+ \frac{1}{2 \mathbf{Tr}_{rel}U(T_c)} \mathbf{Tr}_{rel}(\mathbf{p}_{sp}^2/m_1)U(T_c),
\] (III.205)

and
\[
n_b \epsilon_b^{K, le}(r, t) = \int dp_b \mathbf{Tr}_{int} \left[ \frac{(p_b - m_b v_0)^2}{2m_b} + H_{int} \right] f_{b12}^{le} \\
= n_b \left[ \frac{3}{2} kT_b + \frac{m_b}{2} (v_b - v_0)^2 + E_{int} \right].
\] (III.206)
Note that $n_c$ is the (effective) number of particles that are correlated so that $\frac{3}{4}kT_c$ is the average center of mass energy per particle. Similarly, the $\frac{1}{2}$ multiplying the kinetic energy of relative motion partitions this between the two correlated particles. The terms involving $(v_f - v_0)^2$, $(v_c - v_0)^2$ and $(v_b - v_0)^2$ are second order in gradients and so will be dropped from further consideration. $E_{int}$ is the average internal energy per bound pair

$$E_{int} = \frac{1}{q_b}\text{Tr}_{int}H_{int}e^{-H_{int}/kT_b}, \tag{III.207}$$

which is included as part of the bound pair kinetic energy expression for simplicity.

Energy conservation can be treated in several different ways. In non-reactive binary collision processes there are three types of relevant energies:

1. the relative energy of the colliding fragments;
2. the internal energy of the bound pairs if they are involved;
3. the potential energy of two colliding fragments.

Consequently there are three basic energy transfer mechanisms:

1. the energy transfer between the relative motion of the two colliding fragments and the internal states of the colliding (bound) partner(s) during a collision;
2. the energy transfer between the relative motion energy and the potential energy of the two colliding fragments due to the non-locality of the collision;
3. the energy transfer between the internal energies of the bound pair(s) and the potential energy of two colliding fragments during a collision.
It appears that a comprehensive treatment including all three different energy transfer mechanisms is appropriate. But further analysis indicates that there is some inconsistency in doing this. The potential energy does not play any role if the collisions are treated as local. Non-local collisions inherently involve various correlations (see Section III-4.1) depending on the colliding partners, for example in the case of a two particle non-local collision, the pair particle correlation is involved whereas a non-local monomer-dimer collision induces monomer-dimer correlations. Therefore including potential energies between monomer and dimer and between two dimers is inconsistent with the present treatment of ignoring the monomer-dimer and dimer-dimer correlations. Consequently it is important to consider only those parts of the potential energies that are consistent with those collision non localities that have been treated. The latter in turn have to eventually agree with the correlations that have been included in the treatment. From this analysis only the potential energy of monomer-monomer collisions is to be considered in the rest of the discussion.

The potential energy is determined by the density operators of two colliding particles which, to second order in density $n_f$, involves both the product of free density operators and the pair correlation density operator, thus

$$n_1^c V^{le}_1(r, t) = \frac{1}{4} \text{Tr}_{12} [\delta (r - r_{op,1}) + \delta (r - r_{op,2})] V_{12} \rho_{ub12}^{(2),le}$$

$$= \frac{1}{2} n_f^2 \int V_{12} dr_{12} + \frac{1}{2} n_c^2 \frac{\text{Tr}_{rel} V_{12} U(T_c)}{\text{Tr}_{rel} U(T_c)},$$

(III.208)

where $\rho_{ub12}^{(2),le}$ denotes the unbound part of the full local equilibrium pair density operator

$$\rho_{ub12}^{(2),le} = \rho_{12}^{(2),le} - \rho_{b12}^{le}.$$  

(III.209)
The total local equilibrium energy of the renormalized particle 1 is given by

$$n_1 \varepsilon^{le}_1 = n_1 \varepsilon^{Kle}_1 + n_1 \varepsilon^{Ve}_1, \quad (III.210)$$

and the total local equilibrium energy of the gas mixture is

$$n \varepsilon^{le} = n_1 \varepsilon^{le}_1 + n_b \varepsilon^{Kle}_b. \quad (III.211)$$

The auxiliary condition for the energy involves the total energy, so requiring

$$\int \frac{(P_1 - m_1 v_0)^2}{2m_1} f_{f1}^e \phi_1 dP_1 + \frac{1}{2} \int \int V_{12} f_{f1}^{le} f_{f2}^{le} (\phi_1 + \phi_2) d\tau_{12} dP_1 dP_2$$

$$+ \frac{1}{2} \mathrm{Tr}_{rel} \int \left( \frac{(P_2 - m_1 v_0)^2}{4m_1} + H_{rel} \right) f_{c12}^{le} \phi_c dP$$

$$+ \mathrm{Tr}_{int} \int \left[ \frac{(P_b - m_b v_0)^2}{2m_b} + H_{int} \right] f_{b12}^{le} \phi_b dP_b = 0. \quad (III.212)$$

Provided the equilibrium conditions $n_c = n_f^2 \Lambda \varepsilon^{Tr_{rel}} U$, $T_f = T_c = T_b = T$ and $v_f = v_c = v_b = v_0$ are satisfied then $\varepsilon^{K}_1$ reduces to the equilibrium thermodynamic kinetic energy per particle, and $\varepsilon^{V}_1$ to the potential energy per particle.

The pressure tensor and the heat flux have contributions arising from several sources. In particular the kinetic contribution to the pressure tensor is

$$P^K(r, t) \equiv P^K_1(r, t) + P^K_b(r, t), \quad (III.213)$$

where the kinetic pressure contribution from the renormalized particle 1 is

$$P^K_1(r, t) = \int dP_1 \frac{(P_1 - m_1 v_0)(P_1 - m_1 v_0)}{m_1} f_1(r, P_1, t)$$

$$= n_f [kT_f U + m_1 (v_f - v_0)(v_f - v_0)]$$

$$+ n_c \left[ \frac{1}{2} kT_c U + m_1 (v_c - v_0)(v_c - v_0) + \frac{\mathrm{Tr}_{rel}(P_{op}^2/m_1)U(T_c)}{3 \mathrm{Tr}_{rel} U(T_c)} U \right]$$
\[ + \int dp_1 \frac{(p_1 - m_1v_0)(p_1 - m_1v_0)}{m_1} f_{f_1}^e \phi_1 \]
\[ + Tr_{rel} \int dP \left[ \frac{(P - 2m_1v_0)(P - 2m_1v_0)}{4m_1} + \frac{P_{op}P_{op}}{m_1} \right] f_{b12}^{le} \phi_e. \quad \text{(III.214)} \]

\( U \) is the second rank identity tensor\(^{131,204} \) and the kinetic pressure contribution from the bound pairs is
\[
P_b^K(r, t) = \int dp_b Tr_{int} \frac{(p_b - m_bv_0)(p_b - m_bv_0)}{m_b} f_{b12}(r, p_b, t)
= n_b[kT_b U + m_b(v_b - v_0)(v_b - v_0)]
+ \int dp_b Tr_{int} \frac{(p_b - m_bv_0)(p_b - m_bv_0)}{m_b} f_{b12}^{le} \phi_b. \quad \text{(III.215)}
\]

The kinetic contribution to the heat flux is
\[
q^K(r, t) \equiv q_1^K(r, t) + q_b^K(r, t), \quad \text{(III.216)}
\]
where the renormalized particle 1 contributes
\[
q_1^K(r, t) = \int dp_1 \frac{(p_1 - m_1v_0)^2}{2m_1} f_1(r, p_1, t)
= 5 \frac{n_fkT_f(v_f - v_0)}{2} + n_e \left[ \frac{kT_c}{2} + \frac{Tr_{rel}(p_{op}^2/m_1)U(T_c)}{3Tr_{rel}U(T_c)} \right] (v_c - v_0)
+ \int dp_1 \frac{(p_1 - m_1v_f)^2}{2m_1} f_{f_1}^e(r, p_1, t) \phi_1
+ Tr_{rel} \int dP \left[ \frac{(P - 2m_1v_c)^2}{4m_1} + \frac{P_{op}^2}{m_1} \right] \frac{(P - 2m_1v_c)}{4m_1}
- \frac{(P - 2m_1v_c) \cdot P_{op}P_{op}}{2m_1^2} f_{b12}^{le} \phi_e, \quad \text{(III.217)}
\]
and the bound pair contributes
\[
q_b^K(r, t) = \int dp_b Tr_{int} \frac{(p_b - m_bv_0)^2}{2m_b} \left[ \frac{(p_b - m_bv_0)^2}{2m_b} + H_{int} \right] f_{b12}(r, p_b, t)
= n_b \left( \frac{5}{2} kT_b + E_{int} \right) (v_b - v_0) + \int dp_b Tr_{int}
\times \left( \frac{p_b}{m_b} - v_b \right) \frac{(p_b - m_bv_b)^2}{2m_b} + H_{int} \right] f_{b12}^{le}(r, p_b, t) \phi_b. \quad \text{(III.218)}
\]
The two particle collisional transfer contribution to the pressure tensor is

\[ P_{\text{coll}}(r,t) = -\frac{1}{2} \text{Tr}_{12} \rho_{op} \nabla V_{12} \delta(R_{op} - r) \Omega \rho_{11} \rho_{f2} \Omega^\dagger \]

\[ = -\frac{n_f^2 \Lambda^2}{6} \text{Tr}_{rel} \rho_{op} \cdot \nabla V_{12} e^{-H_{rel}/kT} \mathbf{U} \]

\[ - \frac{n_f^2 \Lambda^2}{4kT} \text{Tr}_{rel} \rho_{op} \nabla V_{12} \Omega \left[ e^{-K_{rel}/kT} \rho_{op}, \rho_{op} \right] + \Omega^\dagger : \nabla \mathbf{v}_f \]

\[ - \frac{n_f^2 \Lambda^6}{16 \hbar^2 \text{Tr}_{rel}} \int d\mathbf{p} e^{-K_{CM}/kT} \rho_{op} \nabla V_{12} \Omega e^{-K_{rel}/kT} (\phi_1 + \phi_2) \Omega^\dagger. \quad (\text{III.219}) \]

Provided \( T_c = T_f = T \) and \( n_c = n_f^2 \Lambda \rho^3 \text{Tr}_{rel} U \), the local equilibrium collisional transfer contribution to the pressure is of virial form which, when combined with the kinetic contribution gives the standard expression \( P_1 = n_1 kT + n_f^2 kTB_c \) for the total pressure if there are no bound pairs. \( B_c \) is the equilibrium pair correlation contribution to the second virial coefficient.

The collisional transfer of kinetic energy is

\[ q_{\text{coll}} = -\frac{1}{4m_1} \text{Tr}_{12} \left[ \rho_{op} - m_1 \mathbf{v}_0 \right] \cdot \nabla V_{12} \Omega \rho_{f1} \rho_{f2} \Omega^\dagger \]

\[ = -\frac{1}{6} (\mathbf{v}_f - \mathbf{v}_0) \text{Tr}_{rel} \rho_{op} \cdot \nabla V_{12} e^{-H_{rel}/kT_f} \]

\[ - \frac{n_f^2 \Lambda^3}{4m_1} \text{Tr}_{rel} \int d\mathbf{G} e^{-\mathbf{G}^2/\pi \hbar^2} \rho_{op} (\mathbf{P} - 2m_1 \mathbf{v}_0) \cdot \nabla V_{12} \]

\[ \times \Omega e^{-K_{rel}/kT_f} (\phi_1 + \phi_2) \Omega^\dagger. \quad (\text{III.220}) \]

where the dimensionless velocity \( \mathcal{G} \equiv (\mathbf{P} - 2m_1 \mathbf{v}_c)/\sqrt{4m_1 kT_c} \).

The local equilibrium contribution to the potential heat flux is given by

\[ q_1^V = -\frac{1}{4m_1} \text{Tr}_{12} \left[ \rho_{op,1} - m_1 \mathbf{v}_0, \delta_1 \right] V_{12} \rho_{ub12}^{(2)} \]

\[ = -\frac{1}{4m_1} \text{Tr}_{12} (\mathbf{P} - 2m_1 \mathbf{v}_0) \delta(R_{op} - r) V_{12} \rho_{ub12}^{(2)} \]

\[ = \frac{1}{2} \left[ n_f^2 (\mathbf{v}_f - \mathbf{v}_0) \int V_{12} \mathbf{d}r_{12} + \frac{n_c}{\text{Tr}_{rel} U(T_c)} (\mathbf{v}_c - \mathbf{v}_0) \text{Tr}_{rel} V_{12} U(T_c) \right] \]

\[ 201 \]
Clearly the leading term of these quantities vanish if $v_f = v_c = v_0$, then leaving only the perturbation contributions.

Finally the kinetic energy production term is

$$
\sigma^K = -\frac{1}{4m_1} \text{Tr}_{12} \left\{ \left[ \delta(r-r_{op,1}) + \delta(r-r_{op,2}) \right] \times (p_{op} \cdot \nabla V_{12} + \nabla V_{12} \cdot p_{op}) \right\}_s \Omega \rho_{f1} \rho_{f2} \Omega^f. \quad (\text{III.222})
$$

This completes the description of the macroscopic variables for a non-reactive moderately dense "binary" gas mixture with one component being a renormalized particle 1 and the other a bound pair. It is noted that these results can be easily modified to describe a moderately dense gas system without the presence of the bound pairs, which is also a very important kinetic system. In that case the generalized Boltzmann equation (III.153) reduce to the renormalized Boltzmann equation (III.103) of Snider$^{52}$ and the solution of the latter, together with that of the modified pair correlation equation (III.161) is presented in Section III-4.2. The macroscopic variables appropriate for this system with no bound state are given by Eqs. (III.192), (III.199), (III.205), (III.208), (III.210), (III.214), (III.217), (III.219), (III.220), (III.221) and (III.222), with the simplified constraints that

$$
\int dp_1 p_1 f^{le}_f \phi_1 + \text{Tr}_{rel} \int P f^{le}_{c12}(r, P, t) \phi_c dP = 0, \quad (\text{III.223})
$$

and

$$
\int \frac{(p_1 - m_1 v_0)^2}{2m_1} f^{le}_f \phi_1 dp_1 + \frac{1}{2} \int \int V_{12} f^{le}_{f1} f^{le}_{f2}(\phi_1 + \phi_2) d\mathbf{r}_{12} dp_1 dp_2
$$

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These are special case of Eqs. (III.198) and (III.212).

$$+ \frac{1}{2} \text{Tr}_{rel} \int \left( \frac{(P - 2m_1v_0)^2}{4m_1} + H_{rel} \right) f_{c12}^e \phi_c dP = 0. \quad (III.224)$$

These are special case of Eqs. (III.198) and (III.212).

### III-3.6 Discussion

Macroscopic properties have been described by using both abstract density operators and their equivalent phase space representations. In the operator method the equations of change have been derived from the three coupled kinetic equations within the non-reactive collision approximation. The equations of change for the generalized Boltzmann equation is particularly similar to those for the renormalized Boltzmann equation presented by Snider\(^{52}\) except for the possible coupling to the bound pair and/or interacting pair through two or three fragment collisions. The equations of change for the dimer parallel those of Sze, Ali and Snider\(^{58,191}\). The latter have included reactive collision terms which involve necessarily the delocalizations due to switching between molecular and atomic pictures for the description of break-up and recombination collisions. The discussion in Section III-3.1 is more general than that in the rest of this chapter. In particular the secondary asymptotic channel, essentially the interacting pair, which is particularly important for the various macroscopic quantities associated with the pair correlations, is kept in Section III-3.1.

In order for an explicit solution to the three coupled kinetic equations (III.100-III.102) to be feasible, the collision processes are further restricted to non-reactive binary collisions in Section III-3.2. With such an approximation, the three kinetic equations (III.153), (III.156) and (III.161) for a non-ideal monomer and dimer mixture are obtained. The equation for the pair correlations within the constraint of non-reactive binary collisions de-
couples from the other kinetic equations. From the physical point of view the correlations can not live forever no matter what approximation is used. For this reason a decay term characterized by a relaxation time \( \tau \) is introduced. In this manner two coupled equations, namely the generalized Boltzmann equation (III.153) and the bound pair equation (III.156), in additional to a modified pair correlation equation (III.161), need to be solved. This is done in Section III-4.3.

The Wigner function representation of \( \rho_{f1}, \rho_{c12}, \rho_{b12} \) and of the collision operator \( T^{(i,j)} \rho_i \rho_j \) for two arbitrary fragments is presented in Section III-3.3. In the case of \( \rho_{c12} \) and \( \rho_{b12} \), the Wigner representation is for the center of mass motion while the relative motion remains in operator form. The resulting form \( J^{(i,j)} \) for the binary collision operator \( T^{(i,j)} \rho_i \rho_j \) reduces to that of Thomas and Snider\(^{193} \), and of Baerwinkel and Grossmann\(^{194} \) for monomer-monomer collisions. Quantum phase space collision theory has been studied intensively\(^{205,206,207,208,209} \).

Since collisions are assumed to be non-reactive in this chapter, a molecular picture treatment for bound pairs is sufficient. In contrast, a pair correlation has to be treated in both molecular and atomic pictures because it appears in two kinetic equations, namely the modified pair correlation equation and the generalized Boltzmann equation. The atomic picture treatment for \( \rho_{c1} \) leads to a gradient expansion for the delocalization and results in \( \rho_{c1}^{le} \simeq \rho_{c1}^{lh} + \rho_{c1}^{lc} \) [see Eq. (III.182)].

The macroscopic variables are expressed in quantum phase space representation in Section III-3.5. Due to the collisional decoupling of the equation for the pair correlations from the other two kinetic equations within the non-reactive binary collision approximation, it is possible to solve the modified pair correlation equation (III.161) separately. The remaining two cou-
plied equations, namely the generalized Boltzmann equation (III.153) and the bound pair equation (III.156) are to be solved together. With this separation in mind, the macroscopic variables are treated in terms of the renormalized particle \( \rho_1 = \rho_{f1} + \rho_{c1} \), plus a bound pair \( \rho_{b12} \), i.e., as a non-ideal binary gas mixture. It is the role of a renormalized particle, rather than of a free singlet, that has been emphasized throughout the macroscopic description. Macroscopic variables appropriate for a moderately dense gas system \textit{without bound states} are also given, in addition to those appropriate for a moderately dense gas mixture of the renormalized particle and bound pair. Solutions of these two important kinetic systems are presented in Sections III-4.2 and III-4.4, under the names of Schemes I and II respectively.

Energy conservation is quite complicated because the bound state, the pair correlation, collisional non-locality and the free singlet are treated simultaneously. There are three types of energies of importance in collisions, namely the relative, internal, and potential energies, giving rise to three collisional energy transfer mechanisms. Not every combination of the three mechanisms is required when finding a solution to these kinetic equations. A consistent treatment for the energy conservation is to consider only the part of the potential energy that corresponds to the non-local monomer-monomer collisions.
Chapter III-4
Solutions and Transport Coefficients

This chapter presents two schemes of solutions to the quantum kinetic equations (III.103), (III.153), (III.161) and (III.156). Scheme I is to solve the renormalized quantum Boltzmann equation (III.103), together with equation (III.161) for the pair correlations. Scheme II is to solve the generalized quantum Boltzmann equation, (III.153), the bound pair equation (III.156) and equation (III.161) for the pair correlations. Each scheme describes a moderately dense gas with the latter including the presence of, and contributions from, bound states.

Density corrections to ideal gas kinetic theory can be traced back to Enskog's work in the early twenties\textsuperscript{152}. He obtained a modification of the Boltzmann equation\textsuperscript{130} which accounts for non local collisions of hard spheres and also the effect that the presence of a third particle can have on a collision between two particles. For a general (soft) potential, Snider and Curtiss\textsuperscript{62} derived expansions for the non-local corrections to the transport coefficients based on the works of Green\textsuperscript{61} and Bogoliubov\textsuperscript{21}. Three-body collision effects on the transport coefficient have been considered by Hoffman and Curtiss\textsuperscript{153}. Numerical work performed by Rainwater and co-workers\textsuperscript{154,155} using realistic potentials found that a combination of the theories of Snider and Curtiss, Hoffman and Curtiss, and of bound state effects described by Stogryn and Hirschfelder\textsuperscript{156}, has been very successful in explaining experimental data for the transport virials.

The renormalized quantum Boltzmann equation (III.103) proposed recently by Snider\textsuperscript{52} was motivated by Laloë and Mullin's\textsuperscript{210} distinguishing between free and full motion for the pair density operator. The solution to
that equation has been pursued by Snider and coworkers over the last few years. The transport coefficients obtained from the present solution include both the non-local collision correction, which is comparable to the classical mechanical treatment of Snider and Curtiss\textsuperscript{62}, and the unbound part of the second virial coefficient.

The kinetic equations are solved within the philosophy of the Chapman-Enskog procedure\textsuperscript{131,16,132,133}. Only the lowest order Sonine polynomials\textsuperscript{132,16} are used for approximating the perturbation functions. The internal state density matrix of the bound pairs is assumed to be diagonal in energy and only the lowest order Wang Chang-Uhlenbeck polynomials\textsuperscript{196} are used for estimating the bound pair density operator. More general methods of treating internal states are given by Waldman\textsuperscript{144}, Snider\textsuperscript{26}, Tip\textsuperscript{145}, and Snider and Sanctuary\textsuperscript{32}.

This chapter is divided into six sections. Section III-4.1 is devoted to the linearization of the four kinetic equations which is in part a continuation of Chapter III-3. The linearization is necessary in order to solve the kinetic equations by the Chapman-Enskog method. In such a method the distinction between equilibrium and out of equilibrium contributions to macroscopic and microscopic properties is first required. The local inhomogeneity is responsible for the system being out of non-equilibrium, therefore a set of common macroscopic variables $v_0$ and $T$ for all species at local equilibrium is appropriate for the present purpose. The collision operators, as represented by Wigner functions in Section III-3.3, are parameterized by two different positions since the two colliding fragments start colliding at a finite distance from each other. Since the Chapman-Enskog theory is local, only one macroscopic position variable is allowed and a gradient expansion is necessary to account for this spatial separation. This is accomplished following the meth-
ods of Baerwinkel and Grossmann\textsuperscript{194} and Thomas and Snider\textsuperscript{193}. The four linearized kinetic equations have thus been reduced to essentially linear equations for the perturbations with gradient driving terms.

Under the name of "Scheme I", the solutions and transport coefficients for the renormalized Boltzmann equation and the modified pair correlation equation are presented in Sections III-4.2 and III-4.3 respectively. Since to first order in gradient, the renormalized Boltzmann equation is essentially decoupled from the pair correlation equation, the former is solved independently from the latter. Meanwhile the modified pair correlation equation, despite its apparent dependence on the perturbation $\phi_1$, is also solved independently at the present level of approximation. On the assumption that the pair correlation operator is in complete equilibrium with the free, the time derivatives in the renormalized Boltzmann equation are eliminated by three hydrodynamic equations, namely the equations of continuity, motion and energy balance, to give terms linear in the gradients. For energy conservation, it is the total energy $\varepsilon = \varepsilon^K + \varepsilon^V$ that has been used to determine the temperature equation. The potential energy $\varepsilon^V$ is involved because binary collisions are treated as non-local, which allows the intra-conversion of kinetic energy and potential energy by binary collisions. The non-local collision corrections are also proportional to the gradients. These first order gradient terms are interpreted as general driving forces which cause the system to be out of equilibrium, while it is the collision term on the right hand side of the renormalized Boltzmann equation that relaxes the system back to its equilibrium. The uniqueness of the solution for the renormalized Boltzmann equation is warranted by the Fredholm alternative\textsuperscript{42,195}. The transport coefficients are estimated according to the expressions given in Section III-3.5 but the local inhomogeneity is disallowed for the present purpose. Rotational symmetry
for the system has been assumed both in solving the two kinetic equations and in evaluating the transport coefficients. Most of Sections III-4.2 and III-4.3 is adopted from two papers\textsuperscript{211,212} that are in preparation.

Similarly, under the name of "Scheme II", the solutions and transport coefficients for the generalized Boltzmann equation, the bound pair equation and the modified pair correlation equation are presented in Sections III-4.4 and III-4.5 respectively. For the same reason as stated in the last paragraph, the modified pair correlation equation is treated separately from the two other kinetic equations. The generalized Boltzmann equation and the bound pair equation are then treated as for a binary gas mixture, with one component for the renormalized particle 1, and the other for the bound pair. These two equations, at equilibrium, give rise to the full second virial coefficient. As in Section III-4.2, the density operators in the Wigner representation are treated as functionals of the four hydrodynamic variables, namely the two number densities and the velocity and temperature. Their time derivatives are replaced by those of the three hydrodynamic variables. The total energy includes kinetic energies of the renormalized particle 1 and the bound pair, as well as the potential energy of an interacting pair. Two energy converting mechanisms, namely the transfers between kinetic and potential energies, and between "kinetic" and internal energies are considered. The bound pair density operator is treated in this work as being diagonal in the internal state energy, which simplifies various expressions. Only the two particle collision non-locality associated with the generalized Boltzmann equation is treated because at equilibrium the monomer-dimer collisional non-locality is proportional to the monomer-dimer correlation which has not been considered at present. Only the linear in gradient terms are retained from the two particle non-local expansion. The solutions for the generalized Boltzmann equation
and the bound pair equation are approximated by the lowest order Sonine polynomials\textsuperscript{16} and Wang Chang-Uhlenbeck polynomials\textsuperscript{196} and the five left invariants and the five right invariants are satisfied which guarantees the uniqueness of the solutions. The solution for the modified pair correlation equation basically remains the same as that of Section III-4.2 except for one additional term due to diffusion. The transport coefficients are calculated in the same manner as in Section III-4.2 with extra diffusional contributions to the heat flux and bound pair contributions to all macroscopic quantities. As can be expected from irreversible thermodynamics, the diffusion driving force vectors for the non-ideal binary mixture work out to be determined solely by hydrodynamic (partial) pressures, which is similar to that for an ideal gas mixture\textsuperscript{213,137133} but with appropriate density corrections.

A general discussion is given in Section III-4.6

III-4.1 Linearization

In this section the various quantum kinetic equations given in Section III-3.2 are linearized for the purpose of solving them in the following sections by the Chapman-Enskog method. This section consists of four subsections. The collision operator for an arbitrary two fragment collision is expanded around the macroscopic position $r$ in subsection a). The following three subsections are devoted to the linearization of the three kinetic equations. The linearization of the renormalized Boltzmann equation is presented as a special case of the linearization of the generalized Boltzmann equation.

a) Linearizing the Collision Operators

The operators $f_i$ and $f_j$ in the collision term as shown explicitly in Section
III-3.3 have different position dependences characterized by $x$ and $y$. This difference in positions reflects the fact that the two colliding fragments are interacting over a distance, i.e. the collisional non-locality, which is of the order of magnitude of the potential range. Since in kinetic theory only the macroscopic position $r$ is important, the non-locality is to be treated as a Taylor expansion:

$$f_i(r + \frac{y}{2} + \frac{m_j}{m_i + m_j}x, p_i + \beta - k, t) f_j(r + \frac{y}{2} + \frac{m_i}{m_i + m_j}x, p_j - \beta + k, t)$$

$$= \left\{ \sum_{m, l=0}^{\infty} \frac{1}{m!l!} \left[ \frac{1}{2} \right]^m \left[ \frac{-m_j}{m_i + m_j}x \right]^l \bigotimes^{m+l} [\nabla]^{m+l} f_i(r, p_i + \beta - k, t) \right\}$$

$$\times \left\{ \sum_{m', l'=0}^{\infty} \frac{1}{m'!l'!} \left[ \frac{1}{2} \right]^{m'} \left[ \frac{m_i}{m_i + m_j}x \right]^{l'} \bigotimes^{m'+l'} [\nabla]^{m'+l'} f_j(r, p_j - \beta + k, t) \right\}$$

$$= f_i(r, p_i + \beta - k, t) f_j(r, p_j - \beta + k, t)$$

$$+ \frac{y}{2} \cdot \nabla [f_i(r, p_i + \beta - k, t) f_j(r, p_j - \beta + k, t)]$$

$$+ x \cdot \left[ \frac{m_i}{m_i + m_j} f_i(r, p_i + \beta - k, t) \nabla f_j(r, p_j - \beta + k, t) \right]$$

$$- \frac{m_j}{m_i + m_j} f_j(r, p_j - \beta + k, t) \nabla f_i(r, p_i + \beta - k, t)$$

$$+ \cdots$$

(III.225)

Here the symbol $\bigotimes^{m+l}$ denotes an $m+l$-fold contraction of two tensors. In the subsequent discussion, only the zeroth order and linear in gradient terms are needed because $x$ and $y$ contribute to the collision integral only over the distance of the potential range, which is small for a short range potential in comparison to the position dependence of the macroscopic quantities. In the spirit of the Chapman-Enskog method, for the linear in gradient terms the operators $f_i$ and $f_j$ are to be replaced respectively by their local equilibrium forms $f_i^{le}$ and $f_j^{le}$, which have been discussed in
Section III-3.4 in order to return only those non-equilibrium effects that are linear in gradients. Furthermore, the local equilibrium differences between the different species, characterized by $v_f$, $v_b$, $T_f$ and $T_b$, are associated with non-equilibrium effects and shall also be treated as perturbations. Thus it is reasonable to assume a common velocity $v_0$ and temperature $T$ for the local homogeneous equilibrium operators $f_i^{le}$ and $f_j^{le}$. Hence it is appropriate to write the collision term, Eq. (III.173), as

$$J^{(i,j)}(r, p_i) \simeq -\frac{i}{\hbar^3} \left( \frac{m_i + m_j}{m_i} \right)^3 2^6 \text{Tr}_{m_{i,t}} \int \int \int \int e^{-\frac{\hbar}{2} (\mathbf{x} - \mathbf{q} \cdot \mathbf{y} - \frac{\hbar}{2})}$$

$$\times T^{(i,j)}(\beta \mathbf{q} \kappa \kappa) f_i(r + \frac{\hbar}{2} - \frac{m_j}{m_i + m_j} \mathbf{x}, p_i + \beta - \mathbf{k}, t)$$

$$\times f_j(r + \frac{\hbar}{2} + \frac{m_i}{m_i + m_j} \mathbf{x}, p_j - \beta + \mathbf{k}, t) d\mathbf{k} d\beta d\mathbf{q} d\mathbf{y} d\mathbf{x}$$

$$\simeq J_h^{(i,j)} + J_e^{(i,j)} + J_{r}^{(i,j)} + J_{ne}^{(i,j)}.$$  \hspace{1cm} (III.226)
\[ \times \text{Tr} e^{-K_{\text{rel}}^{i,j}/kT} \left[ V_{i,j}, \Omega_{i,j} \left[ e^{-K_{\text{rel}}^{i,j}/kT} \right] \Omega_{i,j}^\dagger \right], \quad (III.227) \]

where

\[ K_{\text{rel}}^{i,j} = \frac{p_{op}^2}{2\mu_{ij}} + H_{\text{int}(i)} + H_{\text{int}(j)}, \quad (III.228) \]

with the reduced mass \( \mu_{ij} = m_i m_j / (m_i + m_j) \). The intertwining relation gives

\[ \Omega_{i,j} \left[ e^{-K_{\text{rel}}^{i,j}/kT} \right] \Omega_{i,j}^\dagger = \left[ e^{-H_{\text{rel}}^{i,j}/kT} \right] \Omega_{i,j} \Omega_{i,j}^\dagger, \quad (III.229) \]

where the relative full hamiltonian \( H_{\text{rel}}^{i,j} \) is

\[ \Omega_{i,j} \Omega_{i,j}^\dagger = 1. \quad (III.231) \]

The non-reactive binary collision assumption of the Section III-3.2 implies that the channel Møller operators are unitary

\[ H_{\text{rel}}^{i,j} = K_{\text{rel}}^{i,j} + V_{i,j}, \quad (III.230) \]

Hence the localized equilibrium collision term is

\[ J_k^{(i,j)} = -i \frac{\hbar^3}{\hbar} \left( \frac{m_i + m_j}{m_i} \right)^3 \frac{n_i}{(2\pi m_i kT)^{3/2} q_i} \frac{n_j}{(2\pi m_j kT)^{3/2} q_j} x \text{Tr} e^{-K_{\text{rel}}^{i,j}/kT} \left[ V_{i,j}, e^{-H_{\text{rel}}^{i,j}/kT} \right] \]

\[ = i \frac{\hbar^3}{\hbar} \left( \frac{m_i + m_j}{m_i} \right)^3 \frac{n_i}{(2\pi m_i kT)^{3/2} q_i} \frac{n_j}{(2\pi m_j kT)^{3/2} q_j} x \text{Tr} e^{-K_{\text{rel}}^{i,j}/kT} \left[ K_{\text{rel}}^{i,j}, U_{i,j} \right], \quad (III.232) \]

where the operator relation

\[ \left[ V_{i,j}, e^{-H_{\text{rel}}^{i,j}/kT} \right] = \left[ K_{\text{rel}}^{i,j}, U_{i,j} \right] \quad (III.233) \]

has been used. \( U_{i,j} \) describes the \( i-j \)th fragments' equilibrium correlation (see Section II-2.1). On carrying out the trace in Eq. (III.232), which is over
the relative motion of the two fragments, and the internal states of fragment $j$, keeping the momentum $p_i$ of the particle $i$ fixed, gives

$$\text{Tr}_r \left[ K^{i,j}_{\text{rel}}, U_{i,j} \right] = \left[ H_{\text{int}(i)}, \text{Tr}_r U_{i,j} \right]. \quad (\text{III.234})$$

Therefore $J^{(1,1)}_h$ vanishes immediately. For those fragments those density operators are diagonal in the internal state energy, which are the cases for the further discussion, $J^{(i,j)}_h$ vanish too.

The second term in Eq. (III.226) is a correction due to the center of mass of the colliding fragments being not at the macroscopic position $r$

$$J^{(i,j)}_c = \nabla \cdot 2\hbar^3 \left( \frac{m_i + m_j}{2m_i} \right)^3 \text{Tr}_{\text{int}(j)} \int \int \nabla_q T^{(i,j)}(\beta q k 0)|q=0 \times f^{\text{eq}}(r, p_i + \beta - k, t) \right) dk d\beta$$

$$= \nabla \cdot 2\hbar^3 \left( \frac{m_i + m_j}{2m_i} \right)^3 \text{Tr}_{\text{int}(j)} \int \int d\beta dk \nabla_q e^{\frac{2i}{k} \cdot \frac{m_j}{m_i + m_j} q}|q=0 \times < \beta | V_{i,j}, \Omega_{i,j} | k > f^{\text{eq}}(r, p_i + \beta - k, t)$$

$$\times f^{\text{eq}}(r, p_j - \beta + k, t) < k | \Omega^\dagger_{i,j} | \beta >$$

$$= \nabla \cdot 2\hbar^3 \left( \frac{m_i + m_j}{m_i} \right)^3 \left( \frac{2m_j}{m_i + m_j} \right) \frac{n_i}{(2\pi m_i kT)^{3/2} q_i} \frac{n_j}{(2\pi m_j kT)^{3/2} q_j}$$

$$\times \text{Tr}_r e^{-K^{i,j}_{\text{rel}}/kT} \left[ r_{op}, \left[ V_{i,j}, \Omega_{i,j} \left[ e^{-K^{i,j}_{\text{rel}}/kT} \right] \Omega^\dagger_{i,j} \right] \right]. \quad (\text{III.235})$$

Here the derivative with respect to $q$ has been evaluated by considering a position representation of the operators and carrying out the derivative to obtain the anticommutator $[r_{op}, \_\_\]$. Further simplification of this expression is accomplished by using Eqs. (III.229) and (III.233)

$$J^{(i,j)}_c = \nabla \cdot 2\hbar^3 \left( \frac{m_i + m_j}{m_i} \right)^3 \left( \frac{2m_j}{m_i + m_j} \right) \frac{n_i}{(2\pi m_i kT)^{3/2} q_i} \frac{n_j}{(2\pi m_j kT)^{3/2} q_j}$$

$$\times \text{Tr}_r e^{-K^{i,j}_{\text{rel}}/kT} \left[ r_{op}, \left[ K^{i,j}_{\text{rel}}, U_{i,j} \right] \right]. \quad (\text{III.236})$$

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It is seen that the first non-locality correction is related to the fragment-fragment equilibrium correlations. In other words it gives rise to density corrections from the collision terms. Since only the monomer-monomer particle correlations have been considered, it is consistent to drop the nonlocal collision terms involving the bound pairs from further consideration. For the monomer-monomer collision, $J_c^{(1,1)}$ can be simplified using the operator identity

$$[A, [B, C]_-]_+ = [[A, B]_-, C]_+ + [B, [A, C]_+]_-,$$  \hspace{1cm} (III.237)

in the form

$$[r_{op}, [K_{rel}, U]_-]_+ = \frac{i2\hbar}{m_1} [p_{op}, U]_+ + [K_{rel}, [r_{op}, U]_+]_-.$$  \hspace{1cm} (III.238)

On taking the trace, the collision term $J_c^{(1,1)}$ can be written as

$$J_c^{(1,1)} = -\nabla \cdot \frac{n_f^2 \Lambda^6}{m_1 \hbar^3} \text{Tr}_r e^{-K_{CM}/kT} p_{op} U$$

$$= J_{cn} \cdot \nabla \ln n_f + J_{cv} \cdot \nabla v_0 + J_{cT} \cdot \nabla \ln T,$$  \hspace{1cm} (III.239)

with

$$J_{cn} = \frac{-2n_f^2 \Lambda^6}{m_1 \hbar^3} \text{Tr}_r e^{-K_{CM}/kT} p_{op} U,$$  \hspace{1cm} (III.240)

$$J_{cv} = \frac{-2n_f^2 \Lambda^6}{mkT \hbar^3} \text{Tr}_r e^{-K_{CM}/kT} (p_1 + p_{op} - m_1 v_0) p_{op} U,$$  \hspace{1cm} (III.241)

and

$$J_{cT} = -\frac{3}{2} J_{cn} - \frac{n_f^2 \Lambda^6}{mkT \hbar^3} \text{Tr}_r e^{-K_{CM}/kT} p_{op} (K_{CM} U + kT^2 U_T).$$  \hspace{1cm} (III.242)

The second correction term $J_r^{(i,j)}$, according to Eq. (III.225), is

$$J_r^{(i,j)} = -4 \hbar^3 h \left( \frac{m_i + m_j}{2m_i} \right)^3 \int \int \nabla \kappa T^{(i,j)}(\beta 0 \kappa) |\kappa=0$$

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\[
\times \left( \frac{m_i}{m_i + m_j} f^{le}_{i}(r, p_i + \beta - k, t) \nabla f^{le}_{j}(r, p_j - \beta + k, t) \right) \\
- \frac{m_j}{m_i + m_j} f^{le}_{j}(r, p_j - \beta + k, t) \nabla f^{le}_{j}(r, p_i + \beta - k, t) \right) \right) \right) \right) \right) \right) \right) \right) \right) \right) \\
= - \frac{i4\hbar^3}{h} \left( \frac{m_i + m_j}{2m_i} \right) ^3 \text{Tr}_{\text{int}(i)} \int \int d\beta dk \left< [V_{ij}, \Omega_{ij}] \right> \\
x \left[ r_{op}, |k| > \left( \frac{m_i}{m_i + m_j} f^{le}_{i}(r, p_i + \beta - k, t) \nabla f^{le}_{i}(r, p_i + \beta - k, t) \right) \right]_+ \left< f^{le}_{i}(r, p_i + \beta - k, t) \right> < k \right> | \beta > . \\
(III.243)
\]

The gradient can be carried out by recognizing that the macroscopic position \( r \) dependence in operator \( f^{le}_{i} \) is solely through the three hydrodynamic variable \( n_i, v_0, \) and \( T \)

\[
\left( \frac{m_i}{m_i + m_j} f^{le}_{i}(r, p_i + \beta - k, t) \nabla f^{le}_{j}(r, p_j - \beta + k, t) \right) \\
- \frac{m_j}{m_i + m_j} f^{le}_{j}(r, p_j - \beta + k, t) \nabla f^{le}_{j}(r, p_i + \beta - k, t) \right) \right) \right) \right) \right) \right) \right) \right) \right) \\
= \frac{n_i}{(2\pi m_i kT)^{3/2} q_i} \frac{n_j}{(2\pi m_j kT)^{3/2} q_j} \\
\times \text{Tr}_r e^{-K^{ij} c M / kT} e^{-K^{ij} c M / kT} \left\{ \frac{m_i}{m_i + m_j} \nabla \ln n_j - \frac{m_j}{m_i + m_j} \nabla \ln n_i \\
+ \left[ \frac{3(m_j - m_i)}{2(m_i + m_j)} + T \left[ \frac{m_i q_j}{m_i + m_j} \frac{\partial}{\partial T} \left( \frac{1}{q_j} \right) - \frac{m_j q_i}{m_i + m_j} \frac{\partial}{\partial T} \left( \frac{1}{q_i} \right) \right] \\
+ \frac{m_i}{m_i + m_j} \frac{H_{\text{int}(j)}}{kT} - \frac{m_j}{m_i + m_j} \frac{H_{\text{int}(i)}}{kT} + \left( P_{i,j} - (m_i + m_j)v_0 \right) \cdot k \right] \nabla \ln T \\
+ \frac{1}{kT} k \cdot \nabla v_0 \right\} . \\
(III.244)
\]

where

\[
P_{i,j} = p_i + p_j \\
(III.245)
\]
is the momentum of the center of mass of the two colliding molecules. In the case of $J_{r}^{(1,1)}$, only two terms in Eq. (III.244) contribute

$$J_{r}^{(1,1)} = \frac{-in_{f}^{2} \Lambda^{6}}{2kT h^{3}} \text{Tr} e^{-K_{CM}/kT} \left[ V, \Omega \left[ e^{-K_{rel}/kT} p_{op}, r_{op} \right] + \Omega^{\dagger} \right]$$

with gradient corrections having velocity gradient coefficient

$$J_{rv} = \frac{-in_{f}^{2} \Lambda^{6}}{2kT h^{3}} \text{Tr} e^{-K_{CM}/kT} \left[ V, \Omega \left[ e^{-K_{rel}/kT} p_{op}, r_{op} \right] + \Omega^{\dagger} \right]$$

and temperature gradient coefficient

$$J_{rT} = \frac{-in_{f}^{2} \Lambda^{6}}{2m_{1} kT h^{3}} \text{Tr} e^{-K_{CM}/kT} \left[ V, \Omega \left[ e^{-K_{rel}/kT} p_{op}, r_{op} \right] + \Omega^{\dagger} \right]$$

Finally it is useful to write the collision terms $J_{ne}^{(i,j)}$ in terms of relaxation operators

$$J_{ne}^{(i,j)}(r_{i}, p_{i}, t) \equiv -f_{ie}^{(i,j)} R^{(i,j)} \phi$$

where $i, j, k = 1, b$. The collision cross section $\mathcal{C}^{(i,j)}$ is defined as

$$\mathcal{C}^{(i,j)}(f_{i}^{le}, f_{j}^{le}) = \frac{i h^{3}}{\hbar} \left( \frac{m_{i} + m_{j}}{m_{i}} \right)^{3} \text{Tr}_{int(i)} \int \int d\beta d\mathbf{k} < \beta | V_{ij}, \Omega_{ij} | \mathbf{k} >$$

$$\times \left[ f_{i}^{le}(r, \frac{m_{i}}{m_{i} + m_{j}} p_{i,j} - \mathbf{k}, t) \phi_{i}(\frac{m_{i}}{m_{i} + m_{j}} p_{i,j} - \mathbf{k}, t) \right] \times \left[ f_{j}^{le}(r, \frac{m_{j}}{m_{i} + m_{j}} p_{i,j} + \mathbf{k}, t) \right] < k | \Omega_{ij}^{\dagger} > | \beta >$$

$$= \frac{i h^{3}}{\hbar} \left( \frac{m_{i} + m_{j}}{m_{i}} \right)^{3} \frac{n_{i}}{n_{j}} \frac{n_{i}}{(2\pi m_{i} kT)^{3/2} q_{i}} \frac{n_{j}}{(2\pi m_{j} kT)^{3/2} q_{j}}$$

$$\times \text{Tr} e^{-K_{CM}/kT} \left[ V_{ij}, \Omega_{ij} \left[ e^{-K_{rel}/kT} \phi_{i} \right] \Omega_{ij}^{\dagger} \right] ,$$

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and as

\[ 
\mathcal{C}^{(i,j)}(f^{le}_i f^{le}_j \phi_j) = \frac{i\hbar^3}{h} \left( \frac{m_i + m_j}{m_i} \right)^3 \text{Tr}_{int(j)} \int \int d\beta d\mathbf{k} < \beta | V_{i,j}, \Omega_{i,j} | \mathbf{k} > 
\times \left[ f^{le}_i(\mathbf{r}, \frac{m_i}{m_i + m_j} \mathbf{P}_{i,j} - \mathbf{k}, t) f^{le}_j(\mathbf{r}, \frac{m_j}{m_i + m_j} \mathbf{P}_{i,j} + \mathbf{k}, t) 
\times \phi_j \left( \frac{m_j}{m_i + m_j} \mathbf{P}_{i,j} + \mathbf{k}, t \right) \right] < k | \Omega^\dagger_{i,j} > | \beta > 
\]

\[ 
= \frac{i\hbar^3}{h} \left( \frac{m_i + m_j}{m_i} \right)^3 \frac{n_i}{n_j} \left( \frac{2\pi m_i kT}{{\beta}^{3/2}} q_i \right) \left( \frac{2\pi m_j kT}{{\beta}^{3/2}} q_j \right) 
\times \text{Tr}_e e^{-\mathcal{K}^{le}_{i+} / kT} \left[ V_{i,j}, \Omega_{i,j} \left[ e^{-\mathcal{K}^{le}_{i+} / kT} \phi_j \right] \Omega^\dagger_{i,j} \right]. 
\] (III.251)

It is noted that the perturbations \( \phi_i \) and \( \phi_j \) have different momentum dependences. This completes the linearization of the collision operators in Eq. (III.226).

b) Linearizing the Generalized Boltzmann Equation

The Generalized Boltzmann equation (III.153) is now linearized about local equilibrium. In the Chapman-Enskog method, the time derivatives are to be eliminated by use of the equations of continuity, motion and energy, so they are to be treated as linear in position gradients. This implies that only the local equilibrium forms \( f^{le}_{f_1} \) and \( f^{le}_{c_1} \) (see Section III-3.4) are to appear in the time derivative. The collision term gives rise to four types of contributions for each collision as discussed in the last subsection. The expansion of the generalized Boltzmann equation then can be written in Wigner function representation as

\[ 
\frac{\partial (f^{le}_{f_1} + f^{le}_{c_1})}{\partial t} + \frac{\mathbf{P}_1}{m_1} \cdot \nabla (f^{le}_{f_1} + f^{le}_{c_1}) - \sum_{a=1,b} J^{(1,i)}_{\alpha} = \sum_{i=1,b} \sum_{a=h,c,r} J^{(1,i)}_{ne} 
\] (III.252)
with all terms determined solely by the local equilibrium state collected together before the equality sign and the terms dependent on the perturbation φ after the equality sign. Since only the monomer-monomer correlations are treated at present, it is consistent to consider only the nonlocal corrections arising from monomer-monomer collisions, namely the $J^{(1,1)}$ terms, thus

$$\frac{\partial (f^{le}_{cl} + f^{lh}_{cl})}{\partial t} + \frac{p_1}{m_1} \cdot \nabla (f^{le}_{cl} + f^{lh}_{cl}) - J^{(1,1)}_{h} - J^{(1,1)}_{c} - J^{(1,1)}_{r} = \sum_{i=1,\delta} J^{(1,i)}_{ne}. \quad (III.253)$$

Finding the solution to this generalized quantum Boltzmann equation is here referred to as Scheme II, see Section III-4.4.

The linearization of the renormalized quantum Boltzmann equation\(^{52}\) (III.103) is a special case of Eq. (III.253) when the dimers are neglected

$$\frac{\partial (f^{le}_{cl} + f^{lh}_{cl})}{\partial t} + \frac{p_1}{m_1} \cdot \nabla (f^{le}_{cl} + f^{lh}_{cl}) - J^{(1,1)}_{h} - J^{(1,1)}_{c} - J^{(1,1)}_{r} = J^{(1,1)}_{ne}. \quad (III.254)$$

The solution for the renormalized quantum Boltzmann equation (III.254) is presented as Scheme I, see Section III-4.2.

This completes the linearization of the two quantum Boltzmann equations (III.153) and (III.103).

c) Linearizing the Bound Pair Equation

The linearization of the bound pair equation (III.156) follows the same procedure as the linearization of the generalized quantum Boltzmann equation

$$\frac{\partial f^{le}_{b12}}{\partial t} + \frac{p_b}{m_b} \cdot \nabla f^{le}_{b12} - \sum_{i=1,\alpha} J^{(b,i)}_{\alpha} = -\frac{i}{\hbar} [H_{int}, f^{ne}_{b12}]_+ + \sum_{i=1,\delta} J^{(b,i)}_{ne}, \quad (III.255)$$

with all terms discussed either in Section III-3.4 or in the last subsection. Here again, the collisional non-locality involving the bound pairs for a gas
mixture is neglected for a gas that is moderately dense in monomers with relatively few bound pairs. The latter gives rise to a second virial contribution at equilibrium. A possible off diagonality of the density operator in internal states is not of present interest, so the first term in the right hand side is dropped. The resulting linearized bound pair equation is

\[
\frac{\partial f_{b12}^l}{\partial t} + \frac{p_b}{m_b} \cdot \nabla f_{b12}^l = \sum_{i=1, b} J_{ne}^{(b,i)}. \tag{III.256}
\]

This equation is solved in Section III-4.4.

**d) Linearizing the Modified Pair Correlation Equation**

The pair correlation operator in equation (III.161) is first cast into Wigner function form for the center of mass motion, remaining an operator in relative motion, compare Eqs. (III.181) and (III.189). This is written as

\[
\frac{\partial f_{c12}}{\partial t} + \frac{P}{2m_1} \cdot \nabla f_{c12} = -i\mathcal{L}_{rel} f_{c12} - \mathbf{v}_{12} f_{f12} + \frac{f_{c12}^* - f_{c12}}{\tau}, \tag{III.257}
\]

where \( f_{f12} \) is the properly transformed product of free density operators. Since it is the Wigner function form of the free density operator, Eqs. (III.175) and (III.176), that has been used to express the local equilibrium and small gradient behaviour of the free particles, the two particles can be localized at different positions and a gradient expansion of the product around the center of mass position \( R \) is appropriate. On carrying out this computation \( f_{f12} \) is given by

\[
f_{f12}(R,P,t) \equiv f_{f12}^{lh} + f_{f12}^{lnh} + f_{f12}^{lh}(\phi_1 + \phi_2)
= n_2^2 e^{-K_{CM}/kT_f} \Lambda_r^3 \left\{ e^{-K_{rel}/kT_f} + \frac{e^{-K_{rel}/kT_f}}{2kT_f} \text{p}_{op}, \text{r}_{op} \right\} : \nabla f
\]
while the local homogeneous equilibrium form for the pair correlation function is

\[ f_{cl2}(\mathbf{R}, \mathbf{P}, t) = \frac{n_f^2 e^{-K_{CM}/kT_f}}{(4\pi m_1 kT_f)^{3/2}} \Lambda \gamma^3 U(T_f), \quad (\text{III.259}) \]

on the basis that this is the form that would occur if the pair correlations were at complete equilibrium with the free particle motion through interactions with a third "free" particle. This treatment is based on the assumption that the monomer density is larger than the density of the bound pair. The particle momenta \( p_1 \) and \( p_2 \) in the perturbation terms \( \phi_1 \) and \( \phi_2 \) are to be interpreted in terms of center of mass and relative momenta according to \( \frac{1}{2} \mathbf{P} + \mathbf{p}_{op} \). Within the philosophy of the Chapman Enskog procedure, the modified pair correlation equation (III.257) is solved together with the renormalized Boltzmann equation (III.254) in Section III-4.2 and with the generalized Boltzmann equation (III.253) and the bound pair equation (III.256) in Section III-4.4.

III-4.2 Scheme I: Solution

In this section the modified pair correlation equation (III.257) and the renormalized quantum Boltzmann equation (III.254) are solved. The basic philosophy for the solution is that of Chapman-Enskog, while the detailed implementation is not the same as that in the standard theory\(^{131,16,132,133}\) since, for example, the modified pair correlation equation is not a Boltzmann equation and a potential energy contribution is not part of the standard theory of the Boltzmann equation. This section has two subsections.
a) The Modified Pair Correlation Equation

The time derivative is completely expressed in terms of the time dependence of the parameters specifying the density of correlated particles \( n_c \), the mean velocity of correlated pairs \( v_c \) and the local temperature of the correlated pairs \( T_c \). These in turn can be obtained from the equations of change by taking the appropriate moments of Eq. (III.257). In writing down the Wigner function for the correlations, Eqs. (III.181) and (III.189), the correlation density, temperature and mean velocity have all been taken as independent parameters. Since these can differ from their values when the correlations are in equilibrium with the freely moving particles, these differences are associated with the nonuniformity of the gas and thus scale with gradients as do the perturbations \( \phi_1 \) and \( \phi_c \). Rather than introducing separate parameters, it would be equivalent to include the differences as part of the perturbation \( \phi_c \). But having introduced independent explicit parameters, it is necessary to recognize that to avoid redundancy, the perturbation \( \phi_c \) must not contribute to these parameters. As a consequence the three auxiliary conditions

\[
\text{Tr}_{rel} \int f_c^{le} \phi_c dP = 0
\]
\[
\text{Tr}_{rel} \int P f_c^{le} \phi_c dP = 0
\]
\[
\text{Tr}_{rel} \int \left[ \frac{(P-2m_1v_c)^2}{4m_1} + H_{rel} \right] f_c^{le} \phi_c dP = 0
\]

on \( \phi_c \) are imposed. These are exactly the correlation contributions to the general auxiliary conditions discussed in Section III-3.5. With these conditions, integrating Eq. (III.257) over \( P \) and tracing over the relative motion, an equation of change for \( n_c \) is obtained

\[
\frac{\partial n_c}{\partial t} + \nabla \cdot (n_c v_c) = \frac{n^e_c - n_c}{\tau}.
\]
Here $n_e^s \equiv n_f^2 \Lambda_r (T_f) \text{Tr}_{rel} U(T_f)$ is the equilibrium density of pair correlations as determined by $\rho_f$. The corresponding equation for the velocity $v_c$ is, from the $P/2m_1$ moment of Eq. (III.257) and after eliminating a contribution from $\partial n_c/\partial t$,

$$\frac{\partial v_c}{\partial t} + v_c \cdot \nabla v_c + \frac{1}{2n_cm_1} \nabla \cdot P_c = \frac{n_c^s (v_f - v_c)}{n_c \tau},$$

(III.262)

with the correlation pressure tensor

$$P_c = \frac{1}{2m_1} \text{Tr}_{rel} \int (P - 2m_1 v_c)(P - 2m_1 v_c) f_{c12} dP.$$  

(III.263)

Finally the equation of change for the temperature is obtained from the equation of change for the correlation energy

$$\varepsilon_{corr} \equiv \varepsilon_{CM} + \varepsilon_{rel} = \frac{1}{n_c} \text{Tr}_{rel} \int \left[ \frac{(P - 2m_1 v_c)^2}{4m_1} + H_{rel} \right] f_{c12} dP.$$  

(III.264)

The rate of the change for this energy per particle is

$$\frac{\partial \varepsilon_{corr}}{\partial t} + v_c \cdot \nabla \varepsilon_{corr} = -\frac{1}{n_c} P_c : \nabla v_c$$

$$-\frac{1}{n_c} \nabla \cdot q_c + \frac{\sigma_c}{n_c} + \frac{n_c \varepsilon_{corr} - \varepsilon_{corr}}{\tau},$$

(III.265)

with correlation energy heat flux

$$q_c \equiv \text{Tr}_{rel} \int \frac{P - 2m_1 v_c}{2m_1} \left[ \frac{(P - 2m_1 v_c)^2}{4m_1} + H_{rel} \right] f_{c12} dP.$$  

(III.266)

and correlation energy production

$$\sigma_c \equiv -\frac{1}{m_1} \text{Tr}_{rel} \int (p_{op} \cdot \nabla V + \nabla V \cdot p_{op}) f_{f12} dP$$

$$\approx -\frac{n_f^2 \Lambda_r (T_f)}{2m_1 kT_f} \text{Tr}_{rel} (p_{op} \cdot \nabla V + \nabla V \cdot p_{op}) \left[ e^{-K_{rel}/kT_f} p_{op, r_{op}} \right] : \nabla v_f$$

$$= +n_f^2 \int V dr' \nabla \cdot v_f.$$  

(III.267)
The approximation is the result of using Eq. (III.258) and the subsequent evaluation of the trace. Here the "equilibrium" correlation energy is obtained from Eqs. (III.259) and (III.264) as

$$
\varepsilon_{\text{corr}} = \frac{3}{2} kT_f + \frac{\text{Tr}_{rel} H_{rel} U(T_f)}{\text{Tr}_{rel} U(T_f)}.
$$

At local equilibrium, the correlation energy is determined solely by the temperature $T_c$ so that with the correlation heat capacity $C_{\text{corr}} = \partial \varepsilon_{\text{corr}} / \partial T_c$, the energy equation of change is equivalent to an equation of change for $T_c$.

Eliminating the time dependence in the modified pair correlation equation by means of the above results and retaining at most linear in gradient terms, this equation can be written

$$
\frac{\partial f^{le}_{c12}}{\partial t} + \frac{p}{2m_1} \cdot \nabla f^{le}_{c12} - f^{le}_{c12} \frac{n_c^e - n_c}{n_c^e} \frac{n_c}{n_c^e} \frac{\varepsilon_{\text{corr}} - \varepsilon_{\text{corr}}}{C_{\text{corr}} T_c^2}
$$

$$
= f^{le}_{c12} \left[ L_{T_c} \cdot \nabla \ln T_c + L_{vc}^{(2)} : \left[ \nabla v_c \right]^{(2)} + L_{vc}^{(0)} \nabla \cdot v_c \right]
$$

$$
+ n_c^e f^{le}_{c12} \left\{ \frac{p - 2m_1 v_c}{kT_c} \cdot \frac{\varepsilon_{\text{corr}} - \varepsilon_{\text{corr}}}{C_{\text{corr}} T_c^2} \right\}
$$

$$
+ \left[ G^2 - \frac{3}{2} + U^{-1} T_c U_T - \frac{E^U}{kT_c} \right] \frac{\varepsilon_{\text{corr}} - \varepsilon_{\text{corr}}}{C_{\text{corr}} T_c^2}
$$

$$
= -i L_{rel} \left[ f^{le}_{c12}(1 + \phi_{c12}) \right] - i V_{12} f^{lh}_{f12}(1 + \phi_1 + \phi_2)
$$

$$
\frac{1}{2m_1 kT_f} \cdot \nabla \ln T_f
$$

$$
= - \frac{i}{2kT_f} V_{12} \left[ f^{lh}_{f12} p_{op} \right] \cdot \nabla v_f + \frac{1}{\tau} \left\{ f^{le}_{c12} - \frac{n_c^e}{n_c} f^{le}_{c12} - f^{le}_{c12} \Phi_{12} \right\}.
$$

Here the dimensionless center of mass momentum $G \equiv (p - 2m_1 v_c) / \sqrt{4m_1 kT_c}$ has been introduced to simplify the notation. $E^U$ is a short-hand notation for

$$
E^U(T_c) = \frac{\text{Tr}_{rel} \left( H_{rel} e^{-H_{rel}/kT_c} - K_{rel} e^{-K_{rel}/kT_c} \right)}{\text{Tr}_{rel} U(T_c)}.
$$

(III.270)
This quantity enters naturally in the kinetic theory treatment. It is noted that there is no term involving the gradient of $n_c$ in this equation, consistent with the notion that the perturbations are due solely to temperature and velocity gradients. The three expansion coefficients appearing in this equation are

$$L_{Tc} = \left( \mathcal{G}^2 - \frac{5}{2} + U^{-1}T U_T - \frac{E^U}{kT_c} \right) \sqrt{\frac{kT_c}{m_1}} \mathcal{G}, \quad \text{(III.271)}$$

$$L_{v_c}^{(2)} = 2[\mathcal{G}]^{(2)} \quad \text{(III.272)}$$

and

$$L_{v_c}^{(0)} = \left( \frac{2}{3} - \frac{k}{C_{corr}} \right) \left( \mathcal{G}^2 - \frac{3}{2} \right) - \frac{k}{C_{corr}} \left( U^{-1}T U_T - \frac{E^U}{kT_c} \right)$$

$$+ \left( \mathcal{G}^2 - \frac{3}{2} + U^{-1}T U_T - \frac{E^U}{kT_c} \right) \frac{n^2_f}{n_c} \frac{\int V dV}{T_c}. \quad \text{(III.273)}$$

Consistent with the gradient expansions of the perturbations, Eqs. (III.304) and (III.280), all terms in Eq. (III.269) should be proportional to a gradient. Those that are not explicitly of this form involve the differences between the corresponding correlated and free parameters, for example $T_c - T_f$. Since these differ only because of the spatial nonuniformity of the gas, these differences must be expressible in terms of gradients. As there is only the temperature and velocity gradients available, rotational symmetry requires that each difference can only depend on one gradient, specifically

$$n_c - n^e_c = n^e_c \Delta_c \nabla \cdot v_0$$

$$T_c - T_f = T \tau_c \nabla \cdot v_0$$

$$v_c - v_f = D_c \nabla \ln T. \quad \text{(III.274)}$$

The first combination of quantities that needs to be explicitly expressed in terms of the gradients is

$$-i \mathcal{L}_{rel} f^{le}_{c12} - i \mathcal{L}_{12} f^{lh}_{f12}$$
with the dimensionless center of mass momentum \( \mathcal{G}_f = (P - 2m_1v_f)/\sqrt{4m_1kT_f} \).

The other combination is

\[
\mathcal{F}_{c12} - \frac{n_e^c}{n_e} \mathcal{F}_{c12}^{\text{rel}} = -\mathcal{F}_{c12} \left[ \sqrt{\frac{4m_1}{kT}} D_c \mathcal{G} \cdot \nabla \ln T \right. \\
+ \left. \left( \mathcal{G}^2 - \frac{3}{2} + U^{-1}T_cU_T - \frac{E^U}{kT_c} \right) \tau_c \nabla \cdot v_0 \right]. \tag{III.276}
\]

Subsequent to making this expansion of the difference between free and correlated parameters, there is no need for further distinction between these parameters so that, for simplification, all temperatures \( T_f = T_c = T \) are subsequently expressed by the same symbol, as are the mean velocities \( v_f = v_c = v_0 \).

With these evaluations, the linear in gradients form for the modified pair correlation equation splits into three separate equations, first is the equation for the scalar multiplying \( \nabla \cdot v_0 \),

\[
f_{c12}^{(0)} = i\mathcal{L}_{\text{rel}} \left[ f_{c12}^{\text{rel}} C_{c12} \right] + i\mathcal{V}_{12} f_{j12}^{\text{th}} \left[ \mathcal{G}^2 - \frac{3}{2} + \frac{K_{\text{rel}} - E^U}{kT_c} \right] \tau_c + \Delta_c \\
- \frac{i}{6kT} \mathcal{V}_{12} \left[ f_{j12}^{\text{th}} p_{\text{op}}, r_{\text{op}} \right] + i\mathcal{V}_{12} \left[ f_{j12}^{\text{th}} (C_1 + C_2) \right] + \frac{1}{\tau} f_{c12}^{\text{rel}} C_{c12}. \tag{III.277}
\]

Second is the equation for the vector multiplying \( \nabla \ln T \),

\[
f_{c12}^{\text{L}_{\text{T}}C} = i\mathcal{L}_{\text{rel}} \left[ f_{c12}^{\text{rel}} A_{c12} \right] - \frac{i}{\sqrt{4m_1kT_f}} \mathcal{G} \cdot \mathcal{V}_{12} \left[ f_{j12}^{\text{th}} p_{\text{op}}, r_{\text{op}} \right] \\
+ i\mathcal{V}_{12} \left[ f_{j12}^{\text{th}} (A_1 + A_2) \right] + iD_c \sqrt{\frac{4m_1}{kT}} \mathcal{G} \mathcal{V}_{12} f_{j12}^{\text{th}} + \frac{1}{\tau} f_{c12}^{\text{rel}} A_{c12}. \tag{III.278}
\]
Lastly is the equation for the second rank symmetric traceless tensor multiplied by $[\nabla \nu_0]^{(2)}$,

$$f_c^e \mathbf{L}_c^{(2)} = i L_{rel} [f_{c12}^e \mathbf{B}_{c12}] - \frac{i}{2kT} \mathcal{V}_{12} \left[ f_{f12}^p \mathbf{p}_0, \mathbf{r}_0 \right]^{(2)} + i \mathcal{V}_{12} \left[ f_{f12}^h (\mathbf{B}_1 + \mathbf{B}_2) \right] + \frac{1}{\tau} f_{c12}^e \mathbf{B}_{c12}. \tag{III.279}$$

These three equations are to determine the three functions $C_c$, $A_c$ and $B_c$ arising in the gradient expansion of $\phi_c$

$$\phi_c = -A_c \cdot \nabla \ln T_c - B_c : [\nabla \nu_0]^{(2)} - C_c \nabla \cdot \nu_c. \tag{III.280}$$

This will be done by picking appropriate functional forms for these functions and taking moments. It is to be noted that the time derivatives of Eq. (III.257) were eliminated by the use of moments associated with number, velocity and energy averages and these required the auxiliary conditions (III.260). In terms of the three functions $C_c$, $A_c$ and $B_c$, these auxiliary conditions become

$$\text{Tr}_{rel} \int f_c^e C_c dP = 0 \tag{227}$$

$$\text{Tr}_{rel} \int \mathcal{G}_c^e A_c dP = 0 \tag{228}$$

and

$$\text{Tr}_{rel} \int (K_{CM} + H_{rel}) f_c^e C_c dP = 0. \tag{III.281}$$

It is easy to verify that on taking appropriate moments of Eqs. (III.277-III.279), these auxiliary conditions are consistent with these equations.

A one moment approximation to each of the three perturbation functions is now proposed. For this calculation it is assumed that the appropriate moments are proportional to the (energy production free parts of the) corresponding left hand side of Eqs. (III.277-III.279). Thus the form for $C_c$ is

$$227$$
taken as

\[ C_c = \left[ \left( \frac{2}{3} - \frac{k}{C_{corr}} \right) \left( \mathcal{G}^2 - \frac{3}{2} \right) - \frac{k}{C_{corr}} \left( U^{-1}TU_T - \frac{E^U}{kT} \right) \right] c_0^c \]  

\text{Eq. (III.282)}

with expansion coefficient \( c_0^c \). This satisfies the two relevant auxiliary conditions of Eq. (III.281). The moment of Eq. (III.277) is taken with respect to

\[ \frac{2}{3} \left( \mathcal{G}^2 - \frac{3}{2} \right) - \frac{H_{rel} - \varepsilon_{rel}}{C_{rel}T} \]  

\text{Eq. (III.283)}

to give

\[ c_0^c = \tau \left[ 1 + \frac{3}{2C_{rel}T} \Lambda \Theta \frac{3}{2} \int Vdr' \right], \]  

\text{Eq. (III.284)}

with the potential factor arising from the \([f^{\text{th}}_{j12P_{op},r_{op}}]_+\) term in Eq. (III.277).

The analogous choice for the \( A_c \) moment satisfying Eq. (III.281) is

\[ A_c = \mathcal{G} \left( \mathcal{G}^2 - \frac{5}{2} + U^{-1}TU_T - \frac{E^U}{kT} \right) a_1^c. \]  

\text{Eq. (III.285)}

Taking the matrix element of Eq. (III.278) with

\[ \left( \mathcal{G}^2 - \frac{5}{2} + \frac{H_{rel} - \varepsilon_{rel}}{kT} \right) \mathcal{G} \]  

\text{Eq. (III.286)}

gives

\[ a_1^c = \tau \sqrt{\frac{kT}{m_1}} \left[ 1 - \frac{2}{\Lambda \Theta \frac{3}{2} \int Vdr'} \right]. \]  

\text{Eq. (III.287)}

The obvious choice for \( B_c \) is \([\mathcal{G}]^{(2)}b_0^c\). The expansion coefficient is obtained from the \([\mathcal{G}]^{(2)}\) matrix element of Eq. (III.279) to be \( b_0^c = 2\tau \).

b) The Renormalized Boltzmann Equation

The time derivative in Eq. (III.254) involves both the free and correlated local equilibrium Wigner functions which are respectively parameterized by
$n_f$, $v_f$, $T_f$ and $n_c$, $v_c$, $T_c$. Since a time derivative is to scale as a position gradient in the Chapman Enskog theory for the calculation of transport coefficients, any deviation between these parameters that is proportional to a gradient can be ignored when estimating a time derivative and both can be expressed in terms of the fluid parameters $n$, $v_0$ and $T$. Moreover the time derivative always occurs in the combination $\frac{\partial}{\partial t} + \frac{p_1}{m_1} \cdot \nabla$ in the Boltzmann equation. The appropriate set of equations to be used in evaluating the time derivatives is examined first, then the resulting form of the Chapman Enskog equation is discussed.

From the equation of continuity (III.119), the rate of change of the full density is

$$\frac{\partial n_1}{\partial t} + \frac{p_1}{m_1} \cdot \nabla n_1 = \frac{p_1 - m_1 v_0}{m_1} \cdot \nabla n_1 - n_1 \nabla \cdot v_0.$$  \hfill (III.288)

The equation of motion (III.120) gives to terms linear in gradients

$$\frac{\partial v_0}{\partial t} + \frac{p_1}{m_1} \cdot \nabla v_0 = \frac{p_1 - m_1 v_0}{m_1} \cdot \nabla v_0 - \frac{1}{n_1 m_1} \nabla p_1,$$  \hfill (III.289)

where $P_1 = n_1 k T (1 + n_1 B)$ is the local equilibrium pressure with $n_f^2 \rightarrow n_1^2$ appropriate to keeping only second order in density terms. For the local energy $\varepsilon_1 \equiv \varepsilon_1^K + \varepsilon_1^V$, energy conservation, see Eqs. (III.121) and (III.126), implies that to terms linear in the gradient

$$\frac{\partial \varepsilon_1}{\partial t} + \frac{p_1}{m_1} \cdot \nabla \varepsilon_1 = \frac{p_1 - m_1 v_0}{m_1} \cdot \nabla \varepsilon_1 - \frac{p_1}{n_1} \nabla \cdot v_0.$$  \hfill (III.290)

Now it is $T$ and $n_f$ that enter explicitly into the linearized Boltzmann equation. The rate of change of temperature is obtained from the energy equation while the equation for $n_f$ is derived from the relation between $n_f$ and $n_1$, Eqs. (III.192) and at equilibrium

$$\frac{n_c}{n_f^2} = -2B = \Lambda^3 T_{rel} U.$$  \hfill (III.291)
The temperature equation is considered first.

According to Eq. (III.205) the kinetic energy depends on both temperature $T$ and density $n_f$, likewise the potential energy (ignoring gradient corrections)

$$n_1\varepsilon_1^V(\mathbf{r}, t) = \frac{1}{2}\text{Tr}_{12}V_{12}\delta(\mathbf{r}_1 - \mathbf{r})\Omega \rho_{j1}\rho_{j2}\Omega^\dagger$$

$$= \frac{1}{2}n_f^2\Lambda_{\text{rel}}^V\text{Tr}_{\text{rel}}V e^{-H_{\text{rel}}/kT}. \quad (\text{III.292})$$

By thermodynamics, and consistent with the relations between the local equilibrium quantities, the equilibrium energy per particle depends on volume $(1/n_1)$ and temperature $T$ according to

$$d\varepsilon_1 = C_v dT + \left(\frac{\partial \varepsilon_1}{\partial (1/n_1)}\right)_T d(1/n_1)$$

$$= C_v dT - \left[T \left(\frac{\partial P_1}{\partial T}\right)_n - P_1\right] \frac{1}{n_1^2}dn_1$$

$$= C_v dT - kT^2\frac{dB}{dT}dn_1, \quad (\text{III.293})$$

with constant volume heat capacity

$$C_v = (\partial \varepsilon_1/\partial T)_n = \frac{3}{2}k - 2n_1kT\frac{dB}{dT} - n_1kT^2\frac{d^2B}{dT^2}$$

$$= k \left[\frac{3}{2} - n_1 \frac{d}{dT} \left(T^2 \frac{dB}{dT}\right)\right]. \quad (\text{III.294})$$

On combining the equations of change for energy and number density, the equation

$$\frac{\partial T}{\partial t} + \frac{P_1}{m_1} \cdot \nabla T = \frac{P_1 - m_1v_0}{m_1} \cdot \nabla T - \frac{T}{n_1C_v} \left(\frac{\partial P_1}{\partial T}\right)_n \nabla \cdot v_0 \quad (\text{III.295})$$

for the temperature is obtained. In a similar manner, the free density is also dependent on $n_1$ and $T$ through the equilibrium constraint (III.192), so that

$$\frac{\partial n_f}{\partial t} + \frac{P_1}{m_1} \cdot \nabla n_f$$
\[
\begin{align*}
&= (1 + 4n_1 B) \left( \frac{\partial n_1}{\partial t} + \frac{p_1}{m_1} \cdot \nabla n_1 \right) + 2n_1^2 \frac{d B}{d T} \left( \frac{\partial T}{\partial t} + \frac{p_1}{m_1} \cdot \nabla T \right) \\
&= (1 + 4n_1 B) \frac{p_1 - m_1 v_0}{m_1} \cdot \nabla n_1 + 2n_1^2 \frac{d B}{d T} \frac{p_1 - m_1 v_0}{m_1} \cdot \nabla T \\
&\quad - \left[ n_1 (1 + 4n_1 B) + \frac{2n_1^2 kT dB}{C_v} \right] \nabla \cdot v_0. \quad \text{(III.296)}
\end{align*}
\]

Since both the local equilibrium free Wigner function as well as \( f_{cl}^{th} \) are parameterized by \( n_f, v_0 \), and \( T \), the latter through \( n_c = n_f^2 \Lambda^r \text{Tr}_{re} U \), the above set of equations is sufficient for evaluating the time derivatives appearing in Eq. (III.254).

On carrying out the indicated time and space derivatives in Eq. (III.254) and eliminating the time derivatives with the relations in the last paragraph, the left hand side of this equation is formally linear in the gradients \( \nabla n_1, \nabla v_0 \) and \( \nabla T \). Furthermore, it is a necessary condition for consistency with the equation of continuity that there be no dependence on \( \nabla n_1 \). As an aid to writing down the detailed expressions involving the gradients and to prove the lack of dependence on \( \nabla n_1 \), the individual contributions are organized as follows

\[
d \left( f_{f1}^{le} + f_{cl}^{th} \right) = F_n d \ln n_f + F_v d v_0 + F_T d \ln T \quad \text{(III.297)}
\]

with derivatives with respect to \( \ln n_f, v_0 \) and \( \ln T \) given by

\[
F_n = f_{f1}^{le} + 2f_{cl}^{th}, \quad \text{(III.298)}
\]

\[
F_v = \frac{p_1 - m_1 v_0}{kT} f_{f1}^{le} + \frac{2n_f^2 \Lambda^6}{kT h^3} \text{Tr}_{r} (p_{cp} + p_1 - m_1 v_0) e^{-K_{CM}/kT} U \quad \text{(III.299)}
\]

and

\[
F_T = \left( W_1^2 - \frac{3}{2} \right) f_{f1}^{le} + \frac{n_f^2 \Lambda^6}{k^3} \text{Tr}_{r} e^{-K_{CM}/kT} \left[ \left( \frac{K_{CM}}{kT} - 3 \right) U + T U_T \right], \quad \text{(III.300)}
\]

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wherein the dimensionless momentum\textsuperscript{16} \( W_1 \equiv (p_1 - m_1v_0)/\sqrt{2m_1kT} \) has been introduced.

With this breakdown of the various contributions, the dependence of the left hand side of Eq. (III.254) on the gradients can be explicitly obtained. But as stated earlier, there should be no dependence on \( \nabla n_1 \). That this is the case is now demonstrated. Dependence on \( \nabla n_1 \) arises from the time and space derivatives of \( n_f \) and also through the pressure gradient associated with the time derivative of \( v_0 \). Collecting these contributions together gives as the coefficient of \( \nabla n_1 \),

\[
\frac{p_1 - m_1v_0}{n_fm_1}(1 + 4n_1B)F_n - \frac{1}{n_1m_1} \left( \frac{\partial p_1}{\partial n_1} \right)_T F_v - \frac{1}{n_f}(1 + 4n_1B)J_{cn} = \frac{1 + 2n_1B}{n_1m_1} \left[ (p_1 - m_1v_0)F_n - kTF_v - m_1J_{cn} \right] = 0, \tag{III.301}
\]

to terms linear in \( n_1 \). The terms in \( F_n \) and \( F_v \) involving \( f_{j1}^{le} \) clearly cancel and on examining the various contributions from pair correlations these are also easily shown to cancel.

On collecting the various contributions, the linearized Boltzmann equation (III.254) can be written in the form

\[
L_T \cdot \nabla \ln T + L_v^{(2)}: [\nabla v_0]^{(2)} + L_v^{(0)} \nabla \cdot v_0 = -R\phi, \tag{III.302}
\]

where\textsuperscript{204} \( [\nabla v_0]^{(2)} \) is the symmetric traceless part of the second rank tensor \( \nabla v_0 \). \( R\phi \) is given by \( R^{(1,1)}\phi \) of Eq. (III.249). The general weight factor \( f_{j1}^{le} \) has been removed so that the linearized Boltzmann equation can be treated as an operator equation in a Hilbert space with inner product

\[
\langle\langle A | B \rangle \rangle = \int A f_{j1}^{le} (r, p_1, t) B dp_1. \tag{III.303}
\]

The standard form\textsuperscript{16,131} for the perturbation \( \phi \) is

\[
\phi = -A \cdot \nabla \ln T - B: [\nabla v_0]^{(2)} - C \nabla \cdot v_0. \tag{III.304}
\]

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In the general case the coefficients of the generalized forces are given explicitly by retaining only terms up to second order in the density

\[ f_{f_1}^L L_T = \left( F_T + 2n_1^2 T \frac{dB}{dT} \frac{F_n}{n_f} \right) \frac{p_1 - m_1 v_0}{m_1} \]

\[ -F_v \frac{kT}{m_1} \left( 1 + n_1 B + n_1 T \frac{dB}{dT} \right) - \frac{2n_1^2 T}{n_f} \frac{dB}{dT} - J_{cT} - J_{rT} \]

\[ = \left[ W_1^2 - \frac{5}{2} - n_1 B + n_1 T \frac{dB}{dT} \right] \frac{p_1 - m_1 v_0}{m_1} f_{f_1}^L - J_{rT} \]

\[ + \frac{n_1^2 \Lambda^6}{h^3} Tr e^{-K_{CM}/kT} \frac{p_1 - m_1 v_0}{m_1} \]

\[ \times \left[ \left( \frac{K_{CM}}{kT} - 1 \right) U + T \right], \quad (III.305) \]

\[ f_{f_1}^{L(2)} = \left[ F_v \frac{p_1 - m_1 v_0}{m_1} - J_{c_1} - J_{r_{1u}} \right]^{(2)} \]

\[ = 2[W_1]^{(2)} f_{f_1}^L + \frac{2n_1^2 \Lambda^6}{m_1 kT h^3} Tr e^{-K_{CM}/kT} \left[ p_o + p_1 - m_1 v_0 \right]^{(2)} U \]

\[ + \frac{in_1^2 \Lambda^6}{2kT h^3} Tr e^{-K_{CM}/kT} \left[ V, \Omega \left[ e^{-K_{rel}/kT} p_o, r_o \right]^{(2)} + \Omega^l \right] \quad (III.306) \]

where irreducible Cartesian tensors such as \([W_1]^{(2)}\) are defined in reference 204, and

\[ f_{f_1}^{L(3)} = \frac{1}{3} F_v \left( \frac{p_1 - m_1 v_0}{m_1} \right) - \frac{F_n}{n_f} \left[ n_1 (1 + 4n_1 B) + 2n_1^2 kT \frac{dB}{dT} \right] \]

\[ - \frac{k}{C_v} \left( 1 + n_1 B + n_1 T \frac{dB}{dT} \right) - \frac{1}{3} \left( J_{c_1} + J_{r_{1u}} \right) \]

\[ = \frac{1}{3} \left[ 2C_v \frac{W_1}{3k} - 1 - n_1 B - n_1 T \frac{dB}{dT} \right] \left( W_1^2 - \frac{3}{2} \right) - 3n_1 B - 2n_1 T \frac{dB}{dT} \]

\[ - \frac{n_1^2 \Lambda^6}{C_v h^3} Tr e^{-K_{CM}/kT} T \left[ V, \Omega \left[ e^{-K_{rel}/kT} p_o, r_o \right] + \Omega^l \right] \quad (III.307) \]
This completes the identification of the terms in the Chapman Enskog equation (III.302).

The linear equation (III.302) is to be solved for the perturbation \( \phi \). According to the Fredholm alternative\(^{195,42} \), a solution exists only if the given function (left hand side of the equation) is orthogonal to the left invariants (left eigenvectors having zero eigenvalue) of \( \mathcal{R} \), and to make the solution unique, some condition on the perturbation is required for each right invariant. Just as for the standard Boltzmann equation, it is first verified that the left and right invariants are the mass, momentum and (kinetic) energy. It follows easily that the left hand side of Eq. (III.302) is orthogonal to these invariants and the standard Chapman Enskog method requires that the perturbation does not contribute to the mass, momentum or energy densities, see Eqs. (III.193), (III.223) and (III.224) together with Eqs. (III.260), thus making the solution unique.

In order to verify the invariants of \( \mathcal{R} \) it is appropriate to begin by studying matrix elements of the linear superoperator \( \mathcal{R} \). From the definition of inner product (III.303), the contribution to the collisional rate of change of observable \( \psi \) associated with perturbation \( \phi \) is

\[
\langle \langle \psi | \mathcal{R} | \phi \rangle \rangle = \frac{i n^2 A^6}{2 \hbar h^3} \int dp_1 \text{Tr}_r(\psi_1 + \psi_2)e^{-K_{CM}/kT} \\
\times [V, \Omega e^{-K_{rel}/kT}(\phi_1 + \phi_2)\Omega^+]_-. \tag{III.308}
\]

Here a symmetrization of \( \psi \) between particles has been carried out. Since \( V \) commutes with the center of mass motion, the commutator can be changed into the corresponding commutator with the combination of \( \psi \)'s, namely \([\psi_1 + \psi_2, V]_-\). For mass and linear momentum this commutator immediately vanishes, thus these four quantities are left invariants of \( \mathcal{R} \). For \( \psi \) equal to the (kinetic) energy \( H^{(1)} \), the combination of \( \psi \)'s is equal to the sum of center
of mass and relative (kinetic) energies. The former commutes with \( V \) so cannot contribute. The relative kinetic energy contribution can be written in the following form

\[
\int dp_1 \text{Tr}_r K_{rel} e^{-K_{CM}/kT}[V, \Omega X \Omega^\dagger]\]
\[
= \int dp_1 \text{Tr}_r e^{-K_{CM}/kT}[K_{rel}, V]_\Omega X \Omega^\dagger
\]
\[
= \int dp_1 \text{Tr}_r e^{-K_{CM}/kT}[H_{rel}, V]_\Omega X \Omega^\dagger
\]
\[
= - \int dp_1 \text{Tr}_r e^{-K_{CM}/kT}V[H_{rel}, \Omega X \Omega^\dagger]_-
\]
\[
= - \int dp_1 \text{Tr}_r e^{-K_{CM}/kT}V[K_{rel}, X]_\Omega^\dagger. \tag{III.309}
\]

Thus, if \( X \) commutes with \( K_{rel} \), equivalently the perturbation being a function solely of the particles momentum, then the kinetic energy is a left invariant of \( \mathcal{R} \). It should be emphasized that any position dependence of \( \phi \) is to be treated as a parameter for the linearized collision operator. The delocalization effects, which are in particular responsible for conversion between kinetic and potential energy, have already been accounted for by the presence of \( J^{(1,1)}_c \) and \( J^{(1,1)}_r \) in Eq. (III.254). Thus the kinetic energy provides a fifth left invariant for the linearized Boltzmann equation.

The identification of right invariants requires looking at which \( \phi \)'s give a zero contribution to the matrix element (III.308). For each of mass, momentum and kinetic energy, the sum of \( \phi \)'s is either constant, the center of mass momentum or the sum of center of mass and relative kinetic energies. In all cases, the Møller operators act to change the combination \( e^{-K_{rel}/kT}(\phi_1 + \phi_2) \) into a function of center of mass momentum and "total" relative \( (H_{rel}) \) energy operator. Such a quantity commutes with \( H_{rel} \), so that for each of mass,
momentum and kinetic energy, the $\mathcal{R}$ matrix element can be replaced by

$$
\langle \langle \psi | \mathcal{R} | \phi \rangle \rangle = -\frac{i n_f^2 \Lambda_f^6}{2 \hbar h^3} \int d\mathbf{p}_1 \text{Tr}_r(\psi_1 + \psi_2) e^{-K_{CM}/kT} \times [K_{rel}, \Omega e^{-K_{rel}/kT}(\phi_1 + \phi_2)\Omega^\dagger].
$$

(III.310)

This vanishes provided $\psi$ is a function of momentum, since the combination of $\psi$'s then commutes with $K_{rel}$. Thus, since the collision operator $\mathcal{R}$ is localized at one position and acts only to transform the momentum dependence of the Wigner function, its left and right invariants are the standard mass, momentum and kinetic energy. The possibility of a collision delocalization complicates this identification. In this work this problem is overcome by explicitly expanding the delocalization effects and treating them in a different manner than as collision contributions changing the perturbation $\phi$.

As stated earlier, the solvability of the linearized Boltzmann equation (III.302) requires that the left hand side be orthogonal to the left invariants of $\mathcal{R}$. These requirements are now discussed. Since the equations of change for $n$ and $v_0$ have been based on the moments of Eq. (III.254), these equations are exactly the requirements that the left hand side of Eq. (III.302) be orthogonal to the left invariants. Detailed evaluation of the orthogonality conditions using the coefficients $L_T$, $L^{(2)}_v$ and $L^{(0)}_v$ confirm these properties. The equation of change for the kinetic energy was not used in the elimination of the time derivatives to arrive at Eq. (III.302) so the orthogonality of the left hand side of Eq. (III.302) to the kinetic energy needs to be explicitly examined. For the kinetic energy only the $L^{(0)}_v$ orthogonality is not automatically satisfied by rotational invariance. The immediate integral of this orthogonality condition leads to

$$
\int \mathbf{W}_v^2 f^*_L L^{(0)}_v d\mathbf{p}_1 = \frac{3 n_f k}{2 C_v} \left[ \frac{2 C_v}{3 k} - 1 - 4 n_1 B - 3 n_1 T \frac{dB}{dT} \right]
$$

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After making use of the explicit form for $B(T) = -\frac{1}{2}\frac{\Lambda_r^3}{Tr_{rel} V} + \frac{1}{2m_1(kT)^2} Tr_{rel}[p_{op}; \nabla V]_+ \Omega \left[ e^{-K_{rel}/kT} p_{op}; r_{op} \right]_+ \Omega^\dagger$, (III.311)

retaining at most terms of second order in the density, this is simplified to

$$\int W_1 f_{f_1}^{(0)} l_{v_1} dp_1 = \frac{n_1^2 \Lambda_r^3}{3(kT)^2} Tr_{rel} V H_{rel} e^{-H_{rel}/kT}$$

$$- \frac{in_1^2 \Lambda_r^3}{12\hbar(kT)^2} Tr_{rel} V \left[ H_{rel}, \Omega \left[ e^{-K_{rel}/kT} p_{op}; r_{op} \right]_+ \Omega^\dagger \right]_+$$

$$= 0,$$  

(III.313)

where Eqs. (III.229) and (III.231), and commutator relation $[K_{rel}, r_{op}]_+ = \frac{2\hbar}{m_1} p_{op}$ have been used in the last step. This verifies that all of the orthogonality conditions are satisfied. Thus a solution to the linearized Boltzmann equation exists and is unique.

The presence of right invariants for the collision operator $\mathcal{R}$ implies that the solution $\phi$ to Eq. (III.302) is not unique. Uniqueness is obtained from the combination of auxiliary conditions (III.193, III.223, III.224) and (III.260). The auxiliary conditions (III.260) for the pair correlation Wigner function imply that the auxiliary conditions for $\phi$ reduce to the requirements that $\phi$ be orthogonal to mass, momentum and kinetic energy, namely the right invariants of $\mathcal{R}$. To get to this condition for the kinetic energy from Eq. (III.224) it is recognized that the independent particle contribution to the
potential energy
\[
\int \int V_{12} f_{f1}^{le} f_{f2}^{le} (\phi_1 + \phi_2) d\mathbf{r}' dp_1 dp_2 \tag{III.314}
\]
vanishes because of the separate auxiliary conditions (III.193) for \( \phi_1 \) and \( \phi_2 \) [after subtracting the appropriate correlation condition of Eq. (III.260)].

The auxiliary conditions imply certain constraints on the possible forms for \( A, B \) and \( C \), in the gradient expansion (III.304) of \( \phi \). In particular the vector \( A \) is affected only by the momentum constraint, while the scalar \( C \) is affected by both the number density and energy constraint. These constraints are identical to those appearing in dilute gas kinetic theory\(^{16} \), or more comparably to those for a previous classical treatment\(^{62} \) of moderately dense gas kinetic theory. As in that treatment, only the lowest order Sonine polynomials that are necessary to approximate the perturbation \( \phi \) will be retained in this work. Thus the expansion functions are approximated by

\[
A = a_1 W_1 \left( W_1^2 - \frac{5}{2} \right)
B = b_0 [W_1]^{(2)}
C = c_2 \left( \frac{15}{8} - \frac{5}{2} W_1^2 + \frac{1}{2} W_1^4 \right), \tag{III.315}
\]

having unknown coefficients \( a_1, b_0 \) and \( c_2 \).

The Chapman Enskog equation (III.302) together with the form of the perturbation function (III.304) can be split into three equations according to the three different gradients. This gives separate equations for each of \( A, B \) and \( C \). The magnitude \( a_1 \) of \( A = A W_1 \) is found by taking the component of the \( A \) equation along the \( A \) direction, thus

\[
X_A \equiv \int dp_1 \left( W_1^2 - \frac{5}{2} \right) W_1 \cdot f_f^{le} L_T
= a_1 \langle [W_1 \left( W_1^2 - \frac{5}{2} \right) \cdot \mathbf{R} | W_1 \left( W_1^2 - \frac{5}{2} \right) ] \rangle
\]

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where \( \bar{v} \equiv \sqrt{16kT/\pi m_1} \) is the mean velocity of relative motion and \( \Theta_\lambda \) is the appropriate cross section for thermal conductivity \( \lambda \). The driving term \( X_\lambda \) can be partially evaluated. After some simplification, this can be written as, neglecting terms of order \( n_1^3 \),

\[
X_\lambda = \frac{15}{4} n_f^2 a_1 \bar{v} \Theta_\lambda, \tag{III.316}
\]

where \( v \equiv \sqrt{16kT/\pi m_1} \) is the mean velocity of relative motion and \( \Theta_\lambda \) is the appropriate cross section for thermal conductivity \( \lambda \). The driving term \( X_\lambda \) can be partially evaluated. After some simplification, this can be written as, neglecting terms of order \( n_1^3 \),

\[
X_\lambda = \frac{15}{4} \sqrt{\frac{2kT}{m_1}} n_f + \frac{5n_f^2 \Lambda^3}{4} \sqrt{\frac{kT}{2m_1}} \text{Tr}_{rel} \left[ \left( \gamma^2 - \frac{3}{2} \right) TU_T - \left( \frac{5}{2} \gamma^2 - \frac{21}{4} \right) U \right] + \frac{in_f^2 \Lambda^3}{8\sqrt{2m_1}kT} \text{Tr}_{rel} \left[ \gamma^2 U + 2\gamma \gamma, V \right] : \Omega \left[ e^{-K_{rel}/kT} P_{op, r_{op}} \right] \Omega^\dagger. \tag{III.317}
\]

The equation for \( B \) reduces to an equation for the scalar \( b_0 \),

\[
X_n \equiv \int dp_1 [W_1]^{(2)} ; L_0^{(2)} f_{^\lambda} = b_0 \langle [W_1]^{(2)} ; |R|[W_1]^{(2)} \rangle \equiv \frac{5}{2} n_f^2 b_0 \bar{v} \Theta(20). \tag{III.318}
\]

Since the polarization is the same here as in the dilute gas case, the cross section for viscosity is written in standard notation as \( \Theta(20) \). For the determination of \( b_0 \), there remains only the reduction of \( X_n \) to simpler form. This is accomplished in the same manner as previous reductions, to give

\[
X_n = 5n_f (1 - n_f B) + \frac{n_f^2 \Lambda^3}{4m_1(kT)^2} \text{Tr}_{rel}[P_1, \nabla V_1]^{(2)} : \Omega \left[ e^{-K_{rel}/kT} P_{op, r_{op}} \right]^{(2)} \Omega^\dagger. \tag{III.319}
\]

Finally for the calculation of \( c_2 \) there is the determining equation

\[
X_\kappa \equiv \int dp_1 \left( \frac{15}{8} - \frac{5}{2} W_1^2 + \frac{1}{2} W_1^4 \right) f_{^\lambda} L_0^{(0)} = c_2 \langle \left( \frac{15}{8} - \frac{5}{2} W_1^2 + \frac{1}{2} W_1^4 \right) |R| \left( \frac{15}{8} - \frac{5}{2} W_1^2 + \frac{1}{2} W_1^4 \right) \rangle \equiv \frac{15}{8} c_2 n_f^2 \bar{v} \Theta_\kappa. \tag{III.320}
\]
The driving term to order \( n_1^2 \) is calculated to be

\[
X_\kappa = -\frac{n_f^2 \Lambda_r^3}{12} \text{Tr}_{rel} \left( \gamma^4 - 5\gamma^2 + \frac{15}{4} \right) T U_T \\
+ \frac{i n_f^2 \Lambda_r^3}{48 k T} \text{Tr}_{rel} \left[ \gamma^4 - 5\gamma^2, V \right]_\Omega \left[ e^{-K_{rel}/kT} \mathbf{p}_{op}, \mathbf{r}_{op} \right]_+ \Omega^!.
\]

(III.321)

This completes a listing and reduction of all the quantities that determine the perturbation expansion coefficients \( a_1, b_0 \) and \( c_2 \).

III-4.3 Scheme I: Transport Coefficients

Density operator expressions for the heat flux and pressure tensor are given in Section III-3.5. Specifically the pressure tensor arises by means of kinetic and collisional transfer mechanisms while the heat flux has the additional contribution of a potential energy flux. As well, the kinetic contributions involve both free and pair correlation effects. From the standard dilute gas kinetic theory point of view, fluxes are expanded in powers of the spatial inhomogeneity. For a locally homogeneous system there is no heat flux but there is a local equilibrium pressure. It is the formulation of all these contributions that is the object of the present section. The present estimates are made assuming there is only one temperature \( T_f = T_c = T \) and stream velocity \( v_f = v_c = v_0 \), with the correlation density \( n_c = n_f^2 \Lambda_r^3 \text{Tr}_{rel} U \) at equilibrium with the free particle density.

The kinetic pressure tensor is calculated according to

\[
P^K_1 = 2kT \int \mathbf{W}_1 \mathbf{W}_1 f^{(1)} d\mathbf{p}_1 \\
= (n_1 kT + \frac{1}{3} n_f^2 kT \epsilon_1) U + 2n_f kT \int \mathbf{W}_1 \mathbf{W}_1 \frac{e^{-W_1^2}}{\pi^{3/2}} \phi d\mathbf{W}_1
\]
\[
+2n^2_f kT \Lambda^3 \int d\mathbf{r} \mathbf{T}_{rel} \frac{e^{-\mathcal{G}}}{\pi^{3/2}} \mathbf{W}_1 \mathbf{W}_1 U \phi_c \\
= P^K_1 U - 2\eta_K [\nabla \mathbf{v}_0]^{(2)} - \kappa_K \nabla \cdot \mathbf{v}_0 U,
\]

(III.322)

to give contributions \(\eta_K\) and \(\kappa_K\) to the shear and bulk viscosity coefficients. Here

\[
\epsilon_1 = \Lambda^3 \mathbf{T}_{rel} \left( \frac{K_{rel}}{kT} - \frac{3}{2} \right) U
\]

(III.323)
is the correction term introduced by Imam-Rahajoe and Curtiss\textsuperscript{214}. On identifying the coefficients of \([\nabla \mathbf{v}_0]^{(2)}\) and \(\nabla \cdot \mathbf{v}_0\) and simplifying the resulting expressions, the kinetic contributions to the shear and bulk viscosity coefficients become

\[
\eta_K = \frac{1}{2} kT [n_f b_0 + \frac{1}{2} n_c b_0^c]
\]

(III.324)

and

\[
\kappa_K = \frac{2n_c kT c_0^c}{3 C_{corr}} C^V_U.
\]

(III.325)

Here the heat capacity \(C^V_U = d\epsilon^V_U / dT\) associated with the potential energy \(\epsilon^V_U \equiv \frac{1}{2} \mathbf{T}_{rel} \mathbf{V}U / \mathbf{T}_{rel} U\) per particle for the pair correlations has been introduced. The collisional transfer part of the pressure tensor reduces to

\[
P_{\text{coll}} = P^V_1 U - 2\eta_{\text{coll}} [\nabla \mathbf{v}_0]^{(2)} - \kappa_{\text{coll}} \nabla \cdot \mathbf{v}_0 U
\]

(III.326)

with virial pressure \(P^V_1 = n^2_f kT (B - \epsilon_1 / 3)\), shear viscosity

\[
\eta_{\text{coll}} = \frac{n^2_f \Lambda^3}{40 kT} \mathbf{T}_{rel} [r_{\text{op}} \nabla V]^{(2)}; \Omega \left[ e^{-K_{rel}/kT} p_{\text{op}, r_{\text{op}}} \right]_+ \Omega^+ \\
- \frac{n^2_f \Lambda^3}{20} \mathbf{T}_{rel} [r_{\text{op}} \nabla V]^{(2)}; \Omega e^{-K_{rel}/kT} [\gamma]^{(2)} \Omega^+ \tag{III.327}
\]

and bulk viscosity

\[
\kappa_{\text{coll}} = \frac{n^2_f \Lambda^3}{36 kT} \mathbf{T}_{rel} [r_{\text{op}} \cdot \nabla V] \Omega \left[ e^{-K_{rel}/kT} p_{\text{op}, r_{\text{op}}} \right]_+ \Omega^+ \tag{III.327}
\]
The kinetic heat flux vector is

\[
\mathbf{q}^K = \sqrt{\frac{2kT}{m_1}} kT \int d\mathbf{p}_1 \mathbf{W}_1 W_1^2 f_{te}^i \phi \\
+ \sqrt{\frac{2kT}{m_1}} kT \int dP \mathbf{Tr}_{\text{rel}} \mathbf{W}_1 W_1^2 f_{te}^i \phi_{c12} \\
= -\lambda_K \nabla T
\]  
(III.329)

with kinetic contribution to the thermal conductivity

\[
\lambda_K = \frac{5}{4} n_f k \sqrt{\frac{2kT}{m_1}} a_1 + \frac{5}{8} n_c k \sqrt{\frac{kT}{m_1}} a_i^e \left[ 1 + \frac{4 \mathbf{Tr}_{\text{rel}} K_{\text{rel}} U_T}{3 kT_{\text{rel}} U} \right]
\]  
(III.330)

while the collisional heat flux

\[
\mathbf{q}_{\text{coll}} = -\lambda_{\text{coll}} \nabla T
\]  
(III.331)

has thermal conductivity contribution

\[
\lambda_{\text{coll}} = \frac{n_f^2 \Lambda_r^3}{24 T} \mathbf{Tr}_{\text{rel}} \mathbf{r}_{\text{op}} \nabla V : \mathbf{\Omega} \left[ e^{-K_{\text{rel}}/kT} \mathbf{P}_{\text{op}}, \mathbf{r}_{\text{op}} \right] + \Omega \right] + \frac{ka_1}{2 \sqrt{2m_1 kT}} \left[ T \frac{dP^V}{dT} - P^V \right] \\
- \frac{n_f^2 \Lambda_r^3}{3} \mathbf{Tr}_{\text{rel}} \mathbf{r}_{\text{op}} \nabla V : \mathbf{\Omega} e^{-K_{\text{rel}}/kT} \gamma \gamma \mathbf{\Omega} \right].
\]  
(III.332)

Finally there is the potential energy heat flux contribution

\[
\mathbf{q}^V = \frac{1}{2} n_f^2 \Lambda_r^3 \sqrt{\frac{kT}{m_1}} \mathbf{Tr}_{\text{rel}} \int dG \frac{e^{-\frac{G^2}{\pi^2/2}} G V}{\mathbf{Pr}_{\text{rel}}} \left[ e^{-K_{\text{rel}}/kT} (\phi_1 + \phi_2) + U \phi_c \right] \\
= -\lambda_V \nabla T
\]  
(III.333)
with thermal conductivity contribution

\[ \lambda_V = \frac{5}{12} n_f^2 \Lambda_r^3 a_1 \sqrt{\frac{k}{2m_1T}} \text{Tr}_{rel} V e^{-\frac{K_{rel}/k_T}{k T}} \left( \frac{K_{rel}}{k T} - \frac{3}{2} \right) + \frac{1}{2} n_c \sqrt{\frac{k T}{m_1}} C_U^V a_1^c. \]  

(III.334)

Several different contributions to the transport coefficients have been found. Collected together, the shear viscosity is

\[ \eta = \eta_K + \eta_{\text{coll}}, \]  

(III.335)

with detailed formulae given by Eqs. (III.324) and (III.327). For the bulk viscosity,

\[ \kappa = \kappa_K + \kappa_{\text{coll}}, \]  

(III.336)

with formulae Eqs. (III.325) and (III.328). Finally, for the thermal conductivity,

\[ \lambda = \lambda_K + \lambda_{\text{coll}} + \lambda_V, \]  

(III.337)

with formulae from Eqs. (III.330), (III.332) and (III.334).

### III-4.4 Scheme II: Solution

This section examines the solutions of the three quantum kinetic equations appropriate when bound states are present, namely the generalized quantum Boltzmann equation (III.153), the bound pair equation (III.156) and the modified pair correlation equation (III.161). Technically the modified pair correlation equation does not couple to the two other equations by collisions. Therefore it is reasonable to treat the modified pair correlation equation separately as has been done in subsection a) of Section III-4.2. The two other collisionally coupled equations, one for the renormalized particle \( 1 \), the other for the bound pair, are solved simultaneously within the philosophy of Chapman-Enskog procedure\textsuperscript{131,132,133}.  

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a) The Generalized Boltzmann and Bound Pair Equations

The local equilibrium forms \( f_{f1} \), \( f_{c1} \) and \( f_{b12} \) in the generalized Boltzmann equation (III.253) and bound pair equation (III.256) are respectively parameterized by \( n_f, v_f, T_f; n_c, v_c, T_c \) and \( n_b, v_b, T_b \). The differences among the \( v_i \) and \( T_i \) \((i = f, c, b)\) are associated with local inhomogeneities so that these parameters can be treated as differing by linear in gradient terms from the common stream velocity \( v_0 \) and temperature \( T \) respectively. For a first order solution, these differences can be ignored in the time derivatives, since the time derivatives are also proportional to gradients after being eliminated by Euler’s equations. Moreover, the time derivative always occurs in the combination \( \frac{\partial}{\partial t} + \frac{\partial}{\partial t} \cdot \nabla \) in the two equations. The appropriate set of equations to be used in evaluating the time derivatives is examined first, then the resulting form for the pair Chapman Enskog equations is discussed.

From equations (III.253) and (III.256), the rate of change of the full mass density \( \rho \) is

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v_0) = 0 \tag{III.338}
\]

where

\[
\rho = \rho_1 + \rho_b \tag{III.339}
\]

is the sum of mass densities of the renormalized particle

\[
\rho_1 = (n_f + n_c)m_1 = n_1m_1, \tag{III.340}
\]

and bound pair

\[
\rho_b = n_bm_b. \tag{III.341}
\]

For non-reactive binary collisions, which is the only case considered in the following, the number densities are conserved for each of the two species.
Thus a useful form for each linearized equation is

$$\frac{\partial n_i}{\partial t} + \frac{p_i}{m_i} \cdot \nabla n_i = \frac{p_i - m_i v_0}{m_i} \cdot \nabla n_i - n_i \nabla \cdot v_0,$$  \hspace{1cm} (III.342)

where \( i = 1, b \).

The equation of motion of the linearized generalized Boltzmann equation (III.253) is

$$\frac{\partial n_1 v_0}{\partial t} + \frac{1}{m_1} \nabla \cdot \left[ p_1^K U + n_1 m_1 v_0 v_0 - \frac{U}{3} n_1^2 k T E_U \right] = \sum \int \frac{p_1}{m_1} f_{n, i}^{(1, i)} d p_1,$$  \hspace{1cm} (III.343)

where \( p_1^K \equiv n_1 k T + \frac{1}{3} n_1^2 k T e_1 \) and quantity \( E_U \) is defined in terms of dimensionless energy \( \gamma^2 \equiv \frac{p_{op}^2}{m_1 k T} \)

$$E_U \equiv \Lambda^2 T_{rel} \gamma^2 U_c.$$  \hspace{1cm} (III.344)

Here \( U_c \) is the unbound part of the pair particle Ursell operator. Collision operators are defined in Section III-4.1

Similarly the equation of motion of the linearized bound pair equation (III.256) is

$$\frac{\partial n_b v_0}{\partial t} + \frac{1}{m_b} \nabla \cdot \left[ p_b^K U + n_b m_b v_0 v_0 \right] = \sum \text{Tr}_{\text{int}} \int \frac{p_b}{m_b} f_{n, i}^{(b, i)} d p_b,$$  \hspace{1cm} (III.345)

where \( p_b^K \equiv n_b k T \) is kinetic pressure of the bound pairs. The conservation of the total momentum for the free, the pair correlation and the bound pair implies the total momentum is a collisional invariant. Therefore combination of equations (III.343) and (III.345) gives

$$\frac{\partial v_0}{\partial t} + \frac{p_i}{m_i} \cdot \nabla v_0 = \frac{p_i - m_i v_0}{m_i} \cdot \nabla v_0 - \frac{1}{\rho} \nabla P,$$  \hspace{1cm} (III.346)
where the total local equilibrium pressure

\[ P = P^K + P^b = P^K - \frac{1}{3} n_j^2 k T E_u = P^K - \frac{1}{3} n_j^2 k T E_u = P_1 + P^b_1 = n k T + n_j^2 k T B_c \]  

is the hydrodynamic pressure of the system.

The equation of change for the kinetic energy for the (linearized) generalized Boltzmann equation is

\[ \frac{\partial n_1 \varepsilon^K_1}{\partial t} + \nabla \cdot (\mathbf{v}_0 n_1 \varepsilon^K_1) + \left( P_1 - \frac{\sigma}{3} \right) \nabla \cdot \mathbf{v}_0 = \sum_i \int \frac{(P_1 - m_1 \mathbf{v}_0)^2}{2m_1} j^{(i,i)}_{nc} dP_1 \]  

where the local homogeneous kinetic energy for the renormalized particle 1 is

\[ n_1 \varepsilon^K_1 = \int dP_1 \frac{(P_1 - m_1 \mathbf{v}_0)^2}{2m_1} (f_{11}^{le} + f_{11}^{th}) = \frac{3n_1 k T}{2} + \frac{n_j^2 k T \varepsilon_1}{2}. \]  

The kinetic energy production coefficient

\[ \sigma = -\frac{in_j^2 \lambda^3}{4\hbar} \text{Tr}_{\text{rel}} \gamma^2 \left[ V, \Omega_L \left[ e^{-K_{\text{rel}}/k T \mathbf{P}_{op}', \mathbf{r}_{op}} \right], \right] + \]  

arises from the collisional non-locality correction \( J^{(1,1)}_r \). This kinetic energy production must be balanced by potential energy production. The equation of change for the local potential energy is

\[ \frac{\partial n_1 \varepsilon^V_1}{\partial t} + \nabla \cdot (\mathbf{v}_0 n_1 \varepsilon^V_1) - \frac{\sigma}{3} \nabla \cdot \mathbf{v}_0 = 0. \]
The combination of these two energy equations (III.349) and (III.351) gives the equation of change for the total energy of the renormalized particle \( 1 \)

\[
\frac{\partial n_1 \varepsilon_1}{\partial t} + \nabla \cdot (v_0 n_1 \varepsilon_1) + P_1 \nabla \cdot v_0 = \sum_i \int \frac{(p_i - m_1 v_0)^2}{2m_1} J_n^{(1,i)} dp_1. \tag{III.352}
\]

The equation of change for the local equilibrium kinetic energy of the bound pair is

\[
\frac{\partial n_b \varepsilon_b^K}{\partial t} + \nabla \cdot (v_0 n_b \varepsilon_b^K) + P_b \nabla \cdot v_0 = \sum_i T_{\text{int}} \int \left[ \frac{(p_b - m_1 v_0)^2}{2m_1} + H_{\text{int}} \right] J_n^{(b,i)} dp_b \tag{III.353}
\]

where the local equilibrium kinetic energy of the bound pair is

\[
n_b \varepsilon_b^K = \frac{3n_b kT}{2} + n_b E_{\text{int}} \tag{III.354}
\]

The local total energy \( \varepsilon \) is

\[
\varepsilon = \frac{1}{n} \left( \frac{3}{2} n kT + \frac{n_b^2}{2} kT \varepsilon_1 + n_1 \varepsilon_1^V + n_b E_{\text{int}} \right). \tag{III.355}
\]

The total local energy conservation implies

\[
\frac{\partial n \varepsilon}{\partial t} + \nabla \cdot (v_0 n \varepsilon) + P \nabla \cdot v_0 = 0. \tag{III.356}
\]

To terms linear in gradients, an equation of change for the temperature is obtained as

\[
\frac{\partial T}{\partial t} + \frac{p_i}{m_i} \nabla T = \frac{p_i - m_i v_0}{m_i} \nabla T + \frac{z}{nC_v} \nabla \cdot v_0. \tag{III.357}
\]

where the heat capacity \( C_v \) is defined as

\[
C_v \equiv \frac{1}{n} \left( \frac{\partial n \varepsilon}{\partial T} \right)
= \frac{1}{n} \left[ \frac{3}{2} n k + n_b \frac{dE_{\text{int}}}{dT} + \frac{n_1^2 k \varepsilon_1}{2} + \frac{n_b^2 k \varepsilon_1^V}{2} - 3n_b^2 k T \frac{dB_{\text{c}}}{dT} + \frac{d(n_1 \varepsilon_1^V)}{dT} \right]. \tag{III.358}
\]

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It is noted that \( n \) is also a function of temperature even at local equilibrium because \( n_c \) depends on temperature. The number density \( n_b \) is treated as fixed because reactive collisions are excluded in the present treatment. The symbol \( z \) is used as a short-hand notation for

\[
z \equiv -T \left( \frac{\partial P}{\partial T} \right)_n
= -P + n^2 kT \frac{1}{2} \varepsilon_1 + n_1 \varepsilon_Y
= -nkT + n^2 kT(\frac{1}{2} \varepsilon_1 - B_c) + n_1 \varepsilon_Y
= -P + n^2 kT \frac{1}{2} \varepsilon_1 + \frac{1}{2} n_f \Lambda_r^3 Tr_{rel} V e^{-H_{rel}/kT}.
\text{(III.359)}
\]

The three Euler equations (III.342), (III.346) and (III.357) govern the time evolution of the local (macroscopic) hydrodynamic variables, namely the local homogeneous equilibrium number density, velocity and temperature, and are appropriate for eliminating the time derivatives in the (linearized) generalized Boltzmann equation (III.253) and the (linearized) bound pair equation (III.256). The procedure of eliminating the time derivatives in the generalized Boltzmann equation is exactly the same as that discussed in Section III-4.2 for the renormalized Boltzmann equation, while that for the bound pair equation is accomplished in a similar manner. These are discussed as following:

i) Since it is \( n_f \) that enters explicitly into the (linearized) generalized Boltzmann equation (III.253), the rate of change of \( n_f \) is first required and can be derived from the relation between \( n_f \) and \( n_1 \) at local equilibrium

\[
n_1 = n_f + n_c = n_f + n_f^2 \Lambda_r^3 Tr_{rel} U_c.
\text{(III.360)}
\]

Therefore the rate of change for \( n_f \) is obtained as

\[
\frac{dn_f}{dt} = \frac{\partial n_f}{\partial n_1} \frac{dn_1}{dt} + \frac{\partial n_f}{\partial T} \frac{dT}{dt}.
\text{(III.361)}
\]

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where notation \( \frac{dA}{dt} \) is defined as

\[
\frac{dA}{dt} \equiv \left( \frac{\partial}{\partial t} + \frac{p_i}{m_i} \cdot \nabla \right) A \quad \text{with} \quad (i = 1, b).
\] (III.362)

Note this is not the usual substantial time derivative\(^{131,132}\).

On carrying out the indicated time and spatial derivatives in Eq. (III.253) and eliminating the time derivatives with equations (III.342), (III.346), (III.357) and (III.361), the left hand side of this equation is reduced to terms linear in the gradients \( \nabla n_1 \), \( \nabla n \), \( \nabla v_0 \) and \( \nabla T \). The individual contributions are the same as that in the case for the renormalized Boltzmann equation (see Section III-4.2) but are summarized here for convenience:

\[
d \left( f_{f1}^{le} + f_{cl}^{lh} \right) = F_n \, d \ln n_f + F_v \, d v_0 + F_T \, d \ln T
\] (III.363)

with derivatives with respect to \( \ln n_f \), \( v_0 \) and \( \ln T \) given by

\[
F_n = f_{f1}^{le} + 2f_{cl}^{lh},
\] (III.364)

\[
F_v = \frac{p_1 - m_1 v_0}{kT} f_{f1}^{le} + \frac{2n_f^2 \Lambda_6}{kT h^5} \text{Tr}(p_{op} + p_1 - m_1 v_0) e^{-K_{CM}/kT} U_c
\] (III.365)

and

\[
F_T = \left( W_i^2 - \frac{3}{2} \right) f_{f1}^{le} + \frac{n_f^2 \Lambda_6}{h^5} \text{Tr}(p_{op}) e^{-K_{CM}/kT} \left( \left( \frac{K_{CM}}{kT} - 3 \right) U_c + T U_{cT} \right),
\] (III.366)

where the dimensionless momenta\(^{16}\) is defined similar to that in Section III-4.2 as

\[
W_i \equiv \frac{(p_i - m_i v_0) / \sqrt{2m_i kT}}{1, (i = 1, b)}.
\] (III.367)

In contrast to the treatment in Section III-4.2 of the renormalized quantum Boltzmann equation, the number density gradients do not vanish and give rise to diffusion. This is due to the fact that one now deals with a non-ideal gas mixture and the hydrodynamic equations (III.342), (III.346) and
are different from those hydrodynamic equations used in Section III-4.2.

On collecting the various contributions, the dependence of the left hand side of Eq. (III.253) on the gradients can be given explicitly (by retaining only terms up to second order in the density)

\[
\frac{d(f_{cl} + f_{th})}{dt} = J_{c}^{(1,1)} - J_{r}^{(1,1)}
\]

\[
= \left\{ \left[ F_T - \left( 1 + n_1 B_c - n_1 T \frac{dB_c}{dT} \right) F_n \right] \frac{P_1 - m_1 v_0}{m_1} + J_{cn} - J_{cT} - J_{rT} \right\} \nabla \ln T
\]

\[
+ \left[ F_v \frac{P_1 - m_1 v_0}{m_1} - J_{cv} - J_{rv} \right]^{(2)} : [\nabla v_0]^{(2)}
\]

\[
+ \left[ \frac{1}{3} F_v \cdot \left( \frac{P_1 - m_1 v_0}{m_1} - F_n \right) \left( n_1 (1 + 4 n_1 B) + \frac{2 n_1^2 z T B_c}{n C_v} \right) \right.
\]

\[
- \frac{z}{T n C_v} F_T - \frac{1}{3} U : (J_{cv} + J_{rv}) \nabla \cdot v_0
\]

\[
+ \frac{n + n_1^2 B_c k T}{m_1} F_v \cdot d_1. \tag{III.368}
\]

Here the diffusion driving force vector \( d_1 \) for a non-ideal gas mixture is given by

\[
d_1 = \nabla \frac{n_1 + n_1^2 B_c}{n + n_1^2 B_c} + \left( \frac{n_1 + n_1^2 B_c}{n + n_1^2 B_c} - \frac{\rho_1}{\rho} \right) \nabla \ln P
\]

\[
= \nabla \frac{P_1}{P} + \left( \frac{P_1}{P} - \frac{\rho_1}{\rho} \right) \nabla \ln P. \tag{III.369}
\]

The second form is in terms of hydrodynamic pressures. \([\nabla v_0]^{(2)}\) is the symmetric traceless part\(^{204}\) of the second rank tensor \(\nabla v_0\).

ii) The time derivative in the linearized bound pair equation (III.256) is eliminated by the hydrodynamic equations (III.342), (III.346) and (III.357) to give terms linear in the gradients \(\nabla n_s\), \(\nabla n\), \(\nabla v_0\) and \(\nabla T\). Thus the left
hand side of the linearized bound pair equation (III.256), up to second order in the density, can be written as

\[
\frac{df_{lb}^T}{dt} = f_{lb}^T \left\{ \left[ W_b^2 - \frac{5}{2} + \frac{H_{int} - E_{int}}{kT} \right] \frac{P_b - m_b \nu_0}{m_b} \cdot \nabla \ln T \\
+ 2 \left[ W_s \right]^{(2)} : \left[ \nabla \nu_0 \right]^{(2)} \\
+ \frac{2}{3} \left[ q \left( W_b^2 - \frac{3}{2} \right) + (q - 1) \frac{H_{int} - E_{int}}{kT} \right] \nabla \cdot \nu_0 \\
+ \frac{n + n_i^2 B_c}{n_b} \frac{P_b - m_b \nu_0}{m_b} \cdot d_b \right\}, \quad (III.370)
\]

where the diffusion driving force vector \( d_d \) is defined as

\[
d_b = \nabla \frac{n_b}{n + n_i^2 B_c} + \left( \frac{n_b}{n + n_i^2 B_c} - \frac{\theta_b}{\theta} \right) \nabla \ln P \\
= \nabla \frac{P_b^K}{P} + \left( \frac{P_b^K}{P} - \frac{\theta_b}{\theta} \right) \nabla \ln P. \quad (III.371)
\]

It is easy to see that

\[
d_1 + d_b = 0. \quad (III.372)
\]

Both diffusion driving force vectors are expressed solely as functions of (partial) pressures. This structure is similar to the standard form\(^{152,133,137}\) for an ideal gas mixture but with additional density corrections.

Here factor \( q \) is defined as

\[
q = \frac{3}{2} \frac{z}{T n C_v} + 1, \quad (III.373)
\]

similar to that introduced by Wang Chang and Uhlenbeck\(^{196}\).

On collecting the various contributions, the linearized generalized Boltzmann equation (III.253) and the linearized bound pair equation, up to second order in the density, can be written in a unified form

\[
L^i_T \cdot \nabla \ln T + L^i_{\nu_0} : \left[ \nabla \nu_0 \right]^{(2)} + L^i_{\nu_0} \nabla \cdot \nu_0 + L^i_{d_i} \cdot d_i = - \sum_j R^{i,j} \phi_j. \quad (III.374)
\]
These are referred as the two Chapman Enskog equations in the following. Here the various terms for the renormalized particle are

\[
f^{l_e}_{f_1} L^1_T = \left[ F_T - (1 + n_1 B_c - n_1 T \frac{dB_c}{dT}) F_n \right] \frac{p_1 - m_1 v_0}{m_1} + J_{cn} - J_{cT} - J_{rT}, \tag{III.375}
\]

\[
f^{l_e}_{f_1} L^1_{\nu(2)} = \left[ F_\nu \frac{p_1 - m_1 v_0}{m_1} - J_{c\nu} - J_{r\nu} \right], \tag{III.376}
\]

\[
f^{l_e}_{f_1} L^1_\nu^{(0)} = \frac{1}{3} \mathbf{F}_\nu \cdot \left( \frac{p_1 - m_1 v_0}{m_1} - \frac{F_n}{n_f} \left( n_1 (1 + 4 n_1 B_c) + \frac{2 n_1^2 z T dB_c}{n C_v} \right) \right) - \frac{z}{T n C_v} F_T - \frac{1}{3} \mathbf{U} : (J_{c\nu} + J_{r\nu}), \tag{III.377}
\]

and

\[
f^{l_e}_{f_1} L^1_{d_1} = \frac{n + n_1^2 B_c kT}{n_1} \mathbf{F}_\nu \tag{III.378}
\]

and for the bound pair,

\[
L^b_T = \left[ W^2 - \frac{5}{2} + \frac{H_{int} - E_{int}}{kT} \right] p_b - m_b v_0, \tag{III.379}
\]

\[
L^b_{\nu(2)} = 2 [W^2]^{(2)}, \tag{III.380}
\]

\[
L^b_{\nu(0)} = \frac{2}{3} \left[ q(W^2 - \frac{3}{2}) + (q - 1) \frac{H_{int} - E_{int}}{kT} \right], \tag{III.381}
\]

and

\[
L^b_{\nu} = \frac{n + n_1^2 B_c p_b - m_b v_0}{n_b}. \tag{III.382}
\]

The general weight factors \( f^{l_e}_{f_1} \) and \( f^{l_e}_b \) have been removed in Eq. (III.374) so that the two Chapman-Enskog equations can be treated as operator equations in a Hilbert space with inner products, compare Section III-4.2,

\[
\langle \langle A | B \rangle \rangle_1 = \int A f^{l_e}_{f_1}(\mathbf{r},p_1,t) B dp_1, \tag{III.383}
\]

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and

\[(A|B)_b = \text{Tr}_{\text{int}} \int A f_{12}^{le}(r, p_b, t) B dp_b. \quad (III.384)\]

From the tensorial structure of Eqs. (III.374) one can express the perturbation functions as

\[f_a = -A^1 \cdot \nabla \ln T - B^1 : [\nabla v_0]^{(2)} - C^1 \nabla \cdot v_0 - D_1 \cdot d_1 \quad (III.385)\]

and

\[f_b = -A^b \cdot \nabla \ln T - B^b : [\nabla v_0]^{(2)} - C^b \nabla \cdot v_0 - D_b \cdot d_b. \quad (III.386)\]

According to the Fredholm theory of integral equations\(^{42,195}\), for a perturbation solution to exist, the left hand side of the Chapman-Enskog equations Eqs. (III.374) must be orthogonal to the left invariants of the collision operators \(\sum_j \mathcal{R}^{i,j} \). Stated differently, the first order solution of the coupled Chapman-Enskog equations (III.374) exist if its left hand side is orthogonal to the zeroth order solution, namely the Euler equations (III.342), (III.346) and (III.357) are satisfied. To make the solution unique, the perturbation functions are required to be orthogonal to the five right invariants of the collision operator. In other words, the new solution is unique if it does not contribute to the local homogeneous equilibrium mass, momentum, and energy of the system. This requirement is the set of auxiliary conditions (III.193), (III.195) (III.198) and (III.212) imposed on the perturbation functions \(\phi_i (i = f, c, b)\). Since the proof of the existence is lengthy at present, it is claimed in advance that the Fredholm alternative is indeed satisfied.

The collision operators \(\sum_j \mathcal{R}^{i,j} \phi_j\) of Eq. (III.374), as defined in Eq. (III.249) are the usual localized non-reactive binary collision operators therefore they conserve the mass, momentum and kinetic energy\(^{133,132}\)

\[\sum_{i=1,b} \sum_{j=1,b} \int dp_i f_i^{le} \mathcal{R}^{i,j} \phi_j = 0, \quad (III.387)\]

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\[
\sum_{i=1,b} \sum_{j=1,b} \int dp_i f_i^{le} p_i \mathcal{R}^{i,j} \phi_j = 0, \quad (\text{III.388})
\]

\[
\sum_{i=1,b} \sum_{j=1,b} \int dp_i f_i^{le} \left( \frac{p_i - m_i v_0}{2m_i} \right) + H_{int(i)} \mathcal{R}^{i,j} \phi_j = 0, \quad (\text{III.389})
\]

where \( H_{int(i)} \delta_{1i} \equiv 0 \). This has already been used in deriving the three Euler equations (III.342), (III.346) and (III.357), and accounts for the five left invariants of Eq. (III.374). As in the standard binary mixture theory\cite{133,132,196}, for the perturbation functions \( \phi_1 \) and \( \phi_2 \) each chosen as the mass, momentum and kinetic energy, the five right invariants for the collision operators can be easily obtained [the detailed argument is similar to the discussion about Eq. (III.310)].

To establish the existence and uniqueness of the solution, it remains to choose appropriate perturbation functions that satisfy the auxiliary conditions and to verify that the left hand side functions of Eq. (III.374) are orthogonal to the five left invariants. The auxiliary conditions and perturbation functions are discussed first.

The auxiliary conditions are introduced in Section III-3.5 and can be simplified in the following two ways:

i) It is important to recognize that the modified pair correlation equation (III.257) is collisionally decoupled from the two other equations, and couples the two other equations only through the term \(-i \nu_{12} f_{12}\) involving the local equilibrium free singlet. From the point of view of solving the three equations, the modified pair correlation equation can be handled separately as in Section III-4.2. From the point of view of macroscopic properties, the pair correlation contributions to the local equilibrium quantities such as number density, momentum, and energy are accounted for through the renormalized particle.
1, to avoid redundancy, the perturbation $\phi_c$ must not contribute to these quantities. This results in the additional auxiliary conditions (III.260) for the pair correlations. With these restrictions the auxiliary conditions (III.193), (III.195), (III.198) and (III.212) are effectively reduced to

\begin{align*}
\int dp_1 f_{j1}^{ie}(r, p_1, t) \phi_1 &= 0, \\
\int Tr_{int}f_{b12}^{le}(r, p_b, t) \phi_b dp_b &= 0, \\
\int dp_1 p_1 f_{j1}^{ie} \phi_1 + Tr_{int} \int p_b f_{b12}^{le} \phi_b dp_b &= 0
\end{align*}

and

\begin{align*}
\int \frac{(p_1 - m_1 v_0)^2}{2m_1} f_{j1}^{le} \phi_1 dp_1 + \frac{1}{2n_f} \int \int V_{12} f_{j1}^{le} f_{j2}^{le}(\phi_1 + \phi_2) dr'dp_1 dp_2 \\
+ Tr_{int} \int \left[ \frac{(p_b - m_b v_0)^2}{2m_b} + H_{int} \right] f_{b12}^{le} \phi_b dp_b &= 0. 
\end{align*}

ii) The auxiliary conditions (III.390-III.393) are further simplified by eliminating the potential energy contribution. As shown in Section III-4.2, the independent particle contribution to the potential energy perturbation vanishes

\begin{align*}
\int \int \int V_{12} f_{j1}^{le} f_{j2}^{le}(\phi_1 + \phi_2) dr'dp_1 dp_2 &= 0. 
\end{align*}

With this argument the auxiliary conditions (III.193), (III.195), (III.198) and (III.212) are simplified to forms relevant to the Chapman-Enskog equation (III.374). These are Eqs. (III.390), (III.391), (III.392) and

\begin{align*}
\int \frac{(p_1 - m_1 v_0)^2}{2m_1} f_{j1}^{le} \phi_1 dp_1 \\
+ Tr_{int} \int \left[ \frac{(p_b - m_b v_0)^2}{2m_b} + H_{int} \right] f_{b12}^{le} \phi_b dp_b &= 0. 
\end{align*}

With this break down of the auxiliary conditions, the form for the perturbation functions (III.385) and (III.386) can now be discussed. Firstly, the
perturbation functions (III.385) and (III.386) are to be so chosen that they satisfy the auxiliary conditions (III.390-III.395). Secondly, within the philosophy of the Chapman-Enskog method, the lowest order Sonine polynomials are chosen for $A^1, B^1, C^1$ and $D^1$ to approximate the perturbation $\phi_1$. Finally, in the case of the linearized bound pair equation, an appropriate combination of Sonine functions and Wang Chang-Uhlenbeck polynomials for $\phi_b$ is included to account for the collisional internal energy and relative kinetic energy transfers. These are listed explicitly as the follows:

$$A^1 = a^1 \left( W^1_2 - \frac{5}{2} \right) W_1 + a^1_0 W_1,$$

(III.396)

$$A^b = a^b_1 \left[ W^b_2 - \frac{5}{2} + \frac{H_{int} - E_{int}}{kT} \right] W_b + a^b_0 W_b,$$

(III.397)

with

$$a^b_0 = -\frac{n_f}{n_b} \sqrt{\frac{m_1}{m_b} a^1_0},$$

(III.398)

$$B^1 = b^1_0 [W_1]^{(2)},$$

(III.399)

$$B^b = b^b_0 [W_b]^{(2)};$$

(III.400)

$$C^1 = c^1_1 (W^2_1 - \frac{3}{2}),$$

(III.401)

$$C^b = c^b_1 \left[ W^b_2 - \frac{3}{2} + \alpha \frac{H_{int} - E_{int}}{kT} \right],$$

(III.402)

where

$$\alpha = -\frac{3k}{2C_{int}} \left( 1 + \frac{n_f c^1_1}{n_b c^b_1} \right),$$

(III.403)

and

$$C_{int} = \frac{dE_{int}}{dT} = \frac{\langle H^2_{int} \rangle - E^2_{int}}{kT^2},$$

(III.404)
\[ D_1 = D_1 W_1, \quad (\text{III.405}) \]

and

\[ D_b = D_b W_b, \quad (\text{III.406}) \]

having the constraint

\[ D_b = \frac{n_b}{n_b} \sqrt{\frac{m_1}{m_b}} D_1. \quad (\text{III.407}) \]

It is straightforward to check that the auxiliary conditions (III.390), (III.391), (III.392) and (III.395) are satisfied by the \( \phi_i \) with \( A^i, B^i, C^i \) and \( D_i \) chosen according to Eqs. (III.396-III.406).

As stated earlier, the existence of the solution requires that the left hand side of Eq. (111.374) are orthogonal to the five left invariants. It is necessary to explicitly check these orthogonality relations because of the inclusion of the pair correlation, the presence of collisional non locality and the use of the potential energy in the derivation of the Chapman-Enskog equations (III.374). Since this calculation is a little bit lengthy, we start by evaluating various moments and solving Eq. (III.374). The orthogonality relations are verified from this evaluation.

The rotational invariance of the perturbation functions and the generalized force splits the two Chapman-Enskog equations (III.374) into six different equations according to scalars, vectors and symmetric traceless second rank tensors of rank tensors. The decoupling between the temperature gradient \( \nabla T \) and the diffusion driving vectors \( d_i \) splits each vector equation into two. Thus there are eight equations, one for each of \( A^i, B^i, C^i \) and \( D_i \), deduced from the Chapman-Enskog equations (III.374)

\[ L_T^i = \sum_j \mathcal{R}^{i,j} A^j, \quad (\text{III.408}) \]
and

\[ L_{d_i}^i = \sum_j R^{ij}(-1)^{(1-\delta_{ij})}D_j, \]  

where the sign \((-1)^{(1-\delta_{ij})}\) is due to the relation between the two diffusion driving force vectors \(d_1 = -d_b\).

Similar to that in Section III-4.2, those expansion coefficients of \(A^i, B^i, C^i\) and \(D_i\) that have not been specified in Eqs. (III.396-III.407) are to be determined by taking various moments of the eight equations (III.408-III.411).

The magnitude \(a_1^i, a_0^i\) and \(a_0^1\) are determined by taking moments with Eq. (III.408). The momentum moment gives

\[
X_T^1 = \int dp_1 W_1 \cdot f_i^a L_T^i \\
= \sum_i \langle \langle W_1 \cdot |R^{(1,i)}|A^i \rangle \rangle_1 \\
= \sum_i \left\{ \delta_{1i} \sum_k n_i n_k \bar{v}_{1i} \left[ \sqrt{\frac{45}{8}} a_1^{1} \Theta^{(1,k)}(100|110) \\
+ \frac{3}{2} a_0^{1} \Theta^{(1,k)}(100|100) \right] \\
+ n_i n_k \bar{v}_{1i} \left[ \sqrt{\frac{3}{2}} \left( \frac{15}{4} + \theta \frac{C_{\text{int}}}{k} \right) a_1^{1} \Theta^{(1,a)}(100|110) \\
+ \frac{3}{2} a_0^{1} \Theta^{(1,a)}(100|100) \right] \right\} \]  

(III.412)

where

\[
\theta = 0 \quad (\forall i, k = 1) \\
= 1 \quad (\forall i, k = b). 
\]  

(III.413)
\( \Omega^{(1,i)}(110|100) \) are appropriately normalized collision cross section. The first two indices in the bracket label the Sonine polynomials\(^{132} \) and the third labels the Wang Chang-Uhlenbeck polynomials\(^{196} \).

It is easy to check that

\[
X_T^1 = \int dp_1 W_1 \cdot f_i^f L_T^i = 0 \quad (III.414)
\]

and

\[
X_T^b = \text{Tr}_{\text{int}} \int dp_b W_b \cdot f_i^b L_T^b = 0. \quad (III.415)
\]

The heat flux moment for the particle 1 gives

\[
X_1^1 = \int dp_1 \left( W_1^2 - \frac{5}{2} \right) W_1 \cdot f_i^f L_T^i
= \sum_i \left\{ \left( \sum_k n_k \bar{v}_{1k} \right) \left[ \frac{15}{4} a_1^1 \Omega^{(1,i)}(110|110) \right.ight.
\]

\[
+ \sqrt{\frac{45}{8}} a_0^1 \Omega^{(1,i)}(110|100) \left. \right\} 
+ n_1 n_i \bar{v}_{1i} \left[ \sqrt{\frac{15}{4} \left( \frac{15}{4} + \frac{\theta C_{\text{int}}}{k} \right) a_1^1 \Omega^{(1,i)}(110|110) } \right.
\]

\[
+ \sqrt{\frac{45}{8}} a_0^1 \Omega^{(1,i)}(110|100) \right\} 
\]

and

\[
X_1^1 = \frac{15}{4} \sqrt{\frac{2kT}{m_1}} n_f 
+ \frac{5n_2^2 \Lambda^2}{8} \sqrt{\frac{2kT}{m_1}} \text{Tr}_{\text{rel}} \left[ \left( \gamma^2 - \frac{3}{2} \right) T U_T - \left( \frac{5}{2} \gamma^2 - \frac{21}{4} \right) U \right] 
\]

\[
+ \frac{in_2^2 \Lambda^2}{16kT} \sqrt{\frac{2kT}{m_1}} \text{Tr}_{\text{rel}} \left[ \gamma^2 U + 2\gamma \gamma, V \right] \cdot \Omega_\epsilon \left[ e^{-K_{\text{rel}}/kT} p_{\text{op}}, r_{\text{op}} \right]. \quad (III.417)
\]
The heat flux type moment for the bound pair gives

\[ X^b_\lambda \equiv \text{Tr}_{\text{int}} \int d\mathbf{p}_b \left[ W_b^2 - \frac{5}{2} + \frac{H_{\text{int}} - E_{\text{int}}}{kT} \right] \mathbf{W}_b \cdot f_i^e \mathbf{L}_T^b \]

\[ = \sum_j \left\{ \delta_{b_j} \sum_k n_b n_k \bar{v}_{bk} \left[ \frac{15}{4} + \frac{C_{\text{int}}}{k} \right] a_i^b \mathcal{E}^{(b,k)}(111|111) \right. \]

\[ + \sqrt{\left( \frac{15}{4} + \frac{C_{\text{int}}}{k} \right)} \frac{3}{2} a_i^b \mathcal{E}^{(b,k)}(111|100) \]  

\[ + \sqrt{\frac{45}{8} a_i \mathcal{E}^{(b,j)}(111|100)} \right\}, \quad (\text{III.418}) \]

and

\[ X^b_\lambda \equiv \text{Tr}_{\text{int}} \int d\mathbf{p}_b \left[ W_b^2 - \frac{5}{2} + \frac{H_{\text{int}} - E_{\text{int}}}{kT} \right] \mathbf{W}_b \cdot f_i^e \mathbf{L}_T^b \]

\[ = n_b \sqrt{\frac{2kT}{m_i}} \left[ \frac{15}{4} + \frac{3}{2(kT)^2} \left( \langle H_{\text{int}}^2 \rangle - E_{\text{int}}^2 \right) \right] \]

\[ = n_b \sqrt{\frac{2kT}{m_i}} \left[ \frac{15}{4} + \frac{3C_{\text{int}}}{2k} \right] \quad (\text{III.419}) \]

Therefore Eqs.(III.412), (III.414), (III.416), and (III.419) determine \( a_i^b, a_i^1 \)

and \( a_0^1 \).

According to equation (III.409), the equation for \( \mathbf{B}^1 \) reduces to an equation for the scalar \( b_0^1 \)

\[ X^{1}_{\eta} \equiv \text{tr} \int d\mathbf{p}_1 [\mathbf{W}_1]^{(2)} : \mathbf{L}_v^{(2)} f_i^e \]

\[ = \sum_i ^{\langle [\mathbf{W}_1]^{(2)} : [\mathcal{R}^{(1,i)}] \mathbf{B}^i \rangle_1} \]

\[ = \sum_i \left[ \delta_{1i} \sum_k \frac{5}{2} n_i n_k \bar{v}_{ik} b_0^1 \mathcal{E}_\eta^{(1,k)} + \frac{5}{2} n_i n_i \bar{v}_{i} b_0^1 \mathcal{E}_\eta^{(1,i)} \right], \quad (\text{III.420}) \]

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and

$$X_n^1 = 5n_f(1 - n_f B_c)$$

$$+ \frac{in_f^2 \chi^3}{4kT\hbar} \text{Tr}_{\text{rel}}[\gamma \gamma]^{(2)} \left[ V, \Omega_L \left[ e^{-K_{\text{rel}}/kT} p_{\text{op}}, r_{\text{op}} \right]^{(2)} \right]. \quad (III.421)$$

Similarly equation (III.409) gives for the bound pairs

$$X_b^b = \text{Tr}_{\text{int}} \int dp_b [W_b]^{(2)} : L_b^{b(2)} f_b^{t_{\text{e}}}$$

$$= \sum_j (\langle [W_b]^{(2)} : |R^{(b,j)}|B^j \rangle)_b$$

$$= \sum_j \left[ \delta_{bj} \sum_k \frac{5}{2} n_k n_k \bar{v}_{bk} b_0 \mathcal{E}_n^{(k,k)} + \frac{5}{2} n_b n_j \bar{v}_{bj} b_0 \mathcal{E}_n^{(b,j)} \right]. \quad (III.422)$$

and

$$X_b^b = \text{Tr}_{\text{int}} \int dp_b [W_b]^{(2)} : L_b^{b(2)} f_b^{t_{\text{e}}}$$

$$= 5n_b \quad (III.423)$$

Eqs. (III.420) and (III.422) determine $b_0^1$ and $b_0^b$.

From equation (III.410), it is easy to check that

$$X_n^1 = \int dp_1 f_{\text{f}}^{t_{\text{e}}} L_n^{1(0)} = 0, \quad (III.424)$$

and

$$X_b^b = \text{Tr}_{\text{int}} \int dp_b f_b^{t_{\text{e}}} L_b^{b(0)}. \quad (III.425)$$

This verifies the first orthogonality relation between the left hand side functions of the Chapman-Enskog equations (III.374) and the left invariants of the collision operators.
Taking energy type moments form Eq. (III.410) gives for the particle 1

\[ X_1^1 = \int d^3p_1 \left( W_1^2 - \frac{3}{2} \right) f_1 \exp L_{1(0)} \]
\[ = \sum_i \langle \left( W_1^2 - \frac{3}{2} \right) |R^{(1,i)}|C^{(i)} \rangle \]
\[ = \sum_i \left\{ \delta_{i_1} \sum_k \frac{3}{2} n_k \bar{v}_{ik} c_1 \Theta^{(1,k)} (010|010) \right. \]
\[ + n_k \bar{v}_{ik} c_1 \left[ \frac{3}{2} \Theta^{(1,i)} (010|010) + \delta_{i_1} \sqrt{\frac{3C_{int}}{2k}} \alpha \Theta^{(i,i)} (010|001) \right] \}

(III.426)

The left hand side of equation (III.410) gives

\[ X_1^1 = \frac{n_f}{n_C} \left[ n_b \frac{dE_{int}}{dT} \left( 1 - \frac{5}{2} n_f B_e - \frac{1}{2} n_f E_U \right) + \frac{3 n_1 \epsilon_1}{2} \right] \]
\[ - \frac{n_b n_f k \Lambda_r^3}{2 \gamma \gamma - \frac{3}{2}} T \text{Tr}_s \left( \gamma^2 - \frac{3}{2} \right) T U_T \left[ \frac{3C_{int}}{2k} \right] \]

(III.427)

Similar relations for the bound pairs are

\[ X_{\pi}^b = \text{Tr}_b \int d^3p_b \left[ W_b^2 - \frac{3}{2} + \frac{H_{int} - E_{int}}{kT} \right] f_b \exp L_{b(0)} \]
\[ = \sum_j \left\{ \delta_{j_1} \sum_k n_b \bar{v}_{bj} c_1 \left[ \sqrt{\left( \frac{3}{2} + \frac{C_{int}}{k} \right)} \frac{3C_{int}}{2} \Theta^{(b,k)} (011|010) \right] \right. \]
\[ + n_b \bar{v}_{bj} c_1 \left[ \sqrt{\left( \frac{3}{2} + \frac{C_{int}}{k} \right)} \frac{3C_{int}}{2} \Theta^{(b,j)} (011|010) \right. \]
\[ + (1 - \delta_{j_1}) \alpha \sqrt{\left( \frac{3}{2} + \frac{C_{int}}{k} \right)} \frac{C_{int}}{k} \Theta^{(b,j)} (011|001) \}

(III.428)

and

\[ X_{\pi}^b = n_b q + \frac{2}{3} n_b (q - 1) \frac{C_{int}}{k}. \]

(III.429)
It is checked that
\[ X^1_\kappa + X^b_\pi = 0. \]  
(III.430)

This confirms another orthogonality relation for the left hand side of the Chapman-Enskog equations (III.374).

Eqs. (III.426) and (III.428) determine expansion coefficients \( c^1 \) and \( c^b \).

It remains to determine the diffusion coefficients. The momentum moment from equation (III.411) gives

\[
X^1_{d_1} = \int dp_1 W_1 \cdot L^1_{d_1} f^e
= \sum_i \langle (W_1 \cdot R^{(1,i)})(-1)^{(1-\delta_{1i})}D_i \rangle
= \sum_i \left[ \delta_{1i} \sum_k \frac{3}{2} n_i n_k \bar{v}_{1i} D_1 \Theta_D^{(1,k)} \right.
+ \frac{3}{2} n_i n_i \bar{v}_{1i} (-1)^{(1-\delta_{1i})} D_i \Theta_D^{(1,i)} \right], \quad (III.431)
\]

and
\[
X^1_{d_1} = \frac{3}{2} \sqrt{\frac{2kT}{m_1}} (n + n^2 B_c). \quad (III.432)
\]

Similar equation (III.411) gives for the bound pairs

\[
X^b_{d_b} = \text{Tr}_{int} \int dp_b W_b \cdot L^b_{d_b} f^e
= \sum_i \langle (W_b \cdot R^{(b,i)})(-1)^{(1-\delta_{bi})}D_i \rangle
= \sum_i \left[ \delta_{bi} \sum_k \frac{3}{2} n_b n_k \bar{v}_{bi} D_b \Theta_D^{(b,k)} \right.
+ \frac{3}{2} n_b n_i \bar{v}_{bi} (-1)^{(1-\delta_{bi})} D_i \Theta_D^{(b,i)} \right], \quad (III.433)
\]

and
\[
X^b_{d_b} = \frac{3}{2} \sqrt{\frac{2kT}{m_b}} (n + n^2 B_c). \quad (III.434)
\]
It is obvious that

\[ \sqrt{m_1}X_{d_1}^1 + \sqrt{m_b}X_{d_1}^b = 0. \quad \text{(III.435)} \]

Therefore Eq.(III.431) determines \( D_1 \). This completes the determination of all perturbation coefficients appearing in Eqs (III.396-III.406).

The combination of Eqs. (III.414), (III.415) and (III.435) establishes the last three orthogonality relations between the left hand side of equation (III.374) and the five left invariants of the collision operators. Thus the Fredholm alternative\(^{42,195}\) is satisfied and an approximate solution has been found to the Chapman-Enskog equations (III.374).

b) The Modified Pair Correlation Equation

A solution for the (linearized) modified pair correlation equation (III.257) has been provided in subsection a) of Section III-4.2. That equation is solved separate from the renormalized Boltzmann equation (III.254). Such a treatment is based on two assumptions: i) From the kinetic equation point of view, within the non-reactive binary collision approximation, the modified pair correlation equation (III.257) is decoupled from the other two kinetic equations. The only thing that couples the modified pair correlation equation to the renormalized Boltzmann equation is through the term

\[ -i\mathcal{V}_{12}f_{f1}^e(1 + \phi_1)f_{f2}^e(1 + \phi_2). \quad \text{(III.436)} \]

ii) Moreover, from the macroscopic point of view, the contribution from the pair correlations to the macroscopic variables has been taken into account by renormalizing particle 1. This method of handling the modified pair correlation equation (III.257) is still valid for the present situation, namely a moderately dense gas mixture. Actually, most of the results obtained
in subsection a) of Section III-4.2 are still true under the present mixture situation. Only some minor changes are needed due to the possibility of diffusion, which is discussed in the following.

It is noted that the term (III.436) now couples the modified pair correlation equation to the generalized Boltzmann equation (III.253), thus also to the bound pair equation (III.256). This implies a change in the form of the perturbation $\phi_c$ for pair correlations because the structure for $\phi_1$ has changed [compare Eqs. (III.304) and (III.385)]. The appropriate form for the perturbation function $\phi_c$ of the pair correlation at present is

$$\phi_c = -A_c \cdot \nabla \ln T - B_c : [\nabla \mathbf{v}_0]^{(2)} - C_c \nabla \cdot \mathbf{v}_0 - D_c \cdot \mathbf{d}_1.$$  (III.437)

At this point it is recognized that the time derivative in the modified pair correlation equation (III.257) has been eliminated by using the hydrodynamic equations derived from Eq. (III.257). This is not affected by the present modification. Therefore the right hand side of the linearized modified pair correlation equation (III.257) remains as that stated in Section III-4.2. After various manipulations which are the same as that in Section III-4.2, the modified pair correlation equation (III.257) is broken down into four equations according the independent gradients. The first three are exactly Eqs. (III.277), (III.278) and (III.279). Since the left hand side of Eq.(III.257) does not have a diffusion term, the perturbations involving diffusion are to be balanced by themselves, this resulting in an additional equation proportional to the diffusion driving force vector $\mathbf{d}_1$

$$0 = \left\{ i\mathcal{L}_{rel} \left[ f_{c12}^{th} \mathbf{D}_c \right] + i\mathcal{V}_{12} \left[ f_{f12}^{th} (\mathbf{D}_1^1 + \mathbf{D}_2^2) \right] + \frac{1}{\tau} f_{c12}^{le} \mathbf{D}_c \right\} \cdot \mathbf{d}_1.$$  (III.438)

According to the auxiliary condition (III.198) for the whole system and (III.260) for pair correlations, the diffusion term in the perturbation function

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(III.437) must not contribute to any local hydrodynamic variable, particularly not to the total momentum

$$\int d{\mathbf{p}}_1 {\mathbf{p}}_1 \cdot f^{le}_{f_1} {\mathbf{D}}_1 + \text{Tr}_{rel} \int d{\mathbf{P}} \cdot f^{le}_{c_12} {\mathbf{D}}_c + \text{Tr}_{int} \int d{\mathbf{p}}_b {\mathbf{p}}_b \cdot f^{le}_{f}(-1) {\mathbf{D}}_b = 0,$$

(III.439)

and not to the momentum change of a pair correlation

$$\text{Tr}_{rel} \int d{\mathbf{P}} G \cdot \left\{ i{\mathcal{L}}_{rel} f^{le}_{c12} {\mathbf{D}}_c + i{\mathcal{V}}_{12} f^{lh}_{f12} \left( {\mathbf{D}}_1^1 + {\mathbf{D}}_2^2 \right) + \frac{f^{le}_{c12} {\mathbf{D}}_c}{\tau} \right\} = 0. \quad (III.440)$$

As in Section III-4.2, the perturbation $\phi_c$ is determined by taking moments with respect to the linearized modified correlated equation (III.277), (III.278), (III.279) and (III.438). The solutions for $A_c, B_c$ and $C_c$ remain as what have been done in Section III-4.2, while the coefficient for $D_c$ is now determined.

An appropriate choice for $D_c$ satisfying the auxiliary conditions Eqs.(III.439) and (III.440) is

$$D_c = D_{c1} G \left( g^2 - \frac{5}{2} \right). \quad (III.441)$$

To determine $D_{c1}$, a moment is needed which has to couple $D_{c1}$ to the known coefficient $D_1$ through equation (III.438). This can be achieved through the following apparently strange function

$$G^2 \Omega [p_{op}, r_{op}]_+ \Omega^T. \quad (III.442)$$

The diffusion coefficient $D_{c1}$ is determined by taking matrix element of Eq. (III.438) with respect to the moment of (III.442) to give

$$\frac{15 D_{c1} n_c}{\text{Tr}_{rel} U} \text{Tr}_{rel} e^{-K_{rel}/kT} H_{rel} - 15 \sqrt{2} D_1 n_f^2 A_{c1}^3 \text{Tr}_{rel} H_{rel} e^{-K_{rel}/kT} = 0. \quad (III.443)$$

This determines $D_{c1}$ in terms of the known function $D_1$.  

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III-4.5 Scheme II: Transport Coefficients

The general expressions for the hydrodynamic variables have been given in Section III-3.5 where the possibility of local inhomogeneity contributions in addition to the local non-equilibrium perturbation was kept since it is possible to have each species reaching its own local equilibrium before local homogeneous equilibrium is fulfilled\(^2\). Whereas in this section, as well as in Section III-4.3, the hydrodynamic variables are given in a manner consistent with the way the kinetic equations are solved, namely a common stream velocity \(v_0 = v_f = v_c = v_b\) and a common temperature \(T = T_f = T_c = T_b\) are assumed. The transport coefficients are presented from the binary mixture point of view with one species being a renormalized particle 1, and the other a bound pair. Except for coefficients \(a_1^i, b_0, c_0\) and \(C_{corr}\) being given in Section III-4.2, the rest of the coefficients are determined in Section III-4.4. All transport coefficients are obtained in a manner similar to the treatment in Section III-4.3. However, there are three differences. First, there are new contributions from the bound pair to all the transport properties. Second, in addition to two diffusion velocities, there are diffusion contributions to the kinetic, collisional and potential heat fluxes. Finally, the Sonine functions for the energy perturbation in Section III-4.4 is chosen differently from that in Section III-4.2. This difference leads to different transport coefficient expressions, particularly for the bulk viscosity.

The kinetic pressure tensor is calculated according to

\[
P^K = 2kT \sum_i Tr_{int} \int W_i W_i f_i dp_i
\]

\[
= 2kT \int W_1 W_1 f_1 dp_1 + 2kT Tr_{int} \int W_b W_b f_b dp_b
\]
\[
\begin{align*}
&= (nkT + \frac{1}{3}n_f^2kT\epsilon_1)U + 2n_fkT \int W_1W_1 \frac{e^{-\varphi_1^2 \phi_1}}{\pi^{3/2}} dW_1 \\
&\quad + 2n_f^2kT\Lambda^2 \int dGTr_{rel} \frac{e^{-\varphi_1^2 \phi_1}}{\pi^{3/2}} W_1W_1 U \phi_c \\
&\quad + 2n_bkTTr_{int} \int W_bW_b \frac{e^{-\varphi_b^2 \phi_b}}{q_b\pi^{3/2}} dW_b \\
&= P^KU - 2\eta_K[\nabla \mathbf{v}_0]^{(2)} - \kappa_K \nabla \cdot \mathbf{v}_0 U,
\end{align*}
\]

(III.444)

to give contributions \(\eta_K\) and \(\kappa_K\) to the shear and bulk viscosity coefficients.

On identifying the coefficients of \([\nabla \mathbf{v}_0]^{(2)}\) and \(\nabla \cdot \mathbf{v}_0\) and simplifying the resulting expressions, the expressions for the viscosity coefficients become

\[
\begin{align*}
\eta_K &= \frac{1}{2}kT[n_f b_0^1 + n_b b_0^b + \frac{1}{2}n_c b_0^c] \\
(III.445)
\end{align*}
\]

and

\[
\begin{align*}
\kappa_K &= kT(n_f c_1^1 + n_b c_1^b) \\
&\quad + \frac{kTn_c c_0^c}{2} \left\{ \left( \frac{2}{3} - \frac{k}{C_{corr}} \right) \\
&\quad - \frac{2k}{3} C_{corr} Tr_{rel} U Tr_{rel} \gamma^2 \left( U_T U - U \frac{E_U}{kT} \right) \right\} \\
(III.446)
\end{align*}
\]

The collisional transfer part of the pressure tensor reduces to

\[
\begin{align*}
P_{coll} &\equiv -\frac{1}{2} Tr_{12} r_{op} \nabla \delta (R_{op} - r) \Omega \rho f_1 \rho f_2 \Omega^t \\
&= P^VU - 2\eta_{coll}[\nabla \mathbf{v}_0]^{(2)} - \kappa_{coll} \nabla \cdot \mathbf{v}_0 U \\
(III.447)
\end{align*}
\]

with virial pressure \(P^V = n_f^2kT(B_c - \epsilon_1/3)\), shear viscosity

\[
\begin{align*}
\eta_{coll} &= \frac{n_f^2}{20} \Lambda^2 Tr_{rel} r_{op} \nabla V : \left\{ \Omega c^{-K_{rel}/kT} r_{op} P_{op} \Omega^t \right\}^{(2)} \\
&\quad - b_0^1 \left[ \Omega e^{-K_{rel}/kT} \gamma \gamma^t \right]^{(2)} U, \\
(III.448)
\end{align*}
\]
and bulk viscosity

\[
\kappa_{\text{coll}} = \frac{n_f^2}{12kT} \Lambda^2_{rel} \mathbf{r}_{\text{op}} \cdot \nabla V \cdot \Omega \left[ e^{-\kappa_{\text{rel}}/kT} \mathbf{r}_{\text{op}} \cdot \mathbf{P}_{\text{op}} \right] + \Omega^i + \frac{c^4 n_f^2 kT}{3} \left( \frac{3}{2} E_U - \Lambda^2_{rel} \gamma^2 T U_T \right) \tag{III.449}
\]

The kinetic heat flux vector is estimated as

\[
\mathbf{q}^K = kT \sum_i \mathbf{W}_i \left( \frac{2kT}{m_i} \int dp_i \mathbf{W}_i \left( W_i^2 + \theta H_{int} \right) f_i \right)
\]

\[
= \sqrt{\frac{2kT}{m_1}} kT \int dp_1 \mathbf{W}_1 \left( W_1^2 + \theta H_{int} \right) f_1^{le} \phi_1
\]

\[
+ \sqrt{\frac{2kT}{m_b}} kT \mathbf{Tr}_{\text{int}} \int dp_b \mathbf{W}_b \left( W_b^2 + H_{int} \right) f_b^{le} \phi_b
\]

\[
+ \sqrt{\frac{2kT}{m_1}} kT \int dp_1 \mathbf{W}_1 \left( W_1^2 f_{cl}^{le} \phi_{cl} \right)
\]

\[
= -\lambda_K \nabla T - D^1_K \mathbf{d}_1 - D^b_K \mathbf{d}_b \tag{III.450}
\]

with kinetic contribution to the thermal conductivity

\[
\lambda_K = \frac{5n_f}{4} k \sqrt{\frac{2kT}{m_1}} \left[ a_1^1 + a_0^1 \right]
\]

\[
+ \frac{5n_b}{4} k \sqrt{\frac{2kT}{m_b}} \left[ (a_1^b + a_0^b) + \frac{2}{5} \left( a_1^b (H_{int}^2) - E_{int}^2 + a_0^b E_{int}/kT \right) \right]
\]

\[
+ \frac{5n_c a_1^2}{12} k \sqrt{\frac{2kT}{m_1}} \left[ \frac{3}{2} + \frac{1}{\mathbf{Tr}_{rel} U} \mathbf{Tr}_{rel} \gamma^2 \left( U^{-1} U_T - \frac{E_U}{kT} \right) \right]
\]

and diffusion thermal contributions

\[
D^1_K = \frac{5kT}{4} \sqrt{\frac{2kT}{m_1}} \left( n_f D_1 + \frac{n_c D_{cl}}{2\sqrt{2}} \right), \tag{III.451}
\]

and

\[
D^b_K = \frac{5n_b kT}{4} \sqrt{\frac{2kT}{m_b}} \left( 1 + \frac{2E_{int}}{5kT} \right) D_b. \tag{III.452}
\]
The pair particle collisional heat flux is determined according to

\[
q_{\text{coll}} = -\frac{1}{4m_1} \mathbf{Tr}_{12} \delta(\mathbf{R}_{\text{op}} - \mathbf{r}) \mathbf{r}_{\text{op}}(\mathbf{P} - 2m_1 \mathbf{v}_0) \cdot \nabla V \Omega \rho_{f1} \rho_{f2} \Omega^t
\]

\[
= -\lambda_{\text{coll}} \nabla T - D_{\text{coll}} \mathbf{d}_1, \quad \text{(III.453)}
\]

with thermal conductivity contribution

\[
\lambda_{\text{coll}} = \frac{n_f^2}{24m_1 T} \Lambda^3 \mathbf{Tr}_{\text{rel}} \mathbf{r}_{\text{op}} \nabla V \cdot \Omega \left[ e^{-K_{\text{rel}}/kT} \mathbf{p}_{\text{op}}, \mathbf{r}_{\text{op}} \right]_+ \Omega^t
\]

\[-\frac{a^1_0 n_f^2 k}{6} \sqrt{\frac{2kT}{m_1}} \Lambda^3 \mathbf{Tr}_{\text{rel}} \gamma^2 U
\]

\[+ \frac{a^1_0 n_f^2 k}{12} \sqrt{\frac{2kT}{m_1}} \Lambda^3 \mathbf{Tr}_{\text{rel}} \gamma^2 \left( \frac{5}{2} - U^{-1}TU_T \right) U
\]

\[-\frac{a^1_0 n_f^2}{12} \sqrt{\frac{2kT}{m_1}} \Lambda^3 \mathbf{Tr}_{\text{rel}} \mathbf{r}_{\text{op}} \nabla : \Omega e^{-K_{\text{rel}}/kT} \gamma \gamma \Omega^t \quad \text{(III.454)}
\]

and diffusion thermal contribution

\[
D_{\text{coll}} = -\frac{D_1 n_f^2 k T}{6} \sqrt{\frac{2kT}{m_1}} \Lambda^3 \mathbf{Tr}_{\text{rel}} \gamma^2 U \quad \text{(III.455)}
\]

There is the pair particle potential energy heat flux contribution

\[
q^V = \frac{1}{4m_1} \mathbf{Tr}_{12} [\mathbf{p}_{\text{op},1} - m_1 \mathbf{v}_0, \delta_1]_+ V_{12} \rho_{12}^{(2)}
\]

\[= \frac{1}{2} n_f^2 \Lambda^3 \sqrt{\frac{kT}{m_1}} \mathbf{Tr}_{\text{rel}} \int dG^\gamma e^{-\gamma^2} GV \left[ e^{-K_{\text{rel}}/kT}(\phi_1 + \phi_2) + U \phi_c \right]
\]

\[= -\lambda_V \nabla T - D_V \mathbf{d}_1 \quad \text{(III.456)}
\]

with thermal conductivity contribution

\[
\lambda_V = \frac{5n_f^2 a^1_0}{12} \sqrt{\frac{k}{2m_1 T}} \Lambda^3 \mathbf{Tr}_{\text{rel}} V \left( \gamma^2 - \frac{3}{2} \right) e^{-K_{\text{rel}}/kT}
\]

\[+ \frac{a^1_0 n_f^2}{4} \sqrt{\frac{2k}{m_1 T}} \Lambda^3 \mathbf{Tr}_{\text{rel}} V e^{-K_{\text{rel}}/kT}
\]

\[+ \frac{n_f a^2_c}{4} \sqrt{\frac{k}{m_1 T}} \frac{1}{\mathbf{Tr}_{\text{rel}} U} \mathbf{Tr}_{\text{rel}} V \left( U^{-1}TU_T - \frac{E_U}{kT} \right) U \quad \text{(III.457)}
\]
and diffusion thermal contribution

\[
D_V = \frac{D_1 n_f^2}{4} \sqrt{\frac{2kT}{m_1}} \Lambda^3 \mathrm{Tr}_{rel} V e^{-K_{rel}/kT}.
\]  

(III.458)

Finally the diffusion velocities are

\[
V_i \equiv \frac{1}{n_i} \exp \int \frac{p_i - m_i v_0}{m_i} f_i dp_i.
\]

(III.459)

In particular \( V_1 \) is given by

\[
V_1 \equiv \frac{1}{n_1} \sqrt{\frac{2kT}{m_1}} \left( \int dp_1 W_1 f_{le}^{1e} \varphi_1 + \int dp_1 \mathrm{Tr}_{rel} W_1 f_{c12}^{le} \varphi_{c12} \right) \\
= -D_{1b} d_1 - D_{1T} \nabla \ln T,
\]

(III.460)

where the diffusion coefficient is given by

\[
D_{1b} = \sqrt{\frac{2kT n_f D_1}{m_1}} \frac{n_f}{2n_1},
\]

(III.461)

and the thermal diffusion coefficient is given by

\[
D_{1T} = \sqrt{\frac{2kT n_f a_0^1}{m_1}} \frac{n_f}{2n_1}.
\]

(III.462)

Similarly the diffusion velocity of the bound pair is

\[
V_b \equiv \frac{1}{n_b} \sqrt{\frac{2kT}{m_b}} \mathrm{Tr}_{int} \int dp_b W_b f_{b}^{le} \varphi_b \\
= -D_{b1} d_b - D_{bT} \nabla \ln T
\]

(III.463)

where the diffusion coefficient is given by

\[
D_{b1} = \sqrt{\frac{2kT D_b}{m_b}} \frac{D_b}{2}
\]

(III.464)

and the thermal diffusion coefficient is given by

\[
D_{bT} = \sqrt{\frac{2kT a_0^b}{m_b}} \frac{a_0^b}{2}.
\]

(III.465)

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Recognizing \( D_b = \frac{n_t}{n_b} \sqrt{\frac{m_1}{m_b}} D_1, \quad a_0^b = -\frac{n_t}{n_b} \sqrt{\frac{m_1}{m_b}} a_0^1 \) and \( d_b = -d_1 \), the two diffusion velocities compensate each other,

\[
\varrho_1 V_1 + \varrho_b V_b = 0. \tag*{(III.466)}
\]

Note that means the lighter species with smaller concentration moves faster.

Several different contributions to the transport coefficients have been found. Collected together, the shear viscosity is

\[
\eta = \eta_K + \eta_{\text{coll}}, \tag*{(III.467)}
\]

with detailed formula given by Eq.(III.445). For the bulk viscosity,

\[
\kappa = \kappa_K + \kappa_{\text{coll}}, \tag*{(III.468)}
\]

with formulas Eqs.(III.446), (III.449). For the thermal conductivity,

\[
\lambda = \lambda_K + \lambda_{\text{coll}} + \lambda_V. \tag*{(III.469)}
\]

There are also various contributions to the heat flux associated with diffusion thermal

\[
\left( -D_K^k - D_{\text{coll}} - D_V + D_K^k \right) d_1, \tag*{(III.470)}
\]

with coefficients given in Eqs.(III.451), (III.455), (III.458) and (III.452).

### III-4.6 Discussion

Chapman-Enskog solutions for two sets of quantum kinetic equations, one for a moderately dense gas and the other for a moderately dense gas with bound states, have been found. Various transport coefficients have been expressed in terms of the solutions. The philosophy of the Chapman-Enskog procedure has been utilized for solving the kinetic equations with
the lowest order perturbation contributions to the density operators. Such a program could not be feasible without making the use of the Wigner function representation to clearly separate macroscopic and microscopic properties.

The properties of a renormalized particle 1 is a novel aspect of the present theory both for its distinct role in the two kinetic equations, namely the renormalized Boltzmann equation and the generalized Boltzmann equation, and in various macroscopic quantities. Even the diffusion driving force vector \( d_1 \) depends on the properties of the renormalized particle 1.

While the perturbation is affected only by localized collisions which conserve the kinetic energy, the equation of change for the kinetic energy has a production term due the presence of non local collisions. The potential energy is needed to conserve the total energy in deriving the Euler equations. The Fredholm alternative has been shown to be satisfied for each of the renormalized Boltzmann equation, the generalized Boltzmann equation and the bound pair equation. As for the modified pair correlation equation, the solution is not unique because there are more options for the perturbation functions, involving the two particle relative motion. However it is noted that even if the equilibrium pair correlation operator is of higher order in density, the role of the non-equilibrium pair correlation operator is limited to being second order in density. It is believed the set of perturbation functions chosen are consistent within this level of approximation.

As in the classic work of Snider and Curtiss\(^6\), the second order Sonine function for the kinetic energy perturbation is required for solving the renormalized Boltzmann equation since the kinetic energy is a collisional invariant. On the other hand, in solving the generalized Boltzmann equation the first order Sonine function provides a good estimate because collisions with bound pairs occur.
The transport coefficients derived from both set of solutions have contributions from non-locality and pair correlations. In Scheme II, various heat fluxes also have diffusion thermal contributions. The diffusion velocities are worked out to have two components, one is the usual thermal diffusion due to the variation of collision frequency, the other can be solely expressed in the terms of the non-ideal partial pressure gradients.
General Discussion

As most of the results of this thesis has been summarized in the Abstract, it is not necessary to repeat them here. Instead, a brief discussion of some remaining problems is in order. These are as follows.

The two-Liouville space quantum kinetic theory of reactive gases is formulated without a detailed examination of how macroscopic quantities will be influenced. In particular, various clusters are defined as asymptotic bound fragments in the N-particle asymptotic Liouville space, and the difference of this treatment from the conventional single Liouville space treatment needs to be explored. Such an exploration may be both conceptually involved and time-consuming. Nothing along this line of development has been attempted.

The general correspondence between the connected graphs of the virial expansion and the connected diagrams of few-body scattering theory for four and more particles is a conjecture and needs to be examined in the future.

Whether or not the normalizable resonance states (correlated states) of Part II can lead to a general formulation of a reactive dense gas theory is still unknown. Preliminary attempts at such a formulation were unsuccessful. Other applications of the normalizable resonance states are possible, such as to the transition state theory of chemical reactions, and to the computation (approximation) of collision cross sections. An application to the quantum survival probability has been considered recently.

The formalism of reactive dense gas theory using Kato's chain rule and secondary asymptotic states is provided in Chapter III-2 without being implemented in the detailed evaluation in Chapter III-4. The possible implementation of this formalism is an interesting project.

The scheme of a set of coupled kinetic equations for a reactive moderately
dense gas seems to work at the present level. Certain approximations have been made, the major one being the method of treating the deviation from local equilibrium of the pair correlations. Comparison with experiment would provide one way of judging the validity of this approach. To describe the behaviour of denser gases, it is necessary to systematically include higher ordered correlations and introduce more coupled kinetic equations. Such a program might provide an alternate formulation of dense gas theory without using Bogoliubov's complete weakening of initial correlations\textsuperscript{21}.

Various generalizations to the present solutions in Chapter III-4 are possible. First, reactive collisions can be included. Second, the collision non-locality of monomer-dimer and dimer-dimer collisions need to be considered if the corresponding correlations are included. Third, the internal states of the free singlet and the off diagonality of the pair density operator in internal states can be treated. Finally, a detailed evaluation of transport coefficients using soft potentials and a comparison with the results of Rainwater and Friend\textsuperscript{154,155} are needed.
List of Symbols

A a gradient expansion coefficient of the singlet free perturbation (232)
A_c a gradient expansion coefficient of the correlation perturbation (227)
A^b a gradient expansion coefficient of the bound pair perturbation (253)
A^1 a gradient expansion coefficient of the singlet free perturbation (253)
A(r, p, t) a phase space function (183)
A(t) an arbitrary operator (183)
a_i an expansion coefficient of A_c (228)
a_i^1 an expansion coefficient for the singlet free perturbation (256)
a_i^1 an expansion coefficient for the singlet free perturbation (256)
a_i^b an expansion coefficient for the bound pair perturbation (256)
a_i^b an expansion coefficient for the bound pair perturbation (256)
a_c(T) channel virials (69)
a_1 an expansion coefficient of A (238)
\alpha the list of particles which are monomers (36)
\alpha a factor in the bound pair perturbation coefficient (256)
\mathcal{B}^{(n)} the subspace of the n-particle total bound states (17)
B_2(T) second virial coefficient (68)
B_3(T) third virial coefficient (68)
B second virial coefficient (229)
B_c unbound part of the second virial coefficient (201)
B^1 a gradient expansion coefficient of the singlet free perturbation (253)
B^b a gradient expansion coefficient of the bound pair perturbation (253)
B a gradient expansion coefficient of the singlet free perturbation (232)
B_c a gradient expansion coefficient of the correlation perturbation (227)
b_0 an expansion coefficient of B_c (228)
$b_0$ an expansion coefficient of $B$ (238)

$b_1^b$ an expansion coefficient for the singlet free perturbation (256)

$b_0^b$ an expansion coefficient for the bound pair perturbation (256)

$b_{\omega}(V,T)$ cluster coefficients (70)

$\beta$ relative momentum (185)

$\beta$ the list of pairs of particles which are bound pairs (dimers) (36)

$\beta^{-1} = kT$ (68)

$C$ a gradient expansion coefficient of the singlet free perturbation (232)

$C^1$ a gradient expansion coefficient of the singlet free perturbation (253)

$C^b$ a gradient expansion coefficient of the bound pair perturbation (253)

$C_c$ a gradient expansion coefficient of the correlation perturbation (227)

$C_{\text{corr}}$ correlation heat capacity (224)

$C_{\text{int}}$ bound pair heat capacity (256)

$C_m$ an asymptotic cluster (45)

$|C_{\omega}|$ the number of channels which are compatible to $C^N$ (38)

$|C_{m}|$ the number of fragments compatible to $C_m^N$ in the channel $C^N$ (38)

$C_n$ a rearrangement channel (12)

$C_m^n$ a subchannel (fragment) (12)

$C^n$ the set of channels in the $n$-particle system (15)

$\hat{C}_m^n$ molecular (subchannel) content (37)

$\hat{C}_m^n$ channel content (37)

$\hat{C}_m^n$ the set of all compatible channels (37)

$|\hat{C}_m^n|$ the number of compatible channels (37)

$\{\hat{C}_m^n\}$ the set of all compatible fragments (molecules) (37)

$|\hat{C}_m^n|$ the number of $\hat{C}_m^n$ molecules in the channel $C_m^n$ (37)

$|C_m^n|$ the number of particles in the fragment $C_m^n$ (37)

$C_v$ heat capacity (230)
$C_{ij}^V$ heat capacity (241)
$\sigma^{(i,j)}$ collision cross section (217)
$c_1$ an expansion coefficient for the singlet free perturbation (256)
$c_2$ an expansion coefficient of $C$ (238)
$c_5^b$ an expansion coefficient for the bound pair perturbation (256)
$c_6^b$ an expansion coefficient of $C_c$ (228)
$D$ number of dimers (36)
$D_1$ a gradient expansion coefficient of the singlet free perturbation (253)
$D_6$ a gradient expansion coefficient of the bound pair perturbation (253)
$D_1$ an expansion coefficient for diffusion (257)
$D_K^1$ kinetic diffusion thermal coefficient (269)
$D_T$ thermal diffusion coefficient (271)
$D_6$ an expansion coefficient for diffusion (257)
$D_{31}$ diffusion coefficient (271)
$D_{6T}$ thermal diffusion coefficient (271)
$D_K^b$ kinetic diffusion thermal coefficient (269)
$D_c$ an expansion coefficient for diffusion (265)
$D_{c1}$ an expansion coefficient for diffusion (266)
$D_c$ correlation number density gradient expansion coefficient (225)
$D_{c_n}^\pm$ an observable that confirms a state is in channel $C^n$ (17)
$D_{cool}$ collisional diffusion coefficient (270)
$D(H^{(n)})$ the domain of $H^{(n)}$ (16)
$D(H^{(n)})$ the domain of $H^{(n)}$ (16)
$D_t(E)$ time delay (91)
$D_{1b}$ diffusion coefficient (271)
$D_V$ potential diffusion thermal coefficient (270)
$d$ dimension (90)
$d_1$ diffusion driving force vector (250)
$d_2$ diffusion driving force vector (250)
$\Delta_c$ correlation velocity gradient expansion coefficient (225)
$\Delta(r, p)$ Wigner transform operator (183)
$\Delta_{CM}$ center of mass Wigner transform operator (183)
$\Delta_{rel}$ relative motion Wigner transform operator (183)
$\delta_i = \delta(r - r_i)$ (141)
$E$ two particle relative energy (91)
$E_{int}$ average internal energy per bound pair (197)
$E^U$ difference of average energy (225)
$E_{U}$ reduced kinetic correlation energy (245)
$\epsilon_1$ Imam-Rahajoe and Curtiss notation (241)
$\epsilon_{corr}$ correlation energy for the pair correlations (177)
$\epsilon^K$ kinetic energy (170)
$\epsilon_{CM}$ center of mass energy of pair correlations (223)
$\epsilon_{rel}$ relative energy of pair correlations (223)
$\epsilon_{corr}^e$ equilibrium correlation energy (224)
$\epsilon_1$ total local energy of the renormalized particle 1 (246)
$\epsilon$ local total energy (247)
$\epsilon_{CM}$ negative bound state energy (13)
$\epsilon_n$ bound state energy (91)
$\eta_n(z)$ eigenvalues (80)
$\eta_i(E)$ partial wave phase shift (91)
$\eta_K$ kinetic shear viscosity coefficient (241)
$\eta_{coll}$ collisional shear viscosity (241)
$F_c^e$ a gradient expansion coefficient for the pair correlation operator (191)
$F_{cu}^e$ a gradient expansion coefficient for the pair correlation operator (191)
\( \mathbf{F}_\alpha^\sigma \) a gradient expansion coefficient for the pair correlation operator (191)

\( F(q) \) a matrix element of the difference of resolvents (97)

\( F_n \) a functional derivative coefficient (231)

\( \mathbf{F}_\nu \) a functional derivative coefficient (231)

\( F_T \) a functional derivative coefficient (231)

\( f_{l1}^{th} \) localized pair correlation contribution to singlet (189)

\( f_{l1}^{lc} \) delocalization contribution of pair correlation to singlet (189)

\( f_{le}^{(r,p_b,t)} \) local equilibrium Wigner function for the bound pair (188)

\( f_f^{(r,p_1,t)} \) local equilibrium Wigner function of a free particle (187)

\( f_{nle}^{(r)} \) non-equilibrium bound pair density operator (219)

\( f_{f12} \) the product of two free operators (220)

\( f_{f12}^{th} \) localized part of the product of two singlet free operators (220)

\( f_{f12}^{inh} \) delocalization correction of two singlet free operators (220)

\( f_k \) correlated pole expansion coefficient (102)

\( f^{(n)}(x^n,t) \) \( n \)-particle distribution function (126)

\( f^{(n)}(x^n|f^{(1)}(x_1,t)) \) a functional of \( f^{(1)}(x_1,t) \) (126)

\( f^{(1)}(x_1,t) \) singlet distribution function (126)

\( \mathcal{G} \) the dimensionless velocity (201)

\( \mathcal{G}^{(3)}(z) \) Faddeev's resolvent operators (83)

\([\mathcal{G}]^{(2)} \) symmetric traceless second rank tensor (225)

\( g(N,M,D) \) all the possible ways of partitioning (36)

\( \gamma^2 \) reduced kinetic energy operator (245)

\( \mathcal{S}^{(n)} \) the \( n \)-particle full Hilbert space (10)

\( \mathbf{H}^{(n)} \) an \( n \)-particle Hamiltonian (11)

\( \mathcal{S}_1^{(2)} \) Hilbert space of particle 12 (15)

\( H^{(n)} \) the \( n \)-particle asymptotic Hilbert space (15)

\( \mathbf{H}_c^{\gamma} \) an asymptotic channel Hamiltonian (13)
$H_{C_n}$ an asymptotic subchannel (fragment) Hamiltonian (13)
$H_{C_n}$ an asymptotic channel Hilbert space (13)
$H_{C_n}$ an asymptotic subchannel Hilbert space (13)
$H_{C_n}$ a channel Hamiltonian (12)
$H_{C_n}$ a subchannel Hamiltonian (12)
$S_{C_n}$ channel Hilbert spaces (12)
$S_i$ Hilbert space of particle $i$ (11)
$H_{init(i)}$ internal state hamiltonian of fragment $i$ (213)
$H_{init}$ internal state hamiltonian of a bound pair (188)
$S_{\infty}^{(n)}$ scattering subspace (17)
$H_{rel}^{ij}$ relative full hamiltonian of fragments $i$ and $j$ (213)
$H_{rel}$ relative (two particle) hamiltonian (189)
$H^{(n)}$ an $n$-particle hamiltonian (129)
$I^{(n)}$ the identity on the $H^{(n)}$ (20)
$I^{(n)}$ the identity operator in space $S^{(n)}$ (21)
$I_L^{(n)}$ the identity operator in Liouville space $L^{(n)}$ (27)
$\Re y$ imaginary part of $y$ (92)
$\{i, j, \cdots, s\}$ the set of particles $i, j, \cdots, s$ (12)
$i_{C_n}^j$ a particle in channel $C_n^N$ that belongs to the given set $\{1, \cdots, n\}$ (41)
$J_{C_n}$ channel identification superoperator (25)
$J_{C_n}$ channel identification operator (16)
$J_{C_n}^\dagger$ adjoint channel identification operator (17)
$J_{C_n}$ a gradient expansion coefficient of non local collisions (215)
$J_{C_n}$ a gradient expansion coefficient of non local collisions (215)
$J_{C_n}$ a gradient expansion coefficient of non local collisions (215)
$J(f^{(1)} f^{(1)})$ binary collision term (127)
$J^{(i,j)}(r_i, p_i)$ collision term in phase space representation (185)
\( J_{h(i,j)} \) localized equilibrium collision term (212)
\( J_{c(i,j)} \) a collisional non locality correction (212)
\( J_{r(i,j)} \) a collisional non locality correction (212)
\( J_{ne(i,j)} \) local non-equilibrium collision term (212)
\( \mathcal{J}^{(n)} \) identification superoperator (24)
\( J^{(n)} \) identification operator (16)
\( J^{(n)\dagger} \) adjoint identification operator (16)
\( J_{rv} \) a gradient coefficient of a non-local collision correction (217)
\( J_{rT} \) a gradient coefficient of a non-local collision correction (217)
\( K_{ij}^{(2)} \) two particle kinetic superoperator (145)
\( K_{CM} \) center of kinetic energy operator (190)
\( K(f^{(1)}f^{(1)}f^{(1)}) \) ternary collision term (127)
\( K^{(n)} \) \( n \)-particle kinetic energy operator (11)
\( K^{(n)}(z) \) an \( n \)-particle kernel (79)
\( K^{(3)}(z) \) Faddeev three-body kernel matrix (85)
\( K_{rel}^{ij} \) relative kinetic operator of fragments \( i \) and \( j \) (212)
\( K_{rel} \) relative (two particle) kinetic energy operator (189)
\( k \) average relative momentum (185)
\( k(C^N_m) \) the number of particles in channel \( C^N_m \)
\( k^N_m \) that belong to set \( \{n+1, \ldots, N\} \) (41)
\( \kappa \) relative momentum (185)
\( \kappa_K \) kinetic bulk viscosity coefficient (241)
\( \kappa_{col} \) collisional bulk viscosity (241)
\( \kappa_b \) (1-dim) bound state momentum parameter (110)
\( \kappa_r \) resonance momentum parameter (110)
\( \mathcal{L}_1^{(1)} \) singlet Liouville operator (128)
\( L^2 \) the space of square integrable functions (13)
\( \mathcal{L}_{ij}^{(2)} \) two particle Liouville operator (145)
\( \mathcal{L}_{(\alpha',\beta',\gamma')} \) secondary asymptotic channel Liouville operators (148)
\( \mathcal{L}_{Cn} \) channel Liouville operator (22)
\( \mathcal{L}_{C^*} \) an asymptotic channel Liouville operator (22)
\( \mathcal{L}_{C^*} \) asymptotic channel Liouville space (23)
\( \mathcal{L}(f^{(1)}f^{(1)}f^{(1)}f^{(1)}f^{(1)}) \) quaternary collision term (127)
\( L_{i(c)}^i \) a gradient driving force coefficient (251)
\( L_{i(\rho)}^i \) a gradient driving force coefficient (251)
\( L_{i(d)}^i \) a gradient driving force coefficient (251)
\( \mathcal{L}^{(n)} \) (full) Liouville operator (22)
\( \mathcal{L}^{(n)} \) (full) Liouville space (22)
\( \mathcal{L}^{(n)} \) asymptotic Liouville operator (23)
\( \mathcal{L}^{(n)} \) \( n \)-particle Liouville operator (129)
\( L_{T}^i \) a gradient driving force coefficient (251)
\( L_{T}^i \) a gradient driving force coefficient (232)
\( L_{v(2)}^v \) a gradient driving force coefficient (232)
\( L_{v(0)}^v \) a gradient driving force coefficient (232)
\( L_{Tc}^i \) a gradient expansion coefficient for pair correlation equation (224)
\( L_{v(c)}^i \) a gradient expansion coefficient for pair correlation equation (224)
\( L_{v(0)}^v \) a gradient expansion coefficient for pair correlation equation (224)
\( \mathcal{L}_{(\alpha,\beta,\gamma)} \) conditional Liouville operator (155)
\( \Lambda_r \) the thermal deBroglie wavelength for relative motion (91)
\( \lambda_K \) kinetic thermal conductivity (242)
\( \lambda_{\text{coll}} \) collisional thermal conductivity (242)
\( \lambda_V \) potential thermal conductivity (242)
\( l(C_m^N) \) the number of particles in channel \( C_m^N \)
that belong to the given set \(\{1, \ldots, n\}\) (41)

\(l_{\text{max}}\) the maximum of \(l(C^N_m)\) (42)

\(M\) number of monomers (36)

\(\min(n, |C^N_m|)\) the smaller number between \(n\) and \(|C^N_m|\) (42)

\(m_i\) mass of particle \(i\) (185)

\(\mu_{C_m}\) cluster chemical potential (76)

\(\mu\) reduced mass (91)

\(N\) total number of particles in the system (36)

\(N_j\) normalization factor (109)

\(n\) a subset of particles (36)

\(n_b\) bound particle number density (141)

\(n_b(r, t)\) bound pair number density (188)

\(n_{C_m}\) cluster number density (70)

\(n_c(R, t)\) correlation density (189)

\(n_f(r, t)\) number density of the free (187)

\(n_f\) number density of free singlets (141)

\(n_b\) number density of bound pairs (141)

\(n_c\) number density of pair correlations (141)

\(\nabla = \frac{\partial}{\partial r}\) (171)

\(\Omega_{(\alpha, \beta)}\) channel Møller superoperator (147)

\(\Omega_{(\alpha', \beta', \gamma')(\alpha, \beta)}\) chain Møller operator (147)

\(\Omega_{C_m}^{\pm}\) channel Møller operator (19)

\(\Omega_{D_n, C_n}^{\pm}\) Møller operator (29)

\(\Omega^{(n)}\) Møller operator (19)

\(\Omega^{(n)}\) Møller superoperator (24)

\(\Omega^{(n)}_{2nd-asy}\) secondary asymptotic channel Møller operator (154)

\(\otimes^{m+l}\) \((m + l)\)-fold tensorial contraction (212)
$P$ center of mass momentum (183)

$P$ (equilibrium) pressure (68)

$P$ total hydrodynamic pressure of a mixture (245)

$P_1$ local equilibrium pressure of renormalized particles (229)

$P^V_1$ virial pressure (241)

$\mathcal{P}_{C^*}$ asymptotic channel projection superoperators (26)

$P^{\pm}_{C^*}$ asymptotic channel projection operators (21)

$P_{C^*}$ projection operators (31)

$P_{i,j}$ the center of mass momentum of the two colliding molecules (216)

$P^K_b$ kinetic pressure of bound pairs (245)

$P^K_1$ kinetic pressure of renormalized particles (245)

$P^K$ total kinetic pressure (246)

$P^K_0$ kinetic pressure tensor of bound pairs (175)

$P^K_c$ kinetic pressure tensor of pair correlations (178)

$P^K_1$ total pressure tensor of renormalized particle 1 (173)

$P_{\text{coll}}$ collisional pressure tensor (173)

$P^K_1$ kinetic pressure tensor (171)

$p$ (1-dimensional) momentum (92)

$p_{op}$ momentum operator (214)

$p_1$ momentum (170)

$p_b$ center of mass momentum of bound pairs (175)

$\Phi^{(n)}$ an asymptotic wave function (15)

$\Phi_{C^*}$ an asymptotic channel wave function (13)

$\Psi_{C^*}$ a wave function of channel $C^n$ (12)

$\Psi^{(n)}$ $n$-particle wave functions (11)

$\psi_1$ physical observables of particle 1 (169)

$\phi_n$ a Gamow state (94)

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\( \phi_c \) perturbation function for pair correlation (191)
\( \phi_1 \) singlet free perturbation function (188)
\( Q_{b^n} \) \( n \)-particle totally bound state projection operator (21)
\( Q_{b^n} \) \( n \)-bound projection superoperator (27)
\( Q_{D^n}^\pm \) orthogonal spectral projection of \( D_{D^n}^\pm \) (18)
\( Q_{\mathcal{C}^n}(V, T) \) partition function for compatible channel \( \mathcal{C}^n \) (69)
\( Q_{\pm}^{(n)} \) an orthogonal projection of \( \mathcal{H}_\infty^{(n)} \) onto \( R(\Omega_{\pm}^{(n)}) \) (20)
\( Q^{(n)} \) orthogonal projection of \( \mathcal{L}^{(n)} \) onto \( R(\Omega^{(n)}) \) (26)
\( Q_{\mathcal{C}^n} \) a set of compatible orthogonal channel projection superoperators (69)
\( Q_{C^n} \) orthogonal channel projection superoperator (68)
\( Q(g) \) matrix element of resolvent (92)
\( Q_0(q) \) matrix element of free resolvent (105)
\( Q_{(\sigma, \beta, \gamma|\sigma^1|12)}^{(n)} \) conditional projection superoperator (155)
\( Q_{(\sigma, \beta^*, \gamma^*)}^{(n)} \) projection superoperator (149)
\( Q \) center of mass momentum (184)
\( q \) off-diagonality in the total momentum (185)
\( q \) a symbol for \( \frac{3}{2} \frac{z}{T_0 C_0} + 1 \) (251)
\( q \) complex momentum parameter (93)
\( q_b \) internal state partition function (188)
\( q_j \) momentum poles (92)
\( q_{\text{coll}} \) collisional heat flux (173)
\( q^K_1 \) heat flux (171)
\( q^K_6 \) heat flux of bound pairs (176)
\( q^K_c \) heat flux of pair correlations (179)
\( R \) center of mass position (183)
\( R^{3n} \) Euclidean space of dimension \( 3n \) (11)
\( R^{(2)} \) (two particle) full resolvent operator (78)
$R_0^{(2)}$, (two particle) free resolvent operator (78)
$\mathcal{R}^{(2)}(z)$ the difference of the resolvent operators (78)
$\mathcal{R}^{(3)}(z)$ the (three-body) differences of resolvent operators (82)
$\mathcal{R}^{(i,j)}$ collision operator (217)
$R(\Omega_{m}^{(n)})$ the ranges of Møller operators (19)
$R(\Omega_{c,n}^{(n)})$ ranges of $\Omega_{c,n}^{(n)}$ (19)
$r$ macroscopic position (141)
$r_{op}$ position operator (214)
$r_c$ potential cutoff distance (92)
$\rho^{(n)}$ reduced density operator (22)
$\rho_{C,n}$ channel density operator (22)
$\rho_{M:D}$ density operator (36)
$\rho^{(n)}(1, \ldots, n)$ reduced density operator (36)
$[\rho^{(n)}(t)]_{n-body}$ isolated $n$-particle density operator (45)
$(\rho_{f1} + \rho_{c1})$ density operator of the renormalized particle 1 (128)
$\rho_{c12}$ pair correlation operator (127)
$\rho_{c1\ldots n}^{eq}$ equilibrium density operators (139)
$\rho_{M:D;C}^{(N)}$ $N$-particle density operator (140)
$\rho_{u12}^{(2),c}$ the unbound part of

the full local equilibrium pair density operator (198)
$\rho_{c12}^{eq}$ equilibrium pair correlation operator (182)
$[\rho^{(n)}]_{asy}(t)$ $n$-particle asymptotic density operator (146)
$[\rho^{(n)}]_{2nd-asy}$ secondary asymptotic channel density operator (154)
$[\rho^{(n)}]_{coll}(t)$ density operator of isolated $n$ particles

with collision boundary condition (145)
$[\rho^{(n)}]_{iso}$ density operator of isolated $n$ particles (144)
\( \varrho(r,t) \) total mass density (194)
\( \varrho_1(r,t) \) mass density of the renormalized particles (194)
\( \varrho_b(r,t) \) mass density of the bound pairs (194)
\( S^{(n)} \) scattering operator (20)
\( S_{C_{n},D_{n}} \) channel scattering operator (20)
\( S_l(E) \) partial wave S-matrix (91)
\( s_n^{k_{C_{n}}} \) a particle in channel \( C_{n} \) that belongs to the set \( \{ n+1, \cdots, N \} \) (41)
\( \{ s \} \) the set of particles which are not in the given set \( \{ 1, \cdots, n \} \) (41)
\( \sigma(\theta) \) cross section for viscosity (239)
\( \sigma_\kappa \) cross section for bulk viscosity (239)
\( \sigma_\lambda \) cross section for thermal conductivity (239)
\( \sigma^{(i;j)}(nm|n'm'\ell') \) normalized collision cross section (258)
\( \sigma_c \) correlation energy production (223)
\( \sigma^K \) kinetic energy production (173)
\( \sigma_{n_1} \) number density production (171)
\( \sigma \) kinetic energy production coefficient (246)
\( T \) (equilibrium) temperature (68)
\( T^{(i;j)}(\beta q \kappa \kappa) \) transition superoperator (185)
\( T^{(n)} \) transition superoperator (25)
\( T_{C_{n},B_{n}} \) asymptotic channel transition superoperator from \( B_{n} \) to \( C_{n} \) (27)
\( T_{C_{n}} \) asymptotic channel transition superoperator to \( C_{n} \) (27)
\( T^{(n)} \) (total) transition superoperator (28)
\( T^{(3)}(z) \) three-body transition operator (83)
\( T_c(R,t) \) correlation temperature (189)
\( T_b(r,t) \) bound pair temperature (188)
\( T_f(r,t) \) free particle temperature (187)
\( T^{(n)}_{(\alpha,\beta,\gamma)} \) conditional transition superoperator (155)
t^{(3)}(z) two-body transition operators in three-particle space (83)

t^{(3)}(z) T-matrix in tensorial space of $S^{(3)} \otimes S^{(3)} \otimes S^{(3)}$ (85)

t_{C_m} the total number of subchannels $C_m$ which involve at least one particle from the given set \{1, \ldots, n\} (41)

$\tau$ relaxation parameter (182)

$\tau_c$ correlation temperature gradient expansion coefficient (225)

$U_c$ unbound part of the pair particle Ursell operator (245)

$U_{ij}$ Ursell operator of fragments $i$ and $j$ (213)

$U_{C^n}(t)$ an asymptotic channel evolution group (13)

$U^{(n)}(t)$ $n$-particle full evolution group (11)

$U^{(n)}_L(t)$ full evolution unitary superoperator (24)

$U^{(n)}_L(t)$ asymptotic evolution superoperator (24)

$U_{L_{C^n}}(t)$ asymptotic channel evolution superoperator (26)

$U_{C^n}$ Ursell operators (70)

$U^{(n)}$ $n$-particle Ursell operator (75)

$U$ second rank identity tensor (199)

$U(T_c)$ correlation temperature dependent Ursell operator (189)

$U_T$ the temperature derivative of $U$ (191)

$\cup$ partial direct sum (45)

$V$ (equilibrium) volume (68)

$V$ 1-dimensional Yamaguchi potential (92)

$V_0$ amplitude of the Yamaguchi potential (92)

$V_{1,1}$ potential superoperator of the two singlet free (180)

$V_{C^n,D^n}$ potential between channels $C^n$ and $D^n$ (17)

$V_{ij}$ pair particle potential operator (11)

$V^{(n)}$ $n$-particle potential operator (11)

$V^{(n)}$ potential superoperator (25)
\( V^{(3)} \) a three-body potential (81)
\( V_\alpha \) pair particle potentials (81)
\( \mathcal{V}_{12} \) pair particle potential superoperator (128)
\( \mathcal{V}_1(r, t) \) diffusion velocity of the renormalized particles (195)
\( \mathcal{V}_b(r, t) \) diffusion velocity of the bound pairs (195)
\( \mathcal{V}_1^{(n)} \) conditional channel potential superoperator (155)
\( \mathcal{V}_{1,b} \) potential superoperator of the singlet free and bound (180)
\( \mathcal{V}_{ij} \) two-body potential operator (129)
\( \mathcal{V}_{ij} \) pair particle potential superoperator (129)
\( \mathcal{V}_b(r, t) \) bound pair stream velocity (188)
\( \mathcal{V}_c(R, t) \) correlation velocity (189)
\( \mathcal{V}_t \) stream velocity of renormalized particles (170)
\( \mathcal{V}_f(r, t) \) free particle stream velocity (187)
\( \bar{\mathcal{V}} \) mean velocity of relative motion (239)
\( \mathcal{W}_C^n \) channel probability operator (69)
\( \mathcal{W}_C^n \) compatible channel probability operator (69)
\( \mathcal{W}^{(n)} \) n-particle probability operator (75)
\( \mathcal{W}_1 \) dimensionless momentum for renormalized particles (232)
\( \mathcal{W}_b \) dimensionless momentum for bound pairs (249)
\( \omega(y) \) a \( w \)-function (92)
\( \varphi^{(n)} \) asymptotic channel density operator (22)
\( \varphi^{(n)} \) asymptotic density operator (23)
\( \varphi^{(N)}_{CN} \) \( N \)-particle asymptotic density operator (38)
\( \varphi^{(n)}_{CN} \) reduced \( n \)-particle density operator (39)
\( \varphi_f(1) \) singlet free operator (47)
\( \varphi_b(1, \ldots, n) \) \( n \)-bound density operator (43)
\( X_L^T \) a momentum integral (258)
$X_T^h$ a momentum integral (259)
$X_\lambda^h$ a thermal conductivity integral (259)
$X_\lambda^b$ a thermal conductivity integral (260)
$X_\eta^1$ a pressure tensor integral (260)
$X_\eta^b$ a pressure tensor integral (261)
$X_\kappa^b$ a bulk viscosity integral (261)
$X_\kappa^1$ a bulk viscosity integral (261)
$X_{d_1}$ a diffusion integral (263)
$X_{d_b}$ a diffusion integral (263)
$X_s(p, p')$ a structural pole expansion coefficient (102)
$X_\lambda$ a thermal conductivity integral (239)
$X_\eta$ a pressure tensor integral (239)
$X_\kappa$ a bulk viscosity integral (239)
$x$ relative position vector (185)
$\Xi(V, T, z_{C_m})$ multispecies grand partition function (69)
$\langle \xi_k^{(2)}(z) | \rangle$ left eigenvector in tensor space of $\mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)}$ (86)
$\langle \xi_k (z) | \rangle$ left eigenvector (80)
$|\chi\rangle$ the vector associated with the Yamaguchi potential (92)
y relative position vector (185)
$Z_k(r)$ correlated state in position representation (103)
z complex energy parameter (78)
z a symbol for $-T \left( \frac{\partial F}{\partial T} \right)_n$ (247)
$z_{C_m}$ the fugacity associated with the cluster $C_m$ (69)
$|\zeta_k (z) \rangle$ right eigenvector (80)
$|\zeta_k^{(2)}(z) \rangle$ right eigenvector in tensor space of $\mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)} \otimes \mathcal{H}^{(3)}$ (86)
$|\zeta_{q_k}\rangle$ correlated state (102)
$\zeta_{q_k}(p)$ correlated state in momentum representation (103)
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Appendix A  Faddeev Equations

The full three-body hamiltonian is denoted by (see Section II-2.2)

\[ H^{(3)} = H_0^{(3)} + V^{(3)}, \]  

(A.1)

where \( V^{(3)} \) is the three-body potential

\[ V^{(3)} = \sum_{\alpha=0}^{3} V_{\alpha}, \]  

(A.2)

given in terms of the pair potentials

\[ V_0 \equiv 0, \]  

(A.3)

\[ V_1 \equiv V_{23}, \]  

(A.4)

\[ V_2 \equiv V_{13}, \]  

(A.5)

\[ V_3 \equiv V_{12}. \]  

(A.6)

Channel hamiltonians \( H_\alpha^{(3)} \) are defined by

\[ H_\alpha^{(3)} = H_0^{(3)} + V_\alpha. \]  

(A.7)

The full three-body resolvent operator is defined as

\[ R^{(3)}(z) = \frac{1}{z - H^{(3)}}, \]  

(A.8)

where \( z \) is a complex energy parameter. \( R^{(3)}(z) \) is well defined in whole complex energy plane excluding the spectrum of the hamiltonian \( H^{(3)} \). Similarly, the three-body partial resolvent operators are defined as

\[ R_\alpha^{(3)}(z) = \frac{1}{z - H_\alpha^{(3)}}, \]  

(A.9)
The three-body transition operator is formally given in the same manner as that in the two-body case

\[ T^{(3)}(z) = V^{(3)} + V^{(3)}R^{(3)}(z)V^{(3)} \]

\[ = V^{(3)} + T^{(3)}(z)R_0^{(3)}(z)V^{(3)} \]

\[ = V^{(3)} + V^{(3)}R_0^{(3)}(z)T^{(3)}(z), \quad (A.10) \]

\[ T^{(3)}(z), \text{ however, does not give the scattering cross section in the same manner as does the two-body transition operator. Faddeev introduced the following division} \]

\[ T^{(3)}(z) = \sum_{\alpha=0}^{3} V_\alpha + \sum_{\alpha=0}^{3} V_\alpha R_0^{(3)}(z)T^{(3)}(z) \]

\[ = \sum_{\alpha=0}^{3} T_\alpha^{(3)}(z), \quad (A.11) \]

where

\[ T_\alpha^{(3)}(z) \equiv V_\alpha + V_\alpha R_0^{(3)}(z)T^{(3)}(z). \quad (A.12) \]

Subtracting \( V_\alpha R_0^{(3)}(z)T_\alpha^{(3)}(z) \) from both sides of Eq. (A.12) gives

\[ (1 - V_\alpha R_0^{(3)})T_\alpha^{(3)}(z) = V_\alpha + V_\alpha R_0^{(3)}(z)\left(T^{(3)}(z) - T_\alpha^{(3)}\right). \quad (A.13) \]

Multiplying this by \( (1 - V_\alpha R_0^{(3)})^{-1} \) gives

\[ T_\alpha^{(3)}(z) = (1 - V_\alpha R_0^{(3)})^{-1} V_\alpha \]

\[ + (1 - V_\alpha R_0^{(3)})^{-1} V_\alpha R_0^{(3)}(z)\left(T^{(3)}(z) - T_\alpha^{(3)}\right) \]

\[ = t_\alpha^{(3)}(z) + \sum_{\beta=0}^{3} (1 - \delta_{\alpha,\beta})t_\alpha^{(3)}(z)R_0^{(3)}(z)T_\beta^{(3)}(z) \quad (A.14) \]

where \( t_\alpha^{(3)}(z) \) is a two-body transition operator in the three particle space

\[ t_\alpha^{(3)}(z) \equiv V_\alpha + V_\alpha R_0^{(3)}(z)V_\alpha \quad (A.15) \]
\[ V_\alpha + V_\alpha R_0^{(3)}(z)t_\alpha^{(3)}(z) \]  
\[ = (1 - V_\alpha R_0^{(3)}(z))^{-1} V_\alpha. \]  
\[ (A.16) \]
\[ (A.17) \]

Written in matrix form, the Faddeev equation (A.14) for the transition operator is

\[
\begin{pmatrix}
T_0^{(3)}(z) \\
T_1^{(3)}(z) \\
T_2^{(3)}(z) \\
T_3^{(3)}(z)
\end{pmatrix}
= 
\begin{pmatrix}
t_0^{(3)}(z) \\
t_1^{(3)}(z) \\
t_2^{(3)}(z) \\
t_3^{(3)}(z)
\end{pmatrix}
\]

\[
+ 
\begin{pmatrix}
0 & t_0^{(3)}(z) & t_0^{(3)}(z) & t_0^{(3)}(z) \\
t_1^{(3)}(z) & 0 & t_1^{(3)}(z) & t_1^{(3)}(z) \\
t_2^{(3)}(z) & t_2^{(3)}(z) & 0 & t_2^{(3)}(z) \\
t_3^{(3)}(z) & t_3^{(3)}(z) & t_3^{(3)}(z) & 0
\end{pmatrix}
R_0^{(3)}(z)
\begin{pmatrix}
T_0^{(3)}(z) \\
T_1^{(3)}(z) \\
T_2^{(3)}(z) \\
T_3^{(3)}(z)
\end{pmatrix}
\]

\[ (A.18) \]

It is to be noticed that the Faddeev equation for the transition operator is usually written in a 3 x 3 matrix because

\[ t_0^{(3)}(z) = 0 \]  
\[ (A.19) \]

and

\[ T_0^{(3)}(z) = 0. \]  
\[ (A.20) \]