

DENSITY CORRECTIONS TO TRANSPORT COEFFICIENTS
FROM TIME CORRELATION FUNCTIONS

by

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Abstract

A new method for deriving first order density corrections to transport coefficients using projection operators in the time correlation function formalism is developed.

Low and moderately dense gas transport coefficients are standardly calculated from a form of the generalized Boltzmann equation. This equation being solved to first order density corrections for repulsive potentials at the binary collision level by Snider and Curtiss and later extended to include the effects associated with the static presence of a third particle on a binary collision by Hoffman and Curtiss. Rainwater and Friend added extra contributions for the presence of bound pairs when the molecules have an attractive potential. They utilized the Stogryn - Hirschfelder theory for the bound pairs and performed detailed numerical calculations of the resultant formulas. While the numerical calculations give good agreement with experiment, questions remain as to the nature and rigor of the assumptions made in obtaining the final formulas, especially the ad hoc addition of bound pair contributions to the density corrections of systems with repulsive potentials, and the extent that these approximations affect the final numerical results.

To study these questions, the time correlation function formulas for the transport coefficients were chosen as an alternative route to determine first order density corrections. The time correlation formulas are formally exact and so the density corrections can be usefully compared to those of the generalized Boltzmann equation.

Kawasaki and Oppenheim had previously derived formal expressions for first order density corrections to the shear viscosity for a gas of molecules with a repulsive potential, but their results had not been reduced to a form that could be directly compared to those of Snider and Curtiss. As a first step in the study of the time correlation function formalism, the density corrections of Kawasaki and Oppenheim are shown to be equivalent to those of Snider and Curtiss along with an additional correction for three-body collisions.

The projection operator method developed in this thesis does not have the infinite series resummation procedure used by Kawasaki and Oppenheim and is an alternative route to obtaining density corrections from the time correlation functions. At low pressures, projection operators are defined which only consider kinetic contributions to the flux function and expressions for the lowest order transport coefficients along with their higher moment corrections are derived. These expressions are consistent with the solution of the Boltzmann equation.

The first order density correction from bound pairs on the transport coefficients are approximated by treating the system as a binary gas mixture consisting of free molecules and bound pairs. The results of viewing the system from the molecular picture and the atomic picture with appropriate projection operators are shown to be consistent with one another and also with the Boltzmann equation for binary mixtures.

Density corrections in moderately dense gases also arise from potential contributions to the flux. Projection operators which account for both the kinetic and potential flux contributions are required in order to derive explicit expressions for the first order density corrections to the viscosity and thermal conductivity. It is observed that these corrections are consistent with those of Snider and Curtiss with the added Hoffman and Curtiss correction and a term which takes explicit account of three-particle collisions.

In the treatment of mixtures and potential interaction effects, the calculation of a transport coefficient is reduced to an equivalent matrix inversion problem. The binary collision expansion of the respective resolvent in the matrix elements in these formulas allows the transport coefficient to be expressed in terms of integrals over functions of the intermolecular potential.

The projection operator for each system is determined in a straightforward manner with reference to the particular flux tensor in the time correlation formula. Reduction of the general formula to relations suitable for numerical calculation involves the resolvent expansion onto the appropriate projected subspace, and the subsequent binary collision expansion to reduce the N -particle resolvent to a tractable form.

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Chapter 1

Introduction

The rigorous theory of density corrections to transport coefficients for moderately dense gases has been studied since the late 1950's. Distinct formalisms based on generalizations of the Boltzmann equation and time correlation functions have been used to approach this problem. These developments are summarized briefly in this introduction with relevant references and further details presented in the following chapters.

Historically, studies in this direction began with the generalizations of the Boltzmann equation due to N. N. Bogoliubov who provided a systematic method of extending the Boltzmann equation to all orders of density and with the work of H. S. Green who independently developed a physical method to include first order density corrections in the Boltzmann equation. The Bogoliubov approach involves proposing a generalization of Boltzmann's *Stosszahlansatz* to express the s -particle reduced distribution functions $\rho_{1\dots s}^{(s)}$, in terms of products of the one-particle distribution functions $\rho_j^{(1)}$, $j = 1, \dots, s$ at times in the distant past and also assuming that at all other times, higher order distribution functions can be expressed as functionals of the $\rho^{(1)}$'s. Choh and Uhlenbeck implemented this method to obtain a set of kinetic equations which includes up to ternary collisions among particles. Cohen reformulated the Bogoliubov theory in terms of cluster expansions of the BBGKY hierarchy so as to remove a number of objections with regard to the functional assumption.

The solution of the generalized Boltzmann equation within the Chapman - Enskog framework has been achieved subject to different approximations. To make the general problem tractable, both the method of generalizing the Boltzmann equation and the finding of the solution of the resultant equations require simplifying assumptions. In particular Snider and Curtiss limited the intermolecular interactions to repulsive potentials and binary collisions, and Hoffman and Curtiss included some three-particle effects in the derivation. Necessarily, it is also not clear to what extent these approximations have affected the form and magnitude of the final results.

At approximately the same time, formalisms for determining transport coefficients from time correlation functions appeared. The initial formulas for the time correlation function approach are general and valid to all orders of density, but in order to solve these general expressions, simplifying approximations have to be made.

Historically, the equality of the transport coefficients as calculated via the Boltzmann equation and the time correlation functions has been investigated by many people, especially within the lowest order approximation. But the question also arises as to the relation between the expressions for the density corrections from the generalized Boltzmann equation and from the time correlation function formalism. Advances to answering this question were made by starting from the time correlation functions and relating them to a set of kinetic equations which are then shown to be equivalent to the generalized Boltzmann equation of corresponding order in density. But the method of treating the kinetic equations in the time correlation function formalism is the same as that used in deriving the generalized Boltzmann equations so this comparison does not appear to be completely independent. In this manner the equivalence of the time correlation function formalism with the kinetic equation approach has been demonstrated. Once the comparison of the equations is done, there is still the question of solving the kinetic equations. Presumably, the Chapman - Enskog solution can be used to complete the derivation of the transport coefficient. While this helps to clarify some of the assumptions and conditions under which the generalized kinetic equations are derived, it still leaves unanswered questions regarding the common approximations made in both formalisms.

The generalized Boltzmann equations and the equivalent time correlation function expressions contain collision integrals over operators which for example are convergent when the potential is repulsive. If the potential is attractive, a number of these integrals diverge when calculated for bound states and different approximations have been introduced to account for these problems. These approximations have all been introduced within the framework of the generalized Boltzmann equation. Despite giving rise to reasonable numerical estimates of the first order density corrections, the rigor of the assumptions that have gone into the derivation of the final expressions for the transport coefficients in the presence of attractive forces is under question. To our knowledge, a problem-free study of similar scope has not been performed using the time correlation function approach.

It was with these questions in mind that the following thesis was proposed. It was decided to start with the time correlation function formulas and try to develop a method for their evaluation which is independent of the Chapman - Enskog solution, but in a final form that is suitable for numerical calculation. Simplifying assumptions would undoubtedly

be necessary, but a contrast of the method (and results) would help to clarify the existing questions regarding the rigor of the approaches and the range of validity of the results.

The study involves a number of steps which are presented in this thesis and which roughly follow our chronological development of the work. After a chapter of preliminaries in which the material of this introduction is expanded and relevant references are given, the main study begins.

This thesis owes a lot to the work of Kawasaki and Oppenheim who used the time correlation function approach to obtain expressions for the first order density corrections to the viscosity. They established the equivalence of their final equations to those of the Choh and Uhlenbeck application of Bogoliubov's approach, but they did not reduce their expressions further. In Chapter 3, it is demonstrated that the final equations of Kawasaki and Oppenheim (and thus Choh and Uhlenbeck) indeed reduce to results similar to the Chapman - Enskog solution of the generalized Boltzmann equation for repulsive potentials as obtained by Snider and Curtiss with an added three-particle collision contribution. In this chapter, approximations which can be used to extend the approach to include attractive potentials are proposed. Problems we feel exist in the Kawasaki and Oppenheim theory for the rigorous inclusion of attractive potentials and bound states are also discussed.

The main body of this work is presented from Chapter 4 onwards. In Chapter 4, a projection operator formalism is introduced to obtain expressions for the zeroth order density transport coefficients and their Sonine polynomial corrections. This verifies the well known fact that the zeroth order transport coefficients of the Boltzmann equation are identical to those of the time correlation function expressions. The expressions for transport coefficients of binary mixtures are also obtained with the projection operator formalism. The binary mixture viewpoint is one of the ways of approximating the effects of attractive forces. Attractive forces can lead to the formation of bound pairs which change the detailed nature of the fluxes in the system. In the simplest case, the number of bound pairs are approximated by an equilibrium statistical mechanical calculation, and the system is considered to be a binary mixture of an appropriate number of unbound particles and bound pairs.

In Chapter 5 the inclusion of bound pairs in the system from an atomic viewpoint is presented. This can be considered to be a preliminary step to the rigorous treatment of attractive potentials. The results are the same as viewing the system as a binary mixture, but the bound pairs are considered to be composed of the constituting particles of the system, and not just a general second species as is done in the binary mixture point of view.

In Chapters 6 and 7, the intermolecular potential is incorporated into the projection operator formalism and expressions for the first order density corrections to the transport

coefficients are determined. Chapter 6 deals with general aspects and their application to the shear viscosity while Chapter 7 deals with the application to thermal conductivity. The assumptions made and terms neglected are enumerated and ways of improving on them seem clear in this formalism.

It remains to put these aspects together to derive a formalism which includes both the effects of the intermolecular interactions and the bound pairs in a uniform manner. We feel that this thesis lays the ground work for this.

Chapter 2

Overview of the Kinetic Theory of Transport Coefficients

2.1 Introduction

The *state* of a fluid at equilibrium is completely specified on a macroscopic scale by the density of the components and the temperature, which are uniform throughout the system [1]. With the equation of state, and the use of the three laws of thermodynamics, the hydrostatic pressure and other thermodynamic properties of the fluid are determined. From a microscopic point of view, equilibrium is associated with a Maxwellian distribution of velocities for each of the species with constant temperatures, and a positional dependence of the particles determined by the Boltzmann distribution associated with the intermolecular potentials between the particles.

In a non-equilibrium fluid, the densities of the components, temperature, and/or pressure can be different in different parts of the system. The equation of state no longer necessarily relates these quantities. Moreover, if the fluid is flowing, the pressure can have directional properties and must be described by a pressure tensor. A single scalar hydrostatic pressure is no longer sufficient.

As a consequence of being out of equilibrium, density, temperature and/or velocity gradients arise in the fluid which cause macroscopic flows. Density and concentration gradients lead to mass and species flow, temperature gradients to heat flow, and velocity gradients to momentum flow. The flows may have *conductive* (or *diffusive*) and *convective* components. The rates of the conductive transport for these flows are determined by the diffusion, thermal conductivity and viscosity coefficients respectively, which are the simplest transport coefficients for an electrically neutral, non-reacting fluid. Coupling between flows can occur, leading to other transport coefficients. If the gradients are not sustained by external sources,

they dissipate and the system relaxes to a uniform equilibrium state. The microscopic description of these phenomena for gases is the subject of gas kinetic theory.

If the fluid is not too far from equilibrium, macroscopically small, but microscopically large elements of fluid can still be assigned a set of densities for the components, a temperature, a pressure and a flow velocity. Such volume elements are said to be in *local equilibrium*. Within this approximation a qualitative description of the microscopic origin of the shear viscosity is given in the next section. In this chapter, and indeed in most of this thesis, any molecular internal states are assumed unaffected by the flow and ignored in the discussion.

2.2 Shear Viscosity: A General Survey

An insight into the physical aspects of the theory developed in this thesis can be gained by first describing the phenomena under study. Of the various transports, shear flow is chosen for this purpose.

Viscosity (Latin *viscum*: birdlime) is the phenomenon of the dissipation of a momentum gradient in a fluid system. Just as friction produces a resistive force to the motion of rigid bodies which counters their motion, viscosity opposes non-uniform flow in a fluid. Due to so called “no slip” boundary conditions [2], viscosity is always present when a fluid is flowing adjacent to a stationary object (which may be the walls of its container). Viscosity converts the ordered, directional macroscopic flow of the fluid to random microscopic molecular motions which are manifested as an increase in temperature of the fluid.

The viscosity coefficient is defined for fluids that are microscopically not too far from equilibrium. For a fluid flowing in a container, no slip boundary conditions cause the fluid adjacent to the boundary to be stationary while further away from the wall, the velocity is non-zero. This situation is represented in Fig. 1 by a lengthening of the momentum vectors upon moving away from the wall. The actual momentum profile in a fluid depends on the nature of the flow process. *Newton’s Law of Viscosity*,

$$\frac{F_{xz}}{A} = \eta \frac{\partial v_x}{\partial z} \quad (2.1)$$

defines the viscosity coefficient η in the simple geometric arrangement shown in Fig. 1, as the proportionality constant between the directional tangential force per unit area F_{xz}/A , required to maintain a velocity gradient, and the magnitude of that velocity gradient $\partial v_x/\partial z$ perpendicular to the direction of the flow [3].

The viscosity coefficient of a pure fluid depends on the nature of the substance, the temperature, and at high pressures (more than about 1.5 MPa) the density. Since the

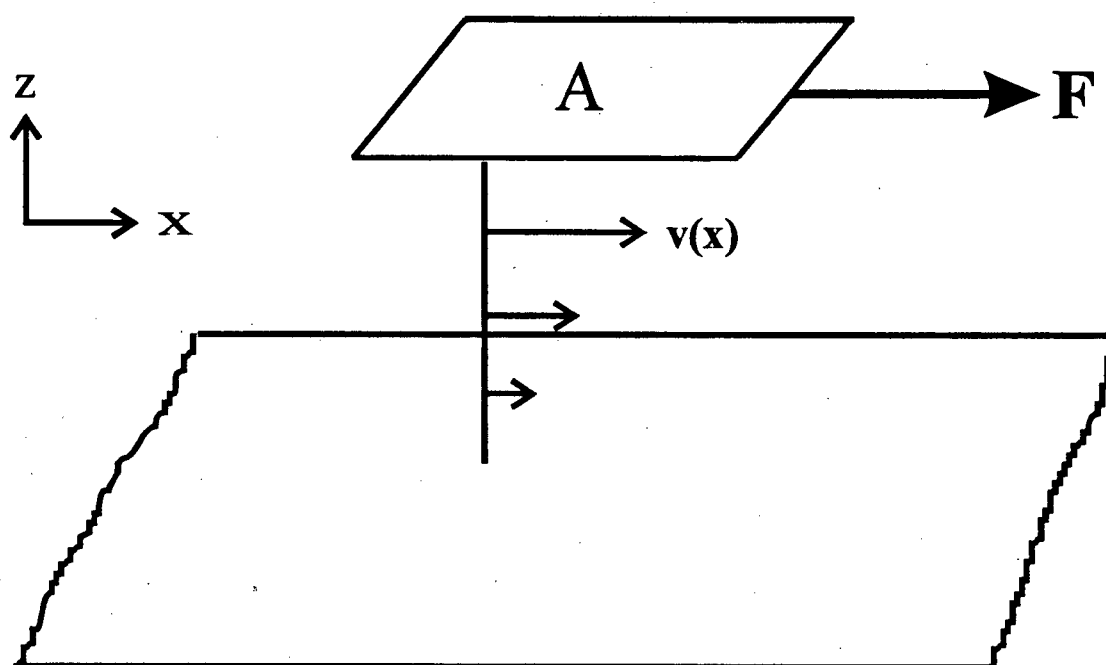


Figure 1. The force F on the surface A establishes a velocity gradient perpendicular to the direction of flow.

fluid in a flow process is not in equilibrium, the definitions of its temperature and density require some care. The temperature and density are assumed to be local properties of macroscopically small but microscopically large volume elements in the fluid. In general, these properties are not equal in different volume elements in the fluid, although in simple flow experiments they can be made constant throughout the fluid. Thus, for example, when viscosity is measured experimentally in the laboratory [4], the temperature and density of the fluid are kept uniform. From a macroscopic point of view, analogous to the virial expansion of equilibrium thermodynamic properties, the temperature and density dependence of the viscosity of a gas can be expressed as a virial expansion, which at least to the first order in density is well defined,

$$\eta = \eta_0(T)[1 + nB_\eta(T) + \dots]. \quad (2.2)$$

η_0 is the low density, ideal gas limit to the viscosity, B_η is called the second viscosity virial coefficient and n is the number density of the gas. Inclusion of terms up to the second viscosity virial coefficient suffices for representing the viscosity for pressures up to about 10 MPa. For comparison, terms up to the third pressure virial coefficient are adequate for the description of equilibrium properties of a gas in this range [5]. A qualitative description of the microscopic nature of the phenomena contributing to $\eta_0(T)$ and $B_\eta(T)$ follows.

Consider as in Fig. 2, two adjacent layers of the fluid in a laminar flow, one having a larger momentum in the direction of flow than the other. If the width of the layers is of the order of the mean free path, the random nature of molecular motions guarantees that a portion of the molecules from each layer wander into the adjacent layer. Molecules from the fast layer entering into the slow layer tend to increase the average momentum of the slow layer. On the other hand, a similar number of molecules from the slow layer enter the fast layer, decreasing its average momentum. The net effect of this transfer of molecules is a decrease in momentum for the fast layer and an increase in momentum for the slow layer. This mechanism for momentum transfer between layers is purely kinetic in nature. The initial velocity gradient is dissipated through the operation of this momentum transfer and in the absence of a tangential external force, the velocity gradient dissipates and the fluid "decays" to an equilibrium state with zero net momentum flow. The average distance a molecule moves before colliding is determined by the mean free path which is inversely related to a collision cross section. A larger collision cross section implies a smaller distance over which the transverse component of the momentum flow is transferred between layers, effectively a smaller transfer of momentum and thus a decrease in the viscosity. At higher temperatures, the particles have a larger momentum and thus transfer more momentum between layers and the viscosity of a gas becomes larger. It is emphasized that in this

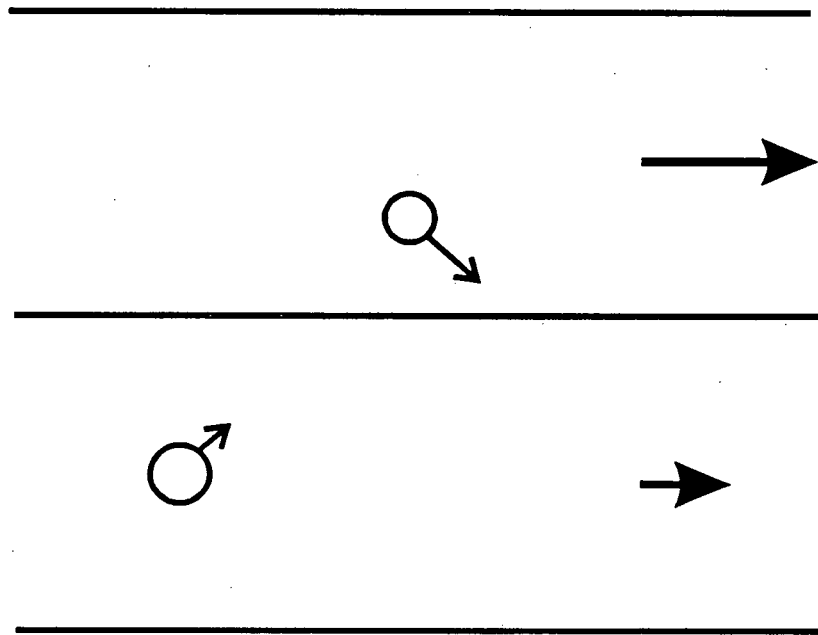


Figure 2. Random motion of molecules in different layers acts to dissipate the momentum gradient among them. There is no net transfer of mass between layers.

process there is a net transfer of momentum between layers without a net transfer of mass.

At higher densities, mechanisms involving the intermolecular potential also contribute to the transverse momentum flux in a fluid. The simplest effect is due to spatial correlations among the particles and is related to the non-ideality in an equilibrium gas. For a given pressure, the density of an ideal gas is different from that of a real gas. The mean free path in a gas is inversely proportional to the density and a correct value for the mean free path will not be obtained if the ideal gas estimate for the density is used. A correction for gas non-ideality must be introduced at higher densities and to first order in density, this leads to a correction to the viscosity that is proportional to the second pressure virial coefficient.

A second mechanism which affects momentum transfer at higher densities is referred to as *collisional transfer*. As illustrated for hard spheres in Fig. 3, collisions can occur in which the centers of mass of both molecules stay within their respective layers. In a binary collision, a molecule with greater momentum loses some of its momentum to the molecule with less momentum. Thus momentum is transferred from the fast layer to the slow layer without an exchange of molecules. As the gas becomes more dense and the mean free path decreases, contributions from these collisions become more important in transferring momentum between layers. The same mechanism for momentum transfer applies to molecules with smooth long range forces. A molecule in the fast layer may exert a force over a distance on a molecule in the slow layer (and vice versa). This force leads to a transfer of momentum between the layers without exchange of molecules. Collisional transfer becomes predominant at high densities. In liquids, where motions are much more restricted, collisional transfer may be up to two orders of magnitude more effective in transferring momentum than the kinetic mechanism of molecular exchange [6]. If interactions between molecules in different layers are attractive, collisional transfer will hamper the relative motion of the layers and give rise to an effective "activation barrier" to the flow. This picture has been used by Eyring as the basis for a theory of viscosity of liquids [7]. At higher temperatures, the average kinetic energy increases, and the molecules can overcome this activation barrier to motion more readily, and collisional transfer contributions to viscosity become smaller. This is consistent with the decrease of viscosity observed in liquids as the temperature is raised. Collisional transfer contributes to first and higher order density corrections since it depends on the interaction of two particles. Another aspect of this momentum transfer mechanism is described in terms of the *non-locality* effect. Even at the distance of closest approach, the centers of mass of two colliding molecules are not at the same point. This allows interconversion of kinetic momentum flow into "virial" (potential; force related) momentum flow and affects the momentum transfer between the layers. The occurrence of at least binary

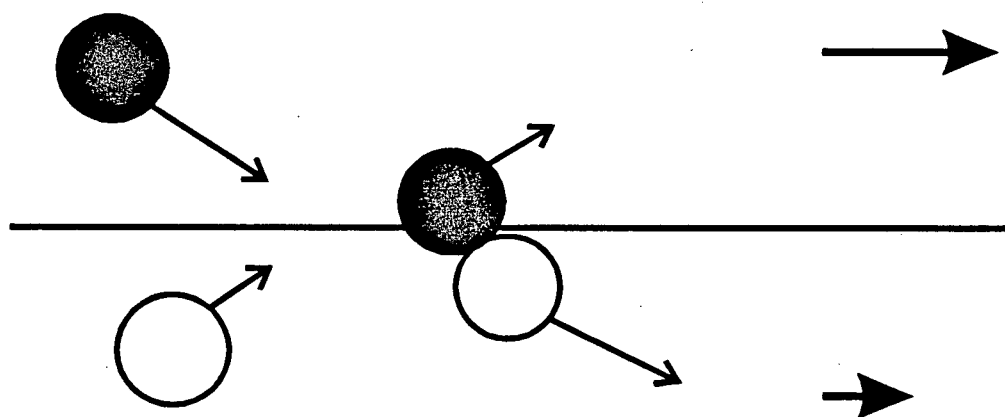


Figure 3. Collisional transfer of momentum from the fast layer to the slow layer, without an exchange of particles.

collisions is required for this mechanism so it contributes to first order or higher density corrections.

The non-ideality and collisional transfer effects require at least two particle interactions and occur even for repulsive intermolecular potentials. At higher densities, the possibility arises for three molecules to interact simultaneously. At a static level, a third particle perturbs the spatial distribution of pairs of colliding molecules and adds a density dependent weight factor to the binary collision cross section. Depending on the range of temperature, this can increase or decrease the viscosity. True three-body collisions also affect momentum transfer in a fluid. The probability of a three-body collision occurring is one order of density higher than a binary collision and so leads to an extra first order density correction to the viscosity.

Finally, in systems with attractive intermolecular potentials, the formation of bound pairs becomes possible. This introduces a new species in the system with its specific collisional properties. The formation of bound pairs also decreases the density of the free species available for momentum transfer. At low abundance, the number of bound pairs is proportional to the square of the density of the fluid. The kinetic transfer of bound pairs between layers contributes to the momentum transfer in the fluid, giving rise to a first order density correction to the viscosity. Calculation of the binary cross sections between free molecules and bound pairs (treating the bound pairs as point particles) [8, 9] indicates that the presence of bound pairs increases the viscosity. This is probably attributed to the fact that bound pairs carry more momentum due to their larger mass and so their transport between layers is more efficient in dissipating the momentum gradient. At higher temperatures where the bound pairs dissociate more readily, their contribution to the viscosity decreases.

Calculations of Najafi et al. [9] for accurate intermolecular potentials, see Fig. 4, show the relative magnitude of the various contributions to the reduced second viscosity virial coefficient at different temperatures. The corrections, designated by (2), are related to two particle potential effects, those indicated by (3), take into account the static effect of a third particle on a binary collision cross section, and finally the $(M - D)$ correction is related to the binary collision cross section between free molecules (monomers) and bound pairs (dimers). To our knowledge, numerical calculations of the contribution of true three-body collisions to the first order density corrections have not been performed.

A theory which sets out to describe the viscosity of a moderately dense gas should account for the above mentioned mechanisms. All density corrections should in principle arise from a unified approach, but in practice, due to conceptual and mathematical difficulties, the mechanisms are usually treated separately.

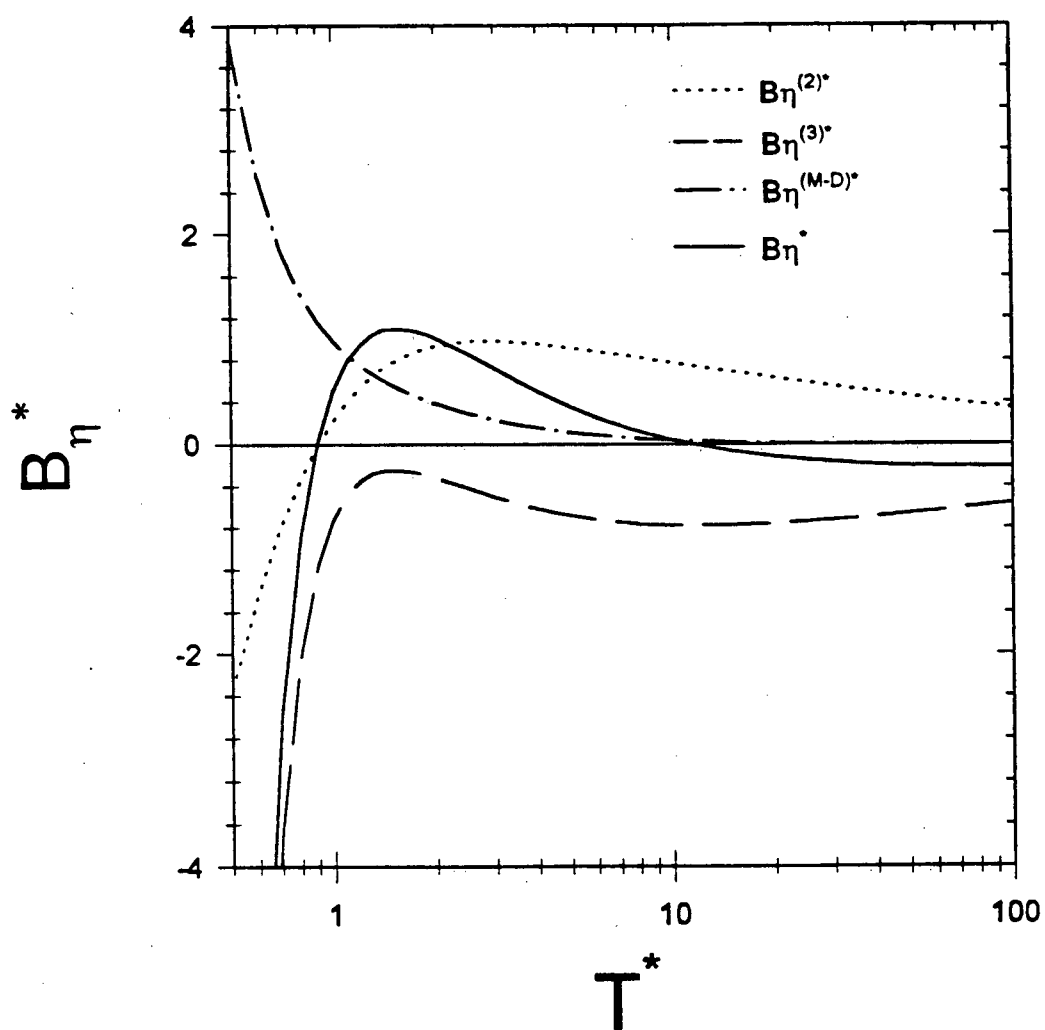


Figure 4. Plots of the different contributions to the reduced second viscosity virial coefficient for argon.

Two general approaches exist for determining the viscosity of a moderately dense gas. The first approach is based on solving the generalized Boltzmann equation, whose method and results are summarized in Section 2.3. The other major approach utilizes the time correlation function formalism. While this is the main topic of this thesis, a short summary of past work is given in Sec. 2.4.

2.3 Generalized Boltzmann Equation for Moderately Dense Gases

Systematic generalizations of the Boltzmann equation which lead to the first order density corrections to the transport coefficients were first developed by N. N. Bogoliubov [10] and H. S. Green [11] and later worked out by Choh and Uhlenbeck [12] to the level of including three-body collisions. M. S. Green [13] and E. G. D. Cohen [14] proposed a derivation for the generalized Boltzmann equation based on cluster expansions which removed a number of objections in the original calculation. Many excellent expositions describing these generalizations [15, 16, 17, 18] are available. Formal derivations are not presented here whereas the emphasis will be on the physical aspects of the theory and establishing connections with the qualitative discussion of the previous section.

The Boltzmann equation describes the time evolution of the state of a non-equilibrium gas at low density. The distribution function $f^{(1)}(\mathbf{v}_1, \mathbf{r}, t)$ for a particle being within the range $d\mathbf{r}$ about a position \mathbf{r} and the range $d\mathbf{v}_1$ about the velocity \mathbf{v}_1 at time t , changes with time if the system is not in equilibrium. Changes in $f^{(1)}(\mathbf{v}_1, \mathbf{r}, t)$ occur due to streaming motion and to collisions which remove or introduce particles from the neighborhood of this phase space point. This leads to the Boltzmann equation which in the absence of external forces, has the form,

$$\frac{\partial f_1^{(1)}(\mathbf{v}_1, \mathbf{r}, t)}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1^{(1)}(\mathbf{v}_1, \mathbf{r}, t)}{\partial \mathbf{r}} = \iiint \left\{ f_1^{(1)}(\mathbf{v}'_1, \mathbf{r}, t) f_2^{(1)}(\mathbf{v}'_2, \mathbf{r}, t) - f_1^{(1)}(\mathbf{v}_1, \mathbf{r}, t) f_2^{(1)}(\mathbf{v}_2, \mathbf{r}, t) \right\} g_{12} b d\mathbf{b} d\mathbf{v}_2. \quad (2.3)$$

In obtaining this equation, the distribution functions of the colliding molecules are both considered to be at the position of the first molecule \mathbf{r} . The collision is also assumed to occur instantaneously at time t . Studied from a macroscopic viewpoint and on hydrodynamic length and time scales, the Boltzmann equation takes the collisions to occur instantaneously, and at a single point in space. In this context, the collision term is said to be *local* in space and time. The assumptions of collision locality are suitable for dilute gases.

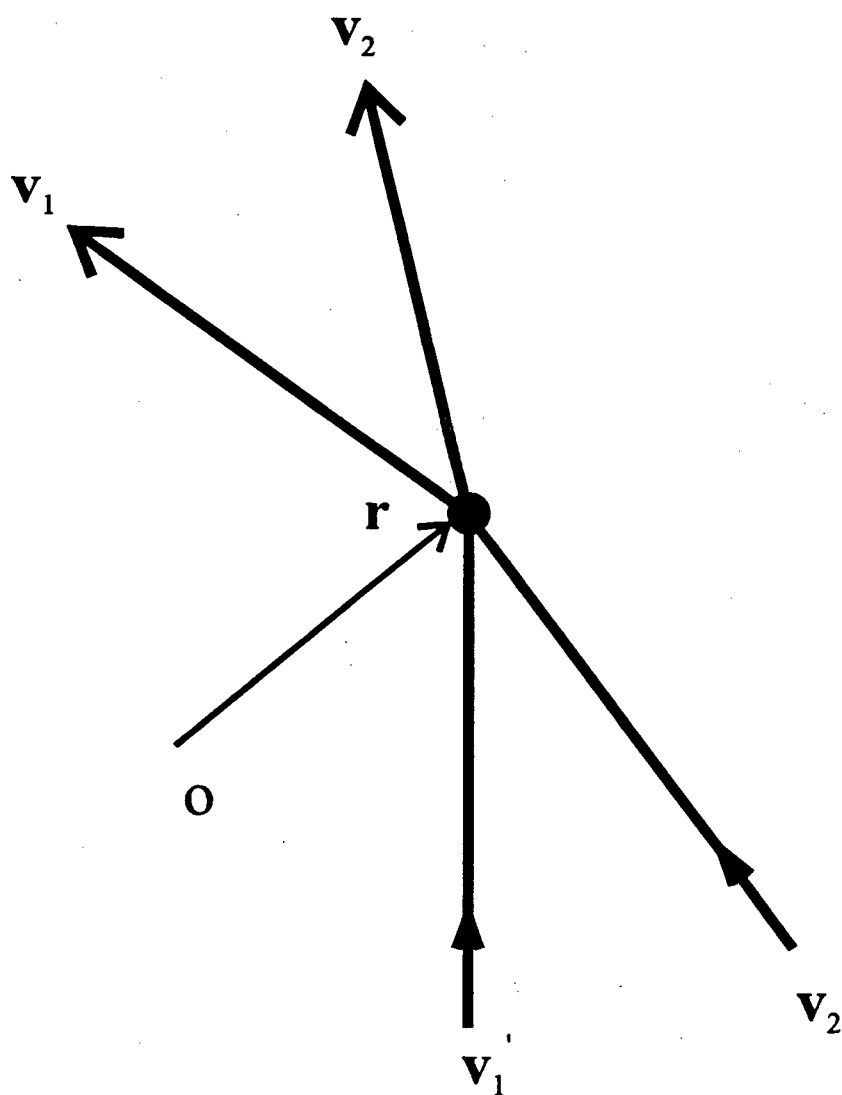


Figure 5. In the Boltzmann equation, the collision is assumed to occur at a single point r .

The initial and final (incoming and outgoing) velocities appearing in the Boltzmann equation are shown in Fig. 5. In deriving the Boltzmann equation, the well known molecular chaos assumption or *Stosszahlansatz* is evoked which states that there are no correlations among one-particle distribution functions prior to collision. The Boltzmann equation describes the time change of the one-particle reduced distribution function, $f_1^{(1)}$, at a point \mathbf{v}_1 and \mathbf{r} in phase space at time t . The terms on the left hand side represent the change in $f_1^{(1)}$ as a result of streaming motion in the fluid, while the right hand side approximates the changes of the distribution function due to collisions. A particle with a velocity \mathbf{v}_1 that collides with a second particle of velocity \mathbf{v}_2 , is transferred outside the vicinity of that particular phase space point. This event decreases the probability of having particles at \mathbf{v}_1 and thus decreases values of the distribution function at \mathbf{r}, \mathbf{v}_1 . On the other hand, a particle with a specific velocity \mathbf{v}'_1 at \mathbf{r} , when colliding with another particle at a specific velocity \mathbf{v}'_2 , produce particles with velocity \mathbf{v}_1 and \mathbf{v}_2 , thus increasing the probability at the phase space point \mathbf{r}, \mathbf{v}_1 . The velocities \mathbf{v}'_1 and \mathbf{v}'_2 involve the inverse collision of particles with velocities \mathbf{v}_1 and \mathbf{v}_2 . This inverse collision is represented by the first term in the integral on the right of Eq. (2.3). The integral is over the velocity of the second particle, $d\mathbf{v}_2$, and also relative volume per unit time, $g_{12}b\delta b d\epsilon$, where g_{12} is the relative speed of approach of the pair of colliding molecules, b is the impact parameter of the collision and ϵ is the azimuthal angle in the cylindrical coordinate system defined by the relative velocity of approach in the collision, cf. Ref. [7]. The values of \mathbf{v}'_1 and \mathbf{v}'_2 are determined from \mathbf{v}_1 and \mathbf{v}_2 with a knowledge of the intermolecular potential by applying binary collision dynamics.

The Chapman - Enskog solution of the Boltzmann equation gives the lowest order in density expressions for the transport coefficients. To obtain higher density corrections, the details of the collision must be studied within smaller length and time scales than that of the Boltzmann equation. The collision can no longer be considered to occur at a single spatial point and a finite collision time must be allowed. Inclusion of these details into the kinetic equation leads to the first generalization of the Boltzmann equation to higher densities.

The quantities involved in a binary collision, when studied on a collisional length and time scale are indicated in Fig. 6. To study the collision, it is convenient to define some cutoff distance R , beyond which the intermolecular force is zero. This distance is later taken to be infinite, but it serves as a useful computational tool. This description gives an indication of the approximations made in the Boltzmann equation. First, in the Boltzmann equation, the sizes of the molecules are neglected, and it is assumed that for particle 2 undergoing a collision in the small interaction region, $f_2^{(1)}(\mathbf{v}_2, \mathbf{r}_2, t) = f_2^{(1)}(\mathbf{v}_2, \mathbf{r}_1, t)$, i.e., the position of particle 2 can be displaced to coincide with the position of particle 1. In essence, this

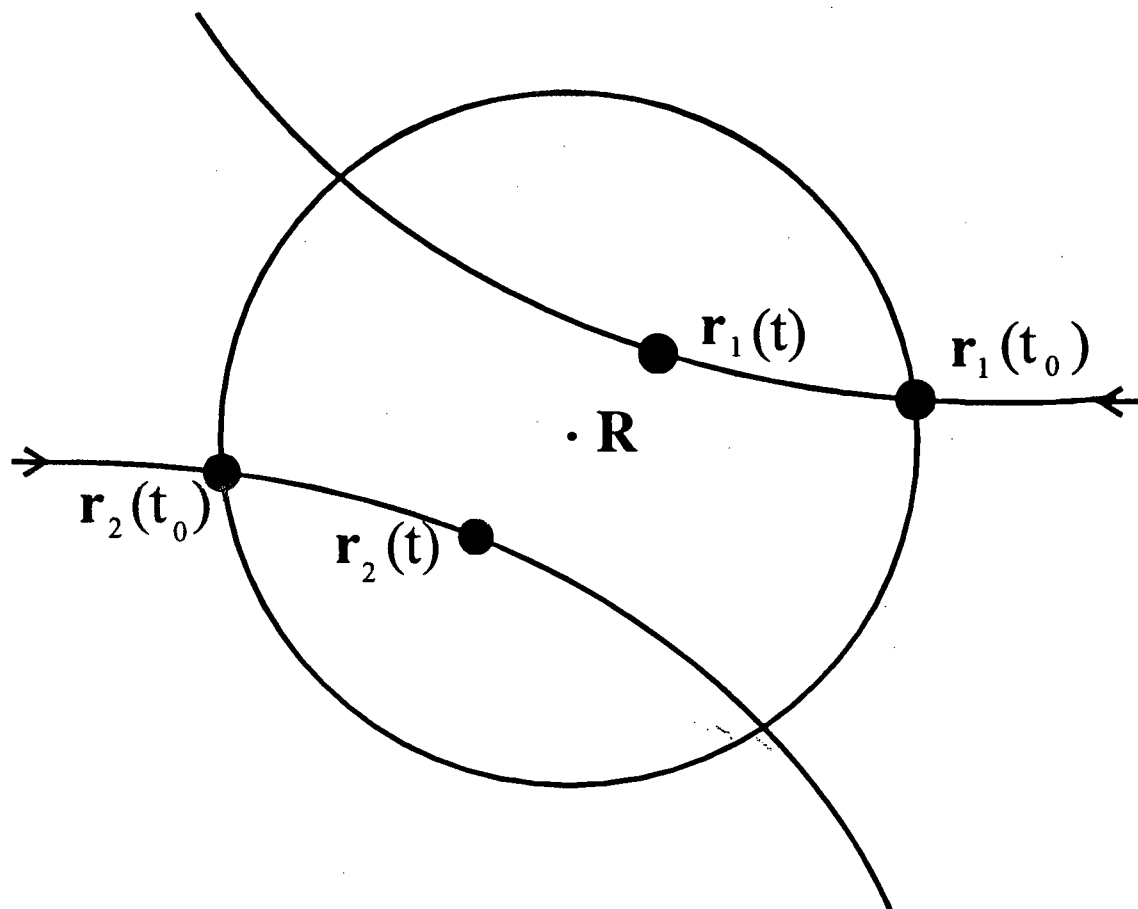


Figure 6. Position coordinates during a binary collision relevant to the generalized Boltzmann equation. The radius of the large circle is the cutoff distance of the potential.

approximation implies the distribution function has no explicit positional dependence inside the interaction region. Second, the particles are taken back from time t , to a time t_0 where their separation is R and they are about to enter the interaction region. Since the interaction region is considered small in the Boltzmann equation, the difference between the times t_0 and t is neglected, the particles are not put at their actual positions of $\mathbf{r}_1(t_0)$ and $\mathbf{r}_2(t_0)$, but at the position \mathbf{r} of particle 1 at time t .

H. S. Green [11] started with the first BBGKY equation to obtain a more rigorous expression for the collision term. In the spirit of the Stosszahlansatz, it is still assumed that the distribution functions of particles 1 and 2 are not correlated at the instant they enter the interaction region of radius R . Considering the details of a binary collision, the time evolution of the one-particle distribution function is written as,

$$\frac{\partial f_1^{(1)}}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1^{(1)}}{\partial \mathbf{r}_1} = \frac{1}{m} \iint \left\{ \frac{\partial f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1(t_0), t_0] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_2(t_0), t_0]}{\partial \mathbf{v}_1} \right\} \cdot \left(\frac{\partial u}{\partial \mathbf{r}_1} \right) d\mathbf{r}_2 d\mathbf{v}_2, \quad (2.4)$$

in which m is the mass of the particles and u the intermolecular potential. H. S. Green demonstrates that the "exact" integral for the effect of collisions on the distribution function as given in Eq. (2.4) differs from the approximate integral of Eq. (2.3) by a correction factor J ,

$$\begin{aligned} \frac{\partial f_1^{(1)}(\mathbf{v}_1)}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1^{(1)}(\mathbf{v}_1)}{\partial \mathbf{r}} \\ = \iint \left\{ f_1^{(1)}(\mathbf{v}'_1) f_2^{(1)}(\mathbf{v}'_2) - f_1^{(1)}(\mathbf{v}_1) f_2^{(1)}(\mathbf{v}_2) \right\} g_{12} b db d\epsilon d\mathbf{v}_2 + J(\mathbf{v}_1, \mathbf{r}_1), \end{aligned} \quad (2.5)$$

where the correction term, $J(\mathbf{v}_1, \mathbf{r}_1)$ is defined as,

$$J(\mathbf{v}_1, \mathbf{r}_1) = \frac{1}{m} \iiint \left(\frac{\partial u}{\partial \mathbf{r}} \cdot \frac{\partial \Delta}{\partial \mathbf{v}_1} \right) d\mathbf{r} d\mathbf{v}_2 = J_1(\mathbf{v}_1, \mathbf{r}_1) + J_2(\mathbf{v}_1, \mathbf{r}_1). \quad (2.6)$$

$\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ is the relative position of particle 1 with respect to particle 2. The decomposition into J_1 and J_2 arises from splitting up of the correction factor Δ into two parts,

$$\begin{aligned} \Delta &= \Delta_1 + \Delta_2 \\ \Delta_1 &= f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1(t_0), t_0] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_2(t_0), t_0] - f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{R}, t] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{R}, t] \\ \Delta_2 &= f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{R}, t] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{R}, t] - f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1, t] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_1, t]. \end{aligned} \quad (2.7)$$

\mathbf{R} is the center of mass of the pair at time t , i.e. $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$. The first correction Δ_1 arises from using the center of mass position of the pair in the distribution functions instead of their actual positions at time t_0 , and also replacing the explicit time t_0 with t .

The second correction Δ_2 is related to using \mathbf{r}_1 , the position of particle 1, at time t , instead of the center of mass position of the pair. These terms account for the explicit dependence of the distribution function on position in the collision region and thus the effect of the intermolecular potential.

The factor Δ_1 introduces a correction involving both a time and a spatial displacement, while Δ_2 only involves spatial displacements. By expanding the Δ_i 's as a Taylor series with respect to the position of particle 1, and retaining only first order gradients, the difference of the terms in Eq. (2.7) are further simplified. Expanding the terms in Δ_1 about \mathbf{r}_1 and time t gives,

$$\Delta_1 = \frac{\mathbf{r}'}{2} \cdot \left\{ f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1, t] \frac{\partial f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_1, t]}{\partial \mathbf{r}_1} - f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_1, t] \frac{\partial f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1, t]}{\partial \mathbf{r}_1} \right\}. \quad (2.8)$$

The center of mass position in Δ_2 is expressed in terms of \mathbf{r}_1 and \mathbf{r} . Using a Taylor expansion about \mathbf{r}_1 gives,

$$\Delta_2 = \frac{\mathbf{r}}{2} \cdot \left\{ \frac{\partial f_1^{(1)}[\mathbf{v}_1(t_0), \mathbf{r}_1, t] f_2^{(1)}[\mathbf{v}_2(t_0), \mathbf{r}_1, t]}{\partial \mathbf{r}_1} \right\}. \quad (2.9)$$

\mathbf{r}' is defined in Section 2.5.1. Snider and Curtiss [19] use these forms in Eq. (2.6) to derive first order density corrections to the viscosity coefficient and thermal conductivity. The first correction reflects both time and position aspects of the collision through \mathbf{r}' , while the second correction only has a positional aspect and is simpler in structure.

2.3.1 Moderately Dense Gas Transport Coefficients from the Generalized Boltzmann Equation

Snider and Curtiss use the Chapman - Enskog method for solving the generalized Boltzmann equation for repulsive potentials, including only binary collisions. This involves solving the Boltzmann equation in the presence of the corrections of Eq. (2.6)

The first step in the solution is linearizing Eq. (2.5),

$$\frac{\partial f_1^{[0]}}{\partial t} + \mathbf{v}_1 \cdot \frac{\partial f_1^{[0]}}{\partial \mathbf{r}_1} = \iint f_1^{[0]} f_2^{[0]} [\phi_1(\mathbf{v}'_1) + \phi_2(\mathbf{v}'_2) - \phi_1(\mathbf{v}_1) - \phi_2(\mathbf{v}_2)] g_{12} b db d\epsilon d\mathbf{v}_2 + J_1 + J_2 \quad (2.10)$$

where $f_i^{[0]}(\mathbf{v}_i, \mathbf{r}_i, t)$ and $f_2^{[0]}(\mathbf{v}_2, \mathbf{r}_2, t)$ are local equilibrium Maxwellian distribution functions in which the densities, mean velocity and temperature are position and time dependent. The ϕ_i 's represent perturbations of the distribution function from Maxwellian.

By recognizing the tensorial properties of a number of the integrals which arise in the Chapman - Enskog solution of Eq. (2.10), Snider and Curtiss were able to simplify the calculation of the transport coefficients. The result was the explicit expression of the first order

density corrections to the transport coefficients for soft repulsive potentials as integrals over functions of the intermolecular potential and the collision parameters. Snider and McCourt [20] later simplified the results considerably by recognizing that some of these integrals can be expressed in terms of the second virial coefficient and its temperature derivatives. These latter forms are stated below.

The viscosity coefficient to first order in density is,

$$\eta = \frac{5kT}{8\Omega^{(2,2)}(T)} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta(T) - \frac{4n\pi^{1/2}\sigma^3}{15} N_\eta(T) \right], \quad (2.11)$$

and the thermal conductivity given as,

$$\lambda = \frac{15k^2T}{32m\Omega^{(2,2)}(T)} \left[5 + 5nB(T) - \frac{20n\sigma^3}{3\pi^{1/2}} F_\lambda(T) - \frac{4n\pi^{1/2}\sigma^3}{3} N_\lambda(T) - \frac{7}{3} nT \frac{dB(T)}{dT} - \frac{5}{3} nT^2 \frac{d^2B(T)}{dT^2} \right]. \quad (2.12)$$

$\Omega^{(2,2)}(T)$ is the omega integral [7] which is proportional to the kinetic cross section, and σ is a scaling parameter, which for attractive potentials corresponds to the separation at which the intermolecular potential is zero. The physical origins of the first order density corrections to the viscosity were discussed in Section 2.2. The thermal conductivity corrections have similar origins.

In Eqs. (2.11) and (2.12), the second virial coefficient, which accounts for the non-ideality of the gas in the equations of change, originates from the non-dynamic (time-independent) J_2 correction. F_σ ($\sigma = \eta, \lambda$) corrections are dynamic in nature and originate from J_1 . The N_η term and the sum of the N_λ and temperature derivatives of the second virial coefficient arise from contribution of the perturbative ϕ_i terms to the potential contributions to the pressure tensor and heat flux vector respectively. The latter are independent of J_1 and J_2 .

The F_σ and N_σ terms are integrals over functions of the relative momentum and position,

$$I = \int d\mathbf{r} \int d\mathbf{p} F(\mathbf{r}, \mathbf{p}) = 8\pi^2 \int_0^\infty r^2 dr \int_0^\infty p^2 dp \int_0^\pi \sin \theta d\theta F(r, p, \theta) \quad (2.13)$$

The reduction of the six-fold integrals to three-fold integrals occurs since the functions $F(\mathbf{r}, \mathbf{p})$ depend only on the magnitudes of the relative separation r , relative momentum p and the angle θ between the \mathbf{r} and \mathbf{p} vectors of the colliding particles. The integrand $F(r, p, \theta)$ may also include one or more of the possible binary collision parameters defined in Section 2.5.1. These collision parameters themselves involve an additional integration, and so evaluation of the density corrections require the numerical calculation of a set of nested four-fold integrals, a far from simple task [8].

Equations (2.11) and (2.12) need to be modified in two ways. First, Snider and Curtiss limited their calculations to systems with repulsive intermolecular potentials which do not support bound states, and second, the occurrence of three-body collisions was not considered in their work. Both these effects contribute extra first order density corrections to transport coefficients.

Bound pairs in moderately dense gas systems were first studied in a modern setting by Stogryn and Hirschfelder. Based on the work of Hill [21], they developed a specific division of the integral of the second virial coefficient into regions of phase space where a pair of particles are free (corresponding to an open collision trajectory), regions where they are bound and regions where they are metastably bound. Making use of equilibrium statistical mechanics, they obtained an expression for the equilibrium constant of the formation of bound pairs and then showed that if a limited amount of association occurs, the mole fraction X_b of bound molecules is proportional to the number density n of the particles in the fluid

$$X_b = nK_{eq}. \quad (2.14)$$

In the above relation K_{eq} is the equilibrium constant for the "dimerization" reaction and the number of double molecules is small relative to the number of free molecules so that $n \approx n_f$.

The presence of bound pairs implies a new mode of momentum transfer in the system. Stogryn and Hirschfelder treat the system as a binary mixture of free and bound molecules. The viscosity for such a mixture with any general composition, not just small bound mole fractions X_b is,

$$\eta = \frac{X_b^2 H_{ff} + X_f^2 H_{bb} - X_f X_b (H_{fb} + H_{bf})}{H_{ff} H_{bb} - H_{fb} H_{bf}}. \quad (2.15)$$

The $H_{\xi\zeta}$ are related to binary collision cross sections of the species ξ with ζ . Considering Eq. (2.14) for low densities of bound molecules to first order in density only free-free and bound-free collisions contribute. The result is expressed as,

$$\begin{aligned} \eta &= \eta^{(M)} [1 + n B_{\eta}^{(MD)}] \\ \lambda &= \lambda^{(M)} [1 + n B_{\lambda}^{(MD)}] \end{aligned} \quad (2.16)$$

where $\sigma^{(M)}$ is the transport coefficient for a system composed of pure monomers (unbound molecules), equivalent to Eqs. (2.11) and (2.12), and $B_{\sigma}^{(MD)}$ is the first order correction from the monomer - dimer (free molecule - bound pair) collisions. This purely kinetic contribution to momentum transfer assumes the flow process does not change the equilibrium population of the bound species. Considering the bound pair to be a point molecule and using estimations for the parameters in the free - bound intermolecular potential, Stogryn

and Hirschfelder obtained numerical values for $B^{(MD)}$. However, they treated non-locality and collisional transfer effects crudely by using adaptations of the Enskog theory, not the rigorous corrections of Eqs. (2.11) and (2.12).

Formal relations for the effect of three-body collisions on the transport coefficients were first developed by Choh and Uhlenbeck [12]. Their expressions however, are difficult to implement in a numerical calculation. Hoffman and Curtiss [22] proposed a different formalism with a similar scope. Starting with the BBGKY equations, they made a factorization assumption for higher order reduced distribution functions similar to the superposition approximation of equilibrium statistical mechanics, and after detailed calculations obtained the Snider - Curtiss density corrections, collectively denoted as $B_\sigma^{(2M)}$, along with an extra first order density correction $B_\sigma^{(3M)}$, which approximates the effects associated with three-body dynamics,

$$\begin{aligned}\eta &= \eta_0 \left[1 + n \left(B_\eta^{(2M)} + B_\eta^{(3M)} \right) \right], \\ \lambda &= \lambda_0 \left[1 + n \left(B_\lambda^{(2M)} + B_\lambda^{(3M)} \right) \right].\end{aligned}\tag{2.17}$$

The $3M$ superscript emphasizes this correction accounts for three monomer collisions. The explicit form of this correction is expressed by Hoffman and Curtiss [22] as,

$$B_\eta^{(3M)} = \frac{1}{8\pi^2} \frac{R(T)}{\Omega^{(2,2)*}}\tag{2.18}$$

where $R(T)$ is an integral which has the general structure of Eq. (2.13) and is defined in Eq. (6.91). The detailed form of the three monomer correction shows that the presence of the third particle in this correction is actually static in nature. It does not involve the dynamics necessary to obtain the contribution of true three-particle collisions to the transport coefficient. In this correction, the third particle affects the spatial distribution of a colliding pair and thus gives an extra weight factor to the binary collision cross section.

For potentials with an attractive well, Curtiss and coworkers [22, 23] calculate the corrections of Eq. (2.17), but use the full second virial coefficient, and not only its free part when it occurs in $B_\sigma^{(2M)}$ of Eqs. (2.11) and (2.12). This includes contributions from the bound pairs, which it should not, since $B_\sigma^{(2M)}$ arises from open collision trajectories.

At this stage of the development, Kuznetsov [24] proposed that only the free part of the second virial coefficient should be used whenever it occurs in $B^{(2M)}$, the density corrections of Curtiss and coworkers, Eq. (2.17). The separate contribution of Stogryn and Hirschfelder for the bound pairs should then be added on to this to account for the presence of bound pairs. Thus

$$\eta = \eta_0 [1 + nB_\eta + O(n^2)],$$

$$\lambda = \lambda_0[1 + nB_\lambda + O(n^2)], \quad (2.19)$$

with the second transport virial expressed as,

$$\begin{aligned} B_\eta &= B_\eta^{(2M)} + B_\eta^{(MD)} + B_\eta^{(3M)}, \\ B_\lambda &= B_\lambda^{(2M)} + B_\lambda^{(MD)} + B_\lambda^{(3M)}. \end{aligned} \quad (2.20)$$

The $B_\sigma^{(2M)}$ and $B_\sigma^{(3M)}$ terms only involve the free part of the second pressure virial coefficient according to the division of Stogryn and Hirschfelder. The argument is that if bound pairs are accounted for by including the Stogryn - Hirschfelder correction, then using the full second virial coefficient in the Snider - Curtiss corrections overcounts the effects of the pairs. Kuznetsov's scheme leads to numerical results in good agreement with experiment for the viscosity coefficient, but in poor agreement for the thermal conductivity. The separate adding of bound pair contributions to the transport coefficients, as proposed by Kuznetsov appears physically reasonable but is not rigorous.

Rainwater [8] accounted for the discrepancies with thermal conductivity data by realizing that for attractive intermolecular potentials, there is an ambiguity in the way which the second pressure virial coefficient can be partitioned into free and bound regions. He studied cases and stated the importance of choosing the appropriate division for the second pressure virial coefficient and its temperature derivatives in the first order density corrections. The first calculation of first order density contributions with correct partitioning for Lennard-Jones fluids appeared in 1984 with the work of Rainwater and Friend [8] which they later extended to lower temperatures in 1987.

The calculations of Rainwater and Friend and their later extension to accurate intermolecular potentials show good agreement with experiment [9]. But from a theoretical point of view the addition of the contributions in Eq. (2.20) is not rigorous. The corrections have not been derived from a uniform starting point which still leaves open the possibility of some overcounting or neglect of contributions. On the other hand, each of the individual evaluations are rather complicated and involve both formalistic and numerical approximations. It is difficult to assess the effect of these approximations on the final expression of the density corrections.

In a recent thesis by Wei [25] a uniform approach was used to derive density corrections in the presence of bound pairs and pair correlations. The method utilized a kinetic equation approach in which the N -particle distribution function accounts for free molecules, bound pairs, and correlated pairs. A system of coupled kinetic equations was derived for these species which was closed and made convergent by introducing a decay time for the correlated pairs. The coupled equations were solved simultaneously with the Chapman - Enskog

method. The solution leads to first order density corrections which include contributions from the free molecules, bound pairs and correlated pairs. Due to the introduction of the particular structure in the N -particle distribution function, the final results are expressed in a manner different from previous theories.

The density corrections discussed above may in principle be derived using the Choh and Uhlenbeck theory [12]. They implement the Bogoliubov method [10] to higher order density corrections, but express their results in a set of integral equations which must still be solved in order to derive explicit density corrections. It is expected that if this program is explicitly carried out, the density corrections of Snider and Curtiss will be obtained, although to our knowledge this has not been demonstrated.

It was with the goal of clarifying the relations among kinetic equation approaches that a study of alternate derivations of the density corrections based on time correlation functions was initiated. This is also desirable from another viewpoint. Numerical calculations of transport coefficients are invariably done with some approximate intermolecular potential. The degree of disagreement with experiment may either be related to the approximate nature of the theoretical expressions for the transport coefficients, or the approximate nature of the potential [26]. An independent verification of the theoretical expressions could help establish the validity of the density correction expressions and so relate any residual disagreement with experiment to the approximate nature of the intermolecular potential.

2.4 Time Correlation Functions for Transport Coefficients

The relation between a transport coefficient and the time correlation of a phase function was introduced by Einstein [27] in 1905 in the study of Brownian motion. The relation states that the diffusion coefficient, D , is related to the integral over all times of the ensemble average of the velocity auto-correlation function,

$$D = \frac{1}{3} \int_0^\infty d\tau \langle\langle \mathbf{v}(0) \cdot \mathbf{v}(\tau) \rangle\rangle. \quad (2.21)$$

The $\langle\langle \rangle\rangle$ notation implies a thermal average over an equilibrium canonical ensemble of an N -particle system of volume V and temperature T (other ensembles can also be used), and $\mathbf{v}(0)$ and $\mathbf{v}(\tau)$ are the velocities of a particle at time 0 and τ . Over all members of the ensemble, the initial velocity of a chosen particle $\mathbf{v}(0)$, has a Maxwellian distribution. For times equivalent to a small number of mean free times, the initial magnitude and direction of the velocity of a particle have not been randomized and $\mathbf{v}(0)$ and $\mathbf{v}(\tau)$ show some correlation.

As time progresses, more collisions randomize the velocities and the initial correlation is lost. The ensemble average of the velocity auto-correlation decays from its classical equipartition value of $3kT/m$ at $\tau = 0$ to very small values over the time scale of several collision times. The nature of this decay can be determined from the study of the detailed dynamics of the system or from numerical simulations. The former approach is pursued in this thesis.

The Einstein relation is an example of a general principle named the *fluctuation - dissipation theorem* which was anticipated by Onsager in 1931 [28], and given a general proof by Callen and Welton in 1951 [29]. This theorem states that the rate of decay to equilibrium of a perturbed non-equilibrium state not very far from equilibrium is related to the time correlation of spontaneous fluctuations at equilibrium [30]. In the case above, the diffusion coefficient which describes the rate of dissipation of a density gradient in a non-equilibrium system, is proportional to the integral over time of the velocity auto-correlation function at equilibrium. This theorem allows the use of equilibrium properties of a system to obtain information about its non-equilibrium properties.

Extensive study of transport coefficients utilizing time correlation function methods began with the pioneering work of M. S. Green [31] and R. Kubo [32] in the mid 1950's. Many excellent introductions [33, 34, 35, 36, 37, 38] and review articles [39, 40] regarding the general principles of time correlation function methods are available.

A multitude of approaches are available for deriving the time correlation function formulas for transport coefficients [39]. In particular, the method due to Helfand [33, 41] obtains the time correlation expression for the transport coefficient from the corresponding equation of change by utilizing an appropriate form for the distribution function of the system.

As a result, the time correlation formula for the viscosity coefficient is

$$\eta = \frac{1}{10VkT} \int_0^\infty d\tau \langle\langle \mathbf{J}_p(0) : \mathbf{J}_p(\tau) \rangle\rangle, \quad (2.22)$$

\mathbf{J}_p is the phase space function for the transverse momentum flux tensor. For a system with only pairwise additive forces, the momentum flux tensor has a kinetic contribution which is a function of the momenta \mathbf{p}_j , of particles and a potential contribution which depends on the relative separation $\mathbf{r}_{j\ell}$ and force $\mathbf{F}_{j\ell}$ between pairs of particles j and ℓ ,

$$\mathbf{J}_p = \sum_{j=1}^N \left(\frac{[\mathbf{p}_j \mathbf{p}_j]^{(2)}}{m} + \sum_{\ell > j}^N [\mathbf{r}_{j\ell} \mathbf{F}_{j\ell}]^{(2)} \right). \quad (2.23)$$

The bracket notation $[]^{(2)}$ indicates a symmetric traceless second rank tensor. From here onwards, when a dyadic tensor is constituted of two identical vectors, the vector is repeated only once within the bracket, i.e.

$$[\mathbf{A}\mathbf{A}]^{(2)} \equiv [\mathbf{A}]^{(2)}. \quad (2.24)$$

For the thermal conductivity,

$$\lambda = \frac{1}{3VkT^2} \int_0^\infty d\tau \langle\langle \mathbf{J}_e(0) \cdot \mathbf{J}_e(\tau) \rangle\rangle, \quad (2.25)$$

where \mathbf{J}_e , the phase space function for the heat flux vector is,

$$\mathbf{J}_e = \sum_{j=1}^N \left\{ \left(\frac{p_j^2}{2m} - h \right) \frac{\mathbf{p}_j}{m} + \frac{1}{2} \sum_{\ell \neq j} (\mathbf{r}_{j\ell} \mathbf{F}_{j\ell} + u_{j\ell} \mathbf{U}) \cdot \frac{\mathbf{p}_j}{m} \right\}. \quad (2.26)$$

$u_{j\ell}$ is the intermolecular potential between particles j and ℓ , h the average enthalpy per particle, and \mathbf{U} the second rank identity tensor. The enthalpy term eliminates any contribution from the convective energy flux. Clearly the heat flux vector also has kinetic and potential contributions. Explicit expressions for other transport coefficients have been derived but will not be stated here.

For an N -particle system, a time correlation function for a transport coefficient has the general form,

$$\mathcal{C}(t) = \frac{1}{2\alpha + 1} \langle\langle \mathbf{J}(0) \overset{\alpha}{\odot} \mathbf{J}(t) \rangle\rangle = \frac{1}{2\alpha + 1} \langle\langle \mathbf{J}(0) \overset{\alpha}{\odot} e^{-it\mathcal{L}} \mathbf{J}(0) \rangle\rangle, \quad (2.27)$$

where \mathbf{J} is a tensor valued phase space function representing the flux of the property of interest. Moreover, \mathbf{J} is a tensor of rank α belonging to an irreducible representation of dimension $2\alpha + 1$ of the three-dimensional rotation group $SO(3)$, $\overset{\alpha}{\odot}$ represents an α -fold dot (tensorial) contraction, and \mathcal{L} is the N -particle Liouville superoperator. With this notation the general expression for transport coefficients in terms of time correlation functions has the following form,

$$\sigma = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{B}{(2\alpha + 1)V} \int_0^\infty dt e^{-\epsilon t} \langle\langle \mathbf{J}(0) \overset{\alpha}{\odot} e^{-it\mathcal{L}} \mathbf{J}(0) \rangle\rangle. \quad (2.28)$$

The thermodynamic limit is needed to eliminate edge effects. The B factor introduces a scale factor for each transport coefficient. ϵ is related to a frequency and the convergence factor $e^{-\epsilon t}$ implies the adiabatic approximation, namely the slow switching on of a perturbation from equilibrium in the distant past [42, 43]. Equations (2.21), (2.22) and (2.25) are consistent with this general form. The flux \mathbf{J} is an extensive property and may be a scalar (bulk viscosity), a vector (diffusion and thermal conductivity) or a symmetric traceless second-rank tensor (shear viscosity). Introduction of the volume factor V recognizes the extensivity of a flux and the intensivity of a transport coefficient. For diffusion and thermal conductivity, α is 1, so the tensorial contraction in the time correlation function reduces to a simple dot product, while for the shear viscosity, α is 2 and the tensorial contraction in the time correlation function is a double dot product.

A transport coefficient σ is the particular limiting form of the Fourier transform of the time correlation function of the flux. Calculation of the time integral specifically leads to,

$$\sigma = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \odot \frac{1}{i\epsilon - \mathcal{L}} \mathbf{J} \rangle\rangle. \quad (2.29)$$

In most of the literature it is standard to use the tensorial components of the transverse momentum flux for the shear viscosity, η ,

$$\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{i}{VkT} \langle\langle \mathbf{J}_{p,xy} \frac{1}{i\epsilon - \mathcal{L}} \mathbf{J}_{p,xy} \rangle\rangle. \quad (2.30)$$

Since $\mathbf{J}_{p,xy}$ is one component of a second rank symmetric traceless tensor, it belongs to a five-dimensional irreducible representation of the rotation group. By the rotational invariance of \mathcal{L} and of the thermal average, the quantity of Eq. (2.30) is 1/5th the sum over all traceless symmetric components, which appears in Eq. (2.29). A factor of 1/2 is also required to symmetrize the components and obtain Eq. (2.22). The advantage of expressing the transport coefficient in a rotationally invariant form is that the rotational properties of the different operators can be used to simplify its evaluation.

2.4.1 Moderately Dense Gas Transport Coefficients from Time Correlation Functions

Before discussing any analytical approach for the evaluation of a transport coefficient using the time correlation function formalism, it is useful to mention simulations on equilibrium systems which utilize Eq. (2.28). The earliest molecular dynamics simulation, and indeed one of the pioneering works in the history of computer simulations is that of Rahman [44] who studied the velocity auto-correlation and the diffusion coefficient through Eq. (2.21). In the liquid range, the work of Hoheisel and coworkers [6] on viscosity and thermal conductivity is notable. Simulations explicitly show the nature of the time decay of the correlation function (an aspect bypassed in our theory) and the magnitude of the kinetic and potential contributions of the flux function.

Much work has been done to show that the results of Eq. (2.28) are equivalent to the generalized Boltzmann equation. Most treatments begin with expressions like Eq. (2.28) and proceed to derive a set of kinetic equations. Résibois [45] uses this approach and with a generalized master equation demonstrates that the time correlation function equations are equivalent to the generalized Boltzmann equation to all orders of density. But the explicit evaluation of a transport coefficient is not attempted in his work. Dufty and Lindenfeld

[46] take this a step farther and show the equivalence between the non-linear Boltzmann equations and the time correlation function expressions.

Other approaches explicitly use the time correlation function formula to obtain expressions for the transport coefficients. Ernst, Dorfman and Cohen's [47] method is in the spirit of Cohen's cluster expansion for generalizing Boltzmann's equation. They introduce a series of reduced time correlation functions in a fashion reminiscent of the definition of reduced distribution functions and proceed to derive a set of kinetic equations for the reduced time correlation functions which are analogous to the BBGKY hierarchy. By utilizing cluster expansions for the reduced time correlation functions, and assuming an appropriate functional dependence of the higher order reduced time correlation functions on the first order reduced time correlation function, this hierarchy is closed and Boltzmann type equations are derived. The nature of the assumptions limits the scope of the work to repulsive potentials. The solution of these equations leads to density corrections for the transport coefficients. To the extent that the resulting equations are similar to the generalized Boltzmann equation, their solution involves the same sort of approximations and limitations mentioned in Section 2.3.1. A solution of the equations to obtain explicit expressions for the transport coefficients is not presented in this work. Later Ernst [48] extended this approach to general orders of density and showed that its results are equivalent to those of the generalized Boltzmann equation to general order in density.

Ono and Shizume [49] calculate the time correlation functions for transport coefficients at moderate densities, but their formulas are not reduced to a form that is easily comparable to other work in this field. They derive an equation which describes the time evolution of the flux function $J(t)$ in terms of an unperturbed Liouville operator and a perturbation. After developing what is equivalent to an interaction representation for the time evolution, they utilize a Mayer cluster expansion technique quite similar to that used in deriving virial coefficients for equilibrium properties. The time evolution is expressed as a series of consecutive binary collisions. The formal development is complete, but no comparison with previous work is given.

Kapral and Desai [50] evaluate transport coefficients for a binary mixture and obtain interesting results for the diffusion and thermal diffusion coefficients. They express transformations of the time correlations in terms of equivalent Boltzmann type kinetic equations. These kinetic equations are solved within certain (two Sonine) approximations and explicit time-decays of the time correlation functions associated with the transport coefficients are obtained.

The work of Kawasaki and Oppenheim [51] is studied in greater detail in the next chap-

ter. This method is an extension of the resolvent expansion of Zwanzig [52] to a flux with both kinetic and potential contributions. Zwanzig introduced an expansion of the resolvent in powers of $1/\epsilon$, which was then resummed to retain a finite expression for the transport coefficient. Zwanzig's treatment was applicable to purely momentum dependent flux functions which are sums of one particle properties, irrespective of their particular functional nature. The Kawasaki and Oppenheim method was initially extended to include potential contributions to the flux function, on condition that the intermolecular potential be repulsive. The final results are a set of integral equations for the various contributions to the viscosity that are similar to the collision integrals of the Boltzmann equation. Unfortunately they do not reduce the final equations to a form suitable for comparison with the results of Snider and Curtiss. However, Kawasaki and Oppenheim do show detailed equivalence of their equations with those of Choh and Uhlenbeck who utilize Bogoliubov's generalized Boltzmann equation. It is recalled that this was also the starting point of the calculations of Snider and Curtiss. The Choh and Uhlenbeck equations themselves have not been independently evaluated to our knowledge. Subsequently, Kawasaki and Oppenheim extended the method to attractive intermolecular potentials [53]. Thus in principle, the theory should account for bound pairs, though explicit expressions for contributions to the viscosity in terms of a functional of the intermolecular potential were not given.

In the next chapter, an explicit derivation of density corrections to the viscosity from the Kawasaki and Oppenheim approach is presented. It is demonstrated that their equations reduce to the Snider and Curtiss formulas within certain well defined approximations. This is encouraging as it provides independent verification of the forms of the density corrections. In our opinion, their treatment of bound states has a number of problems which are also discussed.

2.5 Binary Collisions

2.5.1 Collision Parameters

Detailed knowledge of binary collision dynamics is required in order to calculate the density corrections to the viscosity. Multiple integrals over the relative position and momentum of the type given in Eq. (2.13) arise. The collision parameters in the integrals must be determined as functions of the relative position and momentum so that the phase space integrals can be evaluated. The kinematics and dynamics of a binary collision are summarized in this section and the notation used in later chapters is introduced.

The first step in the kinematic study of binary collisions is the conversion of the positions

and momenta of the pair of particles to the center of mass and relative motion variables (with the position and momentum of particle 2 taken as the origin). The transformations are well known,

$$\mathbf{r} = \mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 \quad \mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2), \quad (2.31)$$

and

$$\mathbf{p} = \frac{1}{2}(\mathbf{p}_1 - \mathbf{p}_2) \quad \mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2, \quad (2.32)$$

$$\mathbf{p}_1 = \frac{1}{2}\mathbf{P} + \mathbf{p} \quad \mathbf{p}_2 = \frac{1}{2}\mathbf{P} - \mathbf{p}. \quad (2.33)$$

The Jacobian for this transform is unity, namely

$$d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 = d\mathbf{r} d\mathbf{R} d\mathbf{p} d\mathbf{P}. \quad (2.34)$$

Within classical mechanics, for a known intermolecular potential, the trajectory of a collision is uniquely determined by the position and momentum of a single point on the trajectory. This reference point is given by the relative position vector \mathbf{r} and relative momentum vector \mathbf{p} . The z axis is chosen to be in the $-\mathbf{p}$ direction. The polar angle θ of the position vector determines whether it is on the incoming or outgoing part of the trajectory, with $\theta < \pi/2$ for the incoming part of the trajectory and $\theta > \pi/2$ for the outgoing part. The angle between \mathbf{r} and \mathbf{p} is $\pi - \theta$. These relations are shown in Fig. 7.

For computational purposes, the potential is considered to have a cutoff distance R , beyond which it is zero. This distance is eventually taken to infinity. The internal states of the colliding molecules are assumed not to change during the collision. If there is no external torque, the collision trajectory is planar and remains in the plane of \mathbf{r} and \mathbf{p} at all times.

A general point on the trajectory is characterized by a position vector $\boldsymbol{\xi}$ and a relative momentum vector \mathbf{p}_ξ . The unit vector along the $\boldsymbol{\xi}$ direction is $\boldsymbol{\kappa}_\xi$ which makes an angle β_ξ with respect to the z -axis. The unit vector along the direction of \mathbf{p}_ξ is $\boldsymbol{\kappa}'_\xi$ which makes an angle of η_ξ with respect to the z -axis. The magnitude of the angular momentum L of the initial reference point,

$$L = |\mathbf{r} \times \mathbf{p}| = rp \sin(\pi - \theta) = rp \sin \theta \quad (2.35)$$

and its direction is the same for all points along the trajectory. The magnitude of the angular momentum for a general point is,

$$L = |\boldsymbol{\xi} \times \mathbf{p}_\xi| = \xi p_\xi \sin(\eta_\xi - \beta_\xi). \quad (2.36)$$

At the cutoff distance R where $\mathbf{p}_\xi = \mathbf{p}_R = \mathbf{p}_0$ (the constant momentum in the absence of interaction), the relation between the angles η_R and β_R is,

$$\eta_R = \beta_R + \pi - \arcsin[L/R(mE)^{1/2}]. \quad (2.37)$$

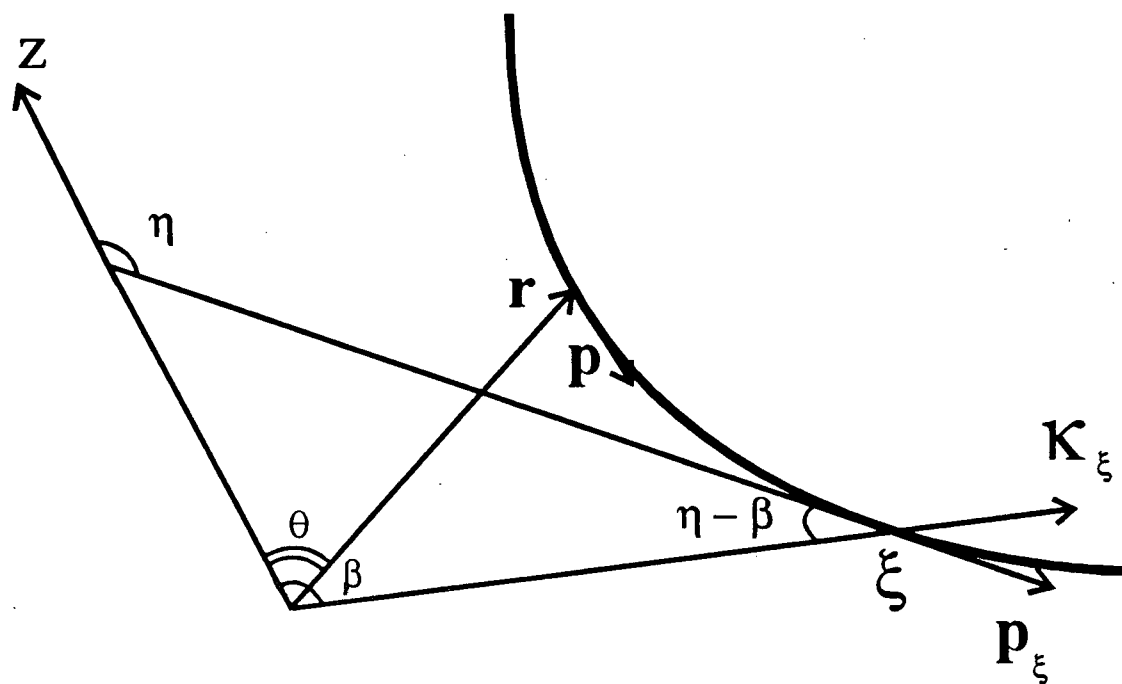


Figure 7. The coordinate system for a binary collision. A reference point of the trajectory, with position \mathbf{r} and momentum \mathbf{p} , and also a general point on the trajectory with position ξ and momentum \mathbf{p}_ξ are indicated on the diagram. Various angles defined in reference to these points are also shown.

If the distance $R \rightarrow \infty$, the above angles approach their asymptotic values on the trajectory, in which case they are no longer denoted by the subscript R , i.e.,

$$\lim_{R \rightarrow \infty} \beta_R = \beta \qquad \lim_{R \rightarrow \infty} \eta_R = \eta \qquad (2.38)$$

The asymptote of the incoming branch of the trajectory makes an angle β with respect to the z -axis. The vector \mathbf{r}_m denotes the point of closest approach of the two particles. The angle between \mathbf{r}_m and the asymptotic direction of approach is $-\omega$ and the angle between \mathbf{r}_m and the reference position \mathbf{r} is denoted by ζ . These relations are illustrated in Fig. 8 for \mathbf{r} on the incoming part of the trajectory. From this figure, it is obvious that the following relations hold among these angles,

$$\beta_R - \theta = \omega_R + \zeta \qquad \text{incoming} \qquad (2.39)$$

$$\beta_R - \theta = \omega_R - \zeta \qquad \text{outgoing} \qquad (2.40)$$

The angles between the position and momentum vectors of the reference point \mathbf{r} and \mathbf{p} with those of the position and momentum vectors at the cutoff distance R are obtained from the following set of dot products,

$$\mathbf{p} \cdot p_0 \boldsymbol{\kappa}'_R = pp_0 \cos(\pi - \eta_R) = -pp_0 \cos \eta_R \qquad (2.41)$$

$$\mathbf{r} \cdot p_0 \boldsymbol{\kappa}'_R = rp_0 \cos(\eta_R - \theta) \qquad (2.42)$$

$$\mathbf{p} \cdot R \boldsymbol{\kappa}_R = pR \cos(\pi - \beta_R) = -pR \cos \beta_R \qquad (2.43)$$

$$\mathbf{r} \cdot R \boldsymbol{\kappa}_R = rR \cos(\beta_R - \theta) \qquad (2.44)$$

$$\mathbf{p} \cdot \mathbf{r} = pr \cos(\pi - \theta) = -pr \cos \theta \qquad (2.45)$$

$$p_0 \boldsymbol{\kappa}'_R \cdot R \boldsymbol{\kappa}_R = p_0 R \cos(\eta_R - \beta_R) \qquad (2.46)$$

Another important collision parameter is the time s_0 it takes to go from $R \boldsymbol{\kappa}_R$ on the incoming part of the trajectory to \mathbf{r} . During this time the momentum changes from \mathbf{p}_0 to \mathbf{p} . A somewhat related collision parameter is $\mathbf{r}' = R \boldsymbol{\kappa}_R + 2\mathbf{p}_0 s_0/m$. The magnitude and direction of this vector are obtained by starting at the vector \mathbf{r} and tracing backwards a time $-s_0$ along the trajectory to reach R . The intermolecular potential is then "turned off" and the relative position allowed to evolve freely forward in time for a duration of s_0 . The value of \mathbf{r} under this transformation is \mathbf{r}' . The relative momentum \mathbf{p} , under the same set of transformations is \mathbf{p}_0 . These quantities are illustrated in Fig. 9.

It is convenient to define two additional collisional parameters, X and Y with reference to Fig. 9. The distance $g_0 s_0 - R$ along the asymptotic direction is denoted by $b(|X| + |Y|)$, where g_0 is the relative speed of approach of the particles and b is the impact parameter.

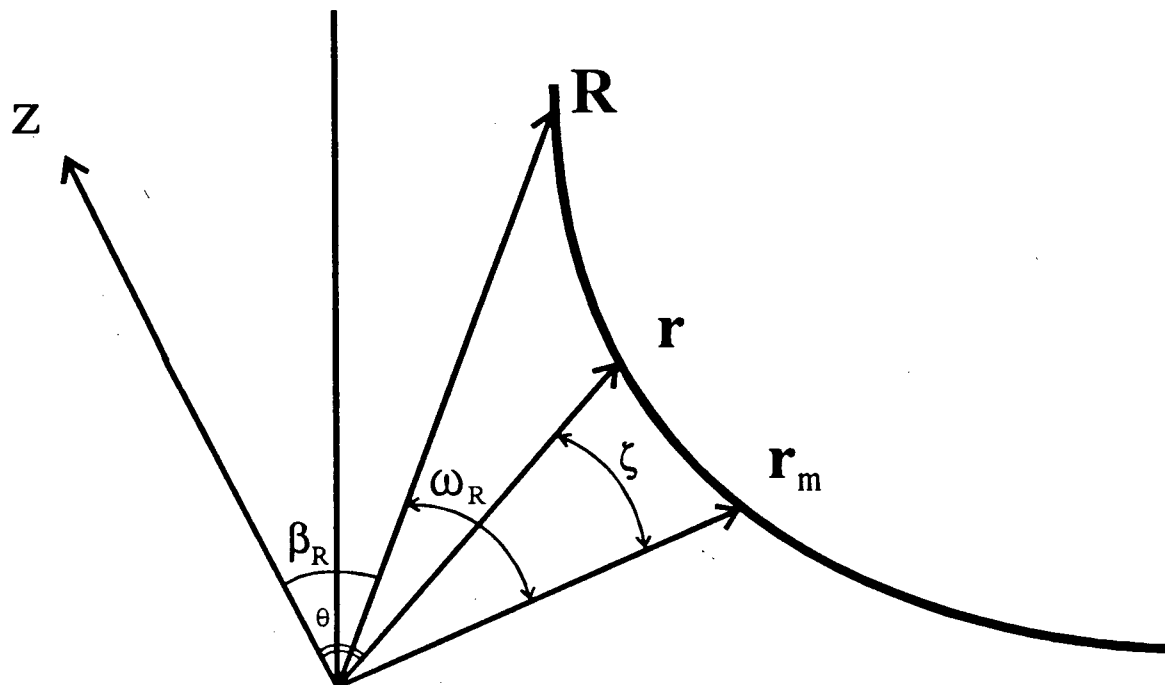


Figure 8. Binary collision parameters. \mathbf{R} is the cutoff distance of the potential and \mathbf{r}_m is the closest distance of approach. Various angles are defined with reference to these vectors.

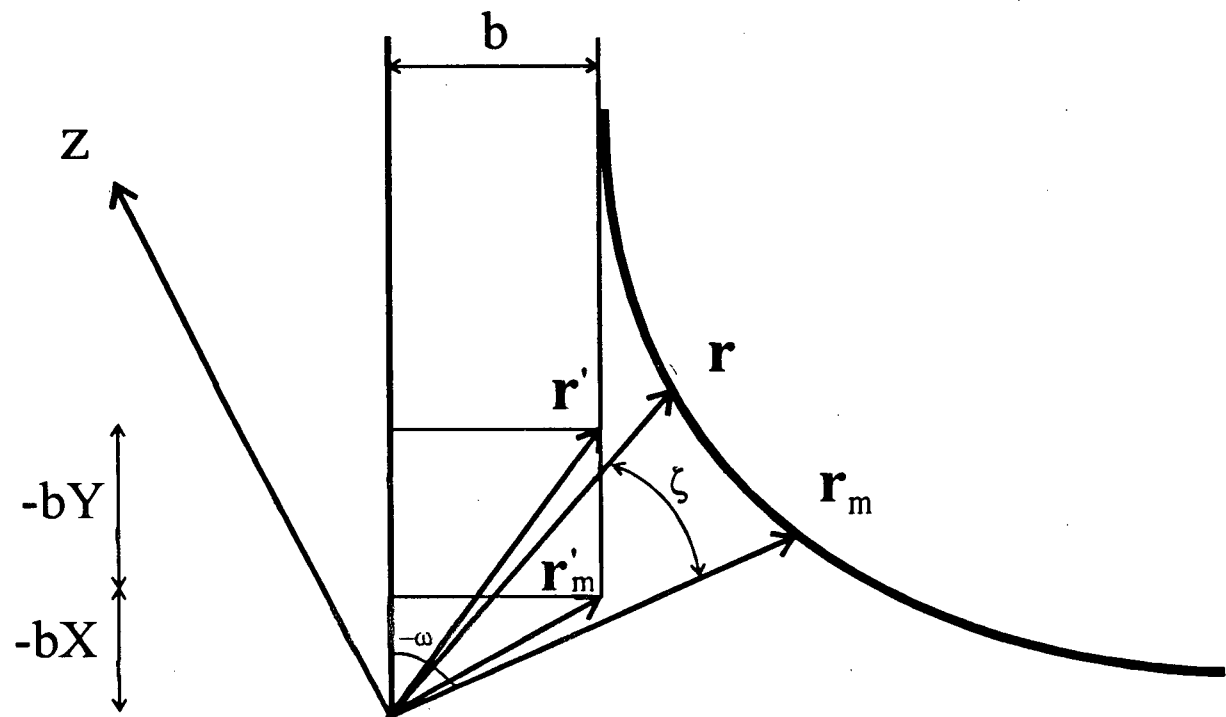


Figure 9. Primed position variables and their related collision parameters. b is the impact parameter.

From the figure, this sum is seen to be the projection of \mathbf{r}' onto the asymptotic direction. If \mathbf{r}_m undergoes the same operations mentioned in deriving \mathbf{r}' , the result is a new vector \mathbf{r}'_m . The projection of this vector along the asymptotic direction of the incoming part of the trajectory is $b|X|$. The parameter Y is defined by the difference of these two projections.

2.5.2 Collision Dynamics

The dynamics of a binary collision allows the determination of the expressions for the collision parameters as integrals over functions of the intermolecular potential. Angular momentum conservation constrains the relative motion to a single plane, taken to be the zx -plane. As stated previously, the z -axis is chosen in the direction of $-\mathbf{p}$. Thus in a Cartesian system, the time behaviour of the x and z components of the relative position coordinate and the conjugate momentum describe the dynamics of the collision. The total relative energy of this system, as given by the Hamiltonian function, is

$$H = \frac{1}{2\mu}(p_z^2 + p_x^2) + u(\xi) \quad (2.47)$$

where it is assumed that the intermolecular potential is spherically symmetric so depends only on the separation between the particles, $\xi = \sqrt{x^2 + z^2}$. Due to planar symmetry, it is more convenient to convert to polar coordinates, based on the relative separation ξ , and the angle β_ξ . With reference to Fig. 8,

$$z = \xi \cos \beta_\xi \implies \dot{z} = \dot{\xi} \cos \beta_\xi - \xi \sin \beta_\xi \dot{\beta}_\xi \quad (2.48)$$

$$x = \xi \sin \beta_\xi \implies \dot{x} = \dot{\xi} \sin \beta_\xi + \xi \cos \beta_\xi \dot{\beta}_\xi \quad (2.49)$$

and so,

$$\frac{1}{2\mu}(p_z^2 + p_x^2) = \frac{1}{2\mu}[(\mu\dot{z})^2 + (\mu\dot{x})^2] = \frac{\mu}{2}(\dot{\xi}^2 + \xi^2\dot{\beta}_\xi^2). \quad (2.50)$$

In this polar coordinate system the Hamiltonian is,

$$H = \frac{\mu}{2}(\dot{\xi}^2 + \xi^2\dot{\beta}_\xi^2) + u(\xi) = \frac{1}{2\mu}\left(p_\xi^2 + \frac{1}{\xi^2}p_{\beta_\xi}^2\right) + u(\xi). \quad (2.51)$$

where $p_\xi = \partial H / \partial \dot{\xi} = \mu\dot{\xi}$ is the radial component of the relative momentum, and $p_{\beta_\xi} = \partial H / \partial \dot{\beta}_\xi = \mu\xi^2\dot{\beta}_\xi$ the angular momentum.

From the conservation of angular momentum, the magnitude of the angular momentum before the collision, $bp_0 = b\mu g_0$ equals that at any other instant during the collision, i.e.

$$p_{\beta_\xi} = \mu\xi^2\dot{\beta}_\xi = b\mu g_0 \implies \frac{d\beta_\xi}{dt} = \frac{bg_0}{\xi^2}. \quad (2.52)$$

This equation shows the variation of the angular coordinate β_ξ with time.

The conservation of energy shows that the energy before the collision, $E = \mu g_0^2/2$ equals that of any other instant during the collision. On substituting Eq. (2.52) into Eq. (2.51),

$$\frac{\mu}{2}g_0^2 = \frac{\mu}{2}\dot{\xi}^2 + \frac{\mu}{2}g_0^2 \left(\frac{b^2}{\xi^2} \right) + u(\xi) \implies \frac{d\xi}{dt} = \pm \left[g_0^2 - g_0^2 \left(\frac{b^2}{\xi^2} \right) - \frac{2u(\xi)}{\mu} \right]^{1/2}. \quad (2.53)$$

This equation shows how the relative separation ξ changes with time. The negative sign corresponds to the incoming part of the trajectory where the relative distance ξ decreases with time and the positive sign is for the outgoing segment of the trajectory where ξ increases with time.

Equations (2.52) and (2.53) are parametric equations in time t . Time can be eliminated from these equations to give the variation of the angle coordinate $d\beta_\xi$ directly as a function of the variation of the relative position coordinate $d\xi$,

$$d\beta_\xi(\xi) = \pm \frac{bd\xi}{\xi^2 \left[1 - \frac{b^2}{\xi^2} - \frac{2u(\xi)}{\mu v_0^2} \right]^{1/2}}. \quad (2.54)$$

Integrating the right hand side of this equation from the position of the reference point \mathbf{r} , assumed to be on the incoming part of the trajectory, to the distance R is equivalent to integrating the left hand side from the angle θ to β_R ,

$$\int_\theta^{\beta_R} d\beta_\xi(\xi) = \beta_R - \theta = - \int_r^R \frac{bd\xi}{\xi^2 \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{1/2}}. \quad (2.55)$$

From the definition of the collision parameters, ω_R and ζ in Eq. (2.39), and with reference to Fig. 8, for \mathbf{r} on the incoming part of the trajectory, the integral of the right of Eq. (2.55) is decomposed to give,

$$\omega_R = - \int_{r_m}^R \frac{bd\xi}{\xi^2 \left[1 - \frac{b^2}{\xi^2} - \frac{2u(\xi)}{\mu v_0^2} \right]^{1/2}} \quad (2.56)$$

$$\zeta = \int_{r_m}^r \frac{bd\xi}{\xi^2 \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{1/2}}. \quad (2.57)$$

A particular case of the first of these equations is

$$\lim_{R \rightarrow \infty} 2\omega_R = \pi - \chi \quad (2.58)$$

with χ being the angle of deflection.

With reference to the definition of s_0 , it is easily seen from Eq. (2.53) that for the incoming part of the trajectory,

$$s_0 = + \int_r^R \frac{d\xi}{g_0 \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{1/2}} \quad (2.59)$$

It is possible to decompose the above integral to obtain contributions corresponding to the collision parameters X_R and Y . Thus with reference to the definitions of X_R and Y ,

$$g_0 s_0 - R = + \int_r^R d\xi \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{-1/2} - R = b(X_R + Y), \quad (2.60)$$

so that,

$$\begin{aligned} X_R &= b^{-1} \int_{r_m}^R d\xi \left\{ \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{-1/2} - 1 \right\} - b^{-1} r_m \\ Y &= -b^{-1} \int_{r_m}^r d\xi \left[1 - \frac{b^2}{\xi^2} - \frac{u(\xi)}{E} \right]^{-1/2} \end{aligned} \quad (2.61)$$

Analogous definitions can be stated for reference points \mathbf{r} and \mathbf{p} on the outgoing part of the trajectory. These relations are stated by Snider and Curtiss [19] and also by Rainwater [54]. In principle all collision parameters can be determined for a particular collision trajectory from a knowledge of the intermolecular potential. The parameters ω_R and X_R are properties of the trajectory as a whole, while ζ and Y are parameters different for each particular reference point, \mathbf{r}, \mathbf{p} of the trajectory.

2.5.3 Collision Operators

A number of processes which occur on a pair of molecules during a binary collision are described by operators. For quantum mechanical calculations, the superoperator equivalents to these operators are used and depending on the context, the operator and/or superoperator forms are used interchangeably throughout this thesis. These arise naturally while studying the dynamics of the system, in particular as a result of the binary collision expansion of the N -particle resolvent as described in future chapters. For completeness of the treatment of binary collisions, two of the relevant superoperators are discussed in this section.

The quantum two-particle transition superoperator [55] is encountered in the study of binary collisions,

$$\mathcal{T}_{12} = \mathcal{V}_{12} + \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} = \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (z - \mathcal{K}_{12}). \quad (2.62)$$

As applied in this thesis, z is a small positive imaginary number which is taken to be zero at the end of the calculation. The classical analog of this, the transition operator, involves the potential part \mathcal{V}_{12} , and the kinetic part \mathcal{K}_{12} of the Liouville operator \mathcal{L}_{12} ,

$$\mathcal{L}_{12} = \mathcal{K}_1 + \mathcal{K}_2 + \mathcal{V}_{12} = -i\frac{\mathbf{p}_1}{m} \cdot \frac{\partial}{\partial \mathbf{r}_1} - i\frac{\mathbf{p}_2}{m} \cdot \frac{\partial}{\partial \mathbf{r}_2} + i\frac{\partial u_{12}}{\partial \mathbf{r}_{12}} \cdot \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2} \right) \quad (2.63)$$

When the transition operator is in an integral of the structure

$$\mathcal{R}_1 \equiv \frac{n}{\varphi_1} \int d\mathbf{x}_2 i\mathcal{T}_{12}(1 + P_{12})\varphi_1\varphi_2 \quad (2.64)$$

and operates on a function of the momentum $F(\mathbf{p}_1)$, the result is related to the linearized (Boltzmann) collision operator \mathcal{R}_1 ,

$$\frac{\varphi_1}{VN} \mathcal{R}_1 F(\mathbf{p}_1) = \int d\mathbf{r}_2 d\mathbf{p}_2 [F(\mathbf{p}'_2) + F(\mathbf{p}'_1) - F(\mathbf{p}_1) - F(\mathbf{p}_2)] \frac{\varphi_1\varphi_2}{V^2} \quad (2.65)$$

where the \mathbf{p}'_j are the momenta before the collision and \mathbf{p}_j are those after the collision. The φ_j are normalized Maxwellian momentum distributions,

$$\varphi_j = \frac{1}{(2\pi m_j kT)^{3/2}} e^{-\mathbf{p}_j^2/2m_j kT} \quad (2.66)$$

The Møller superoperator Ω_{12} for the pair of particles 1 and 2 [56, 57] is also encountered on numerous occasions,

$$\Omega_{12} \equiv \lim_{t \rightarrow \infty} e^{-it\mathcal{L}_{12}} e^{it\mathcal{K}}. \quad (2.67)$$

The classical Møller operator takes an interacting pair of particles back an infinite amount of time to the past (in practice to a time where particles are no longer considered to interact), and then brings them forward in time by the same amount, without the interaction. The Møller operator (superoperator) converts the relative position \mathbf{r} to \mathbf{r}' ,

$$\Omega_{12}\mathbf{r} = \mathbf{r}'. \quad (2.68)$$

and is related, when acting on functions of the momentum, to the two particle resolvent by,

$$\lim_{z \rightarrow 0} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} = \Omega'_{12} - 1. \quad (2.69)$$

The prime is used to indicate that this equality applies only when the resolvents are operating on functions of momentum (functions with zero eigenvalues with respect to the operator \mathcal{K}). A correction term is needed when the resolvent form of the Møller operator operates on functions of the position.

Chapter 3

Moderately Dense Gas Shear Viscosity from the Kawasaki - Oppenheim Approach

In this chapter, the Kawasaki and Oppenheim method of evaluating time correlation functions for first order density corrections to the shear viscosity for gases with repulsive potentials is outlined [51]. Hamer and Oppenheim have carried out similar calculations for thermal conductivity and bulk viscosity [58, 59]. The kinetic and potential contributions to the shear viscosity and the binary collision expansion of the resolvent are introduced in Section 3.1. Of the various terms, the kinetic - kinetic contribution is treated in detail in Section 3.2 and the results for the other contributions are quoted. The Fourier transforms of operators introduced by Kawasaki and Oppenheim are not used as these do not appear to be crucial to the development and their deletion simplifies the notation considerably. Our treatment utilizes the symmetric traceless form of the momentum flux tensor, making the relations rotationally invariant and independent of the choice of coordinate system. The new work of this thesis begins with Section 3.3 where it is demonstrated that the results of Section 3.2 are equivalent to the Snider - Curtiss first order density corrections to the shear viscosity. An extra term which accounts for triple collisions is also obtained in the Kawasaki and Oppenheim approach. A binary mixture calculation based on the method of Section 3.2 follows in Section 3.4. This accounts for bound pairs in the system at the level of the Stogryn and Hirschfelder approximation. By including bound pairs in this manner, it is demonstrated that the approach can produce results equivalent to the Rainwater theory. Section 3.5 outlines the theory originally proposed by Kawasaki and Oppenheim to account for systems with attractive potentials. A discussion on what we believe to be problems in this treatment of attractive potentials is presented.

3.1 Formulation for the Shear Viscosity

From Eq. (2.22), the time correlation function expression for the shear viscosity of a pure fluid of volume V at temperature T , composed of particles of mass m is,

$$\begin{aligned}\eta &= \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \eta(\epsilon) \\ \eta(\epsilon) &= \frac{1}{10VkT} \int_0^\infty dt e^{-\epsilon t} \langle\langle \mathbf{J}(0) : \mathbf{J}(-t) \rangle\rangle, \end{aligned} \quad (3.1)$$

where a convergence factor $e^{-\epsilon t}$ with $\epsilon > 0$ is introduced. The flux at time $-t$ is expressed in terms of the flux at $t = 0$ with the help of the time evolution operator. The time integration of this expression can be equivalently expressed in terms of an N -particle resolvent operator,

$$\begin{aligned}\eta(\epsilon) &= \frac{1}{10VkT} \int_0^\infty dt e^{-\epsilon t} \langle\langle \mathbf{J}(0) : e^{-i\mathcal{L}t} \mathbf{J}(0) \rangle\rangle, \\ &= \frac{1}{10VkT} \langle\langle \mathbf{J}(0) : \frac{i}{z - \mathcal{L}} \mathbf{J}(0) \rangle\rangle \end{aligned} \quad (3.2)$$

Viewed in this manner, the transport coefficient is proportional to the Laplace transform of the time correlation function, $\langle\langle \mathbf{J}(0) : \mathbf{J}(-t) \rangle\rangle$, with a vanishing real variable ϵ (or vanishing complex variable $z = i\epsilon$).

In Eq. (2.23) the momentum flux tensor was seen to have both kinetic and potential parts,

$$\mathbf{J} = \mathbf{J}_K + \mathbf{J}_V \quad (3.3)$$

where $\mathbf{J}_K = \sum_j [\mathbf{p}_j]^{(2)}/m$ and $\mathbf{J}_V = \sum_{j<\ell} [\mathbf{r}_{j\ell} \mathbf{F}_{j\ell}]^{(2)}$. Substituting this sum into Eq. (3.2), the viscosity breaks up into four contributions,

$$\begin{aligned}\eta(\epsilon) &= \frac{1}{10VkT} \left[\langle\langle \mathbf{J}_K : \frac{i}{i\epsilon - \mathcal{L}} \mathbf{J}_K \rangle\rangle + \langle\langle \mathbf{J}_K : \frac{i}{i\epsilon - \mathcal{L}} \mathbf{J}_V \rangle\rangle + \langle\langle \mathbf{J}_V : \frac{i}{i\epsilon - \mathcal{L}} \mathbf{J}_K \rangle\rangle + \langle\langle \mathbf{J}_V : \frac{i}{i\epsilon - \mathcal{L}} \mathbf{J}_V \rangle\rangle \right], \\ &= \eta_{KK}(\epsilon) + \eta_{KV}(\epsilon) + \eta_{VK}(\epsilon) + \eta_{VV}(\epsilon). \end{aligned} \quad (3.4)$$

The evaluation of $\eta_{KK}(\epsilon)$ is presented in detail. Other contributions are obtained by similar arguments but only the final results of these evaluations are given.

Before evaluating the $\eta_{KK}(\epsilon)$, a number of preliminaries need to be discussed. Kawasaki and Oppenheim introduce the notation,

$$G(\epsilon) = \frac{i}{i\epsilon - \mathcal{L}} \quad (3.5)$$

for the resolvent where \mathcal{L} is the N -particle Liouville operator.

Determining the effect of the N -particle resolvent operator on \mathbf{J}_K requires a detailed knowledge of the dynamics of the N -particle system. At low densities where the present

calculations are valid, interactions among particles are predominantly pairwise additive. It is physically reasonable to expect that in this situation, the dynamics of the system are expressed as combinations of binary collisions. Recalling the definition of the transition operator \mathcal{T}_α from Eq. (2.62), (Greek subscripts will designate pairs of particles from this point onwards) and defining G_0 as the resolvent for a system of non-interacting particles and $G_2(\alpha)$ as the resolvent of a system with only the pair α interacting, it is seen that,

$$\begin{aligned}\mathcal{T}_\alpha &= \mathcal{V}_\alpha - i\mathcal{V}_\alpha G_0 \mathcal{T}_\alpha = \mathcal{V}_\alpha - i\mathcal{T}_\alpha G_0 \mathcal{V}_\alpha \\ &= \mathcal{V}_\alpha G_2(\alpha) G_0^{-1} = G_0^{-1} G_2(\alpha) \mathcal{V}_\alpha.\end{aligned}\quad (3.6)$$

With these relations it is straightforward to derive the binary collision expansion of the N -particle resolvent developed originally by Watson [60] and stated in the present form by Siegert and Teramoto [61],

$$G = G_0 - i \sum_{\alpha} G_0 \mathcal{T}_\alpha G_0 - \sum_{\alpha, \beta} G_0 \mathcal{T}_\alpha G_0 \mathcal{T}_\beta G_0 + i \sum_{\alpha, \beta, \gamma} G_0 \mathcal{T}_\alpha G_0 \mathcal{T}_\beta G_0 \mathcal{T}_\gamma G_0 + \dots \quad (3.7)$$

The N -particle resolvent in Eq. (3.7) is decomposed into a free streaming term, a sum of single binary collisions, a sum of two consecutive binary collisions (the prime on the summation indicates that the pairs α and β do not involve the same pair of particles), and so on. The theory of Section 3.2 assumes the potential is repulsive and so none of the pairs in the above expansion are bound. The operators are thus well defined and convergent.

Before proceeding, the normalization convention for reduced distribution functions is defined,

$$\rho^{(s)} = \frac{N!}{(N-s)!} \int d\mathbf{r}^{s+1} d\mathbf{p}^{s+1} \dots d\mathbf{r}^N d\mathbf{p}^N \rho^{(N)}. \quad (3.8)$$

Consistent with this normalization, the expressions for $\rho_1^{(1)}$ and $\rho_{12}^{(2)}$ are,

$$\rho_1^{(1)} = n\varphi_1 \quad \rho_{12}^{(2)} = n^2 \varphi_1 \varphi_2 e^{-\beta u_{12}}. \quad (3.9)$$

φ_i is the normalized Maxwellian momentum distribution and n is the number density.

3.2 Contributions to $\eta(\epsilon)$

To evaluate the shear viscosity, Kawasaki and Oppenheim write the integral of $\eta_{KK}(\epsilon)$ in explicit form,

$$\eta_{KK}(\epsilon) = \frac{1}{10VkT} \iint d\mathbf{r}^N d\mathbf{p}^N \mathbf{J}_K : G(z) \mathbf{J}_K \rho^{(N)}, \quad (3.10)$$

where $\rho^{(N)}$ is the N -particle distribution function. Using the equivalence of the N particles in the system and substituting the binary collision expansion of Eq. (3.7) for the resolvent operator gives,

$$\eta_{KK}(\epsilon) = \frac{n}{10mkT} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : \times G_0 \left\{ 1 - i \sum_{\alpha} \mathcal{T}_{\alpha} G_0 - \sum_{\alpha, \beta} \mathcal{T}_{\alpha} G_0 \mathcal{T}_{\beta} G_0 + \dots \right\} \mathbf{J}_K \rho^{(N)}. \quad (3.11)$$

Since the function to the left of the first G_0 resolvent only depends on the momentum, the equation becomes,

$$\begin{aligned} \eta_{KK}(\epsilon) &= \frac{n}{10mkT} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : \frac{1}{\epsilon} \left\{ 1 - i \sum_{\alpha} \mathcal{T}_{\alpha} G_0 - \sum_{\alpha, \beta} \mathcal{T}_{\alpha} G_0 \mathcal{T}_{\beta} G_0 - \dots \right\} \mathbf{J}_K \rho^{(N)} \\ &= \eta_{KK}^0(\epsilon) + \eta_{KK}^1(\epsilon) + \eta_{KK}^2(\epsilon) + \eta_{KK}^r(\epsilon). \end{aligned} \quad (3.12)$$

The numerical superscript on each term represents the number of transition operators \mathcal{T} , or physically the number of binary collisions involved in its structure. The r superscript represents the contributions from all remaining interactions with at least three collisions.

$\eta_{KK}^0(\epsilon)$ only involves the free streaming of the particles and is simplified to,

$$\begin{aligned} \eta_{KK}^0(\epsilon) &= \frac{n}{\epsilon 10m^2kT} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} \rho^{(N)} \\ &= \frac{n}{\epsilon 10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} \varphi_1. \end{aligned} \quad (3.13)$$

Kawasaki and Oppenheim demonstrate that the only non-zero contributions from \mathbf{J}_K in $\eta_{KK}^1(\epsilon)$ are those in which the index j of $[\mathbf{p}_j]^{(2)}$ is one of the particles in the pair α in the collision operator \mathcal{T}_{α} . Furthermore, one of the particles of the pair α must be particle 1. Therefore,

$$\begin{aligned} \eta_{KK}^1(\epsilon) &= \frac{-n}{\epsilon 10mkT} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : i \sum_{\alpha} \mathcal{T}_{\alpha} G_0 \mathbf{J}_K \rho^{(N)} \\ &= \frac{1}{\epsilon 10m^2kT} \iint d\mathbf{r}_{12} d\mathbf{p}_1 d\mathbf{p}_2 [\mathbf{p}_1]^{(2)} : i \mathcal{T}_{12} G_0 (1 + P_{12}) [\mathbf{p}_1]^{(2)} \rho_{12}^{(2)} \end{aligned} \quad (3.14)$$

P_{12} is the permutation (exchange) operator for the 12 pair, and Eq. (3.8) has been used.

With the introduction of the Mayer f -function $F_0(\mathbf{r}_{12}) = e^{-\beta u_{12}} - 1$, Eq. (3.14) is split up into a sum of a term where the pair 12 do not have any spatial correlation prior to collision and a term where 1 and 2 are spatially correlated prior to colliding,

$$\begin{aligned} \eta_{KK}^1(\epsilon) &= \frac{-n^2}{\epsilon^2 10m^2kT} \iint d\mathbf{r}_{12} d\mathbf{p}_1 d\mathbf{p}_2 [\mathbf{p}_1]^{(2)} : i \mathcal{T}_{12} (1 + P_{12}) [\mathbf{p}_1]^{(2)} \varphi_1 \varphi_2 \\ &\quad - \frac{n^2}{\epsilon 10m^2kT} \iint d\mathbf{r}_{12} d\mathbf{p}_1 d\mathbf{p}_2 [\mathbf{p}_1]^{(2)} : i \mathcal{T}_{12} G_0 (1 + P_{12}) [\mathbf{p}_1]^{(2)} F_0(\mathbf{r}_{12}) \varphi_1 \varphi_2. \end{aligned} \quad (3.15)$$

The operand to the right of G_0 in the first integral in Eq. (3.15) is only momentum dependent and so this operator produces a $1/\epsilon$ factor. The linearized collision operator \mathfrak{L}_1 for an uncorrelated pair of particles is defined as,

$$\mathfrak{L}_1(\mathbf{p}_1) = \int d\mathbf{r}_{12} d\mathbf{p}_2 i\mathcal{T}_{12}(1 + P_{12})\varphi_2. \quad (3.16)$$

Kawasaki and Oppenheim use the script \mathcal{L} rather than the fraktur \mathfrak{L} for this quantity. The \mathfrak{L} is related to the linearized collision operator \mathcal{R}_1 of Eq. (2.65) by,

$$\mathcal{R}_1 = \frac{n}{\varphi_1} \mathfrak{L}_1(\mathbf{p}_1)\varphi_1. \quad (3.17)$$

In the limit of $z \rightarrow 0$ when operating on a function of the momentum $F(\mathbf{p}_1)$, \mathfrak{L}_1 gives,

$$\begin{aligned} \mathfrak{L}_1(\mathbf{p}_1)F(\mathbf{p}_1)\varphi_1 &= - \int d\mathbf{p}_2 \int_0^{2\pi} d\psi \int_0^\infty b db \frac{|\mathbf{p}_1 - \mathbf{p}_2|}{m} \\ &\quad \times [F(\mathbf{p}'_1) + F(\mathbf{p}'_2) - F(\mathbf{p}_1) - F(\mathbf{p}_2)]\varphi_1\varphi_2 \end{aligned} \quad (3.18)$$

Momenta with the prime superscript in $F(\mathbf{p}'_j)$ have values prior to the collision, while momenta without superscripts in $F(\mathbf{p}_j)$ have values after the collision has occurred.

Kawasaki and Oppenheim also define a collision operator for a correlated pair,

$$t_1(\mathbf{p}_1) = \int d\mathbf{r}_{12} d\mathbf{p}_2 i\mathcal{T}_{12}G_0F_0(\mathbf{r}_{12})(1 + P_{12})\varphi_2. \quad (3.19)$$

In terms of these new operators, Eq. (3.15) is written as,

$$\eta_{KK}^1(\epsilon) = \frac{n}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \left\{ -n\epsilon^{-2}\mathfrak{L}_1 - n\epsilon^{-1}t_1 \right\} [\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.20)$$

Evaluation of $\eta_{KK}^2(\epsilon)$ follows in a similar manner. Nonzero contributions are,

$$\begin{aligned} \eta_{KK}^2(\epsilon) &= \frac{-n}{\epsilon 10mkT} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : \sum_{\alpha,\beta} \mathcal{T}_\alpha G_0 \mathcal{T}_\beta G_0 \mathbf{J}_K \rho^{(N)} \\ &= \frac{-1}{\epsilon 10m^2V kT} \int d\mathbf{r}^3 d\mathbf{p}^3 [\mathbf{p}_1]^{(2)} : \mathcal{T}_{12} G_0 (\mathcal{T}_{13} + \mathcal{T}_{23}) G_0 [1 + P_{12} + P_{13}] [\mathbf{p}_1]^{(2)} \rho_{123}^{(3)}. \end{aligned} \quad (3.21)$$

At the level of approximation required for first order density corrections, the position dependent part of $\rho_{123}^{(3)}$ is replaced by $1 + F_0(\mathbf{r}_{13}) + F_0(\mathbf{r}_{23})$. The result is

$$\eta_{KK}^2(\epsilon) \approx \frac{n}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \left[n^2\epsilon^{-3}t_{21} + n^2\epsilon^{-2}t_{22} \right] [\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.22)$$

The operator $t_{21}(\mathbf{p}_1)$ involves two consecutive binary collisions among three particles, with no prior spatial correlation among the particles,

$$t_{21}(\mathbf{p}_1) = - \int d\mathbf{r}_{13} d\mathbf{r}_{23} d\mathbf{p}_2 d\mathbf{p}_3 \mathcal{T}_{12}(\mathcal{T}_{13} + \mathcal{T}_{23})(1 + P_{12} + P_{13})\varphi_2\varphi_3, \quad (3.23)$$

while the operator $t_{22}(\mathbf{p}_1)$ has a similar interpretation but includes spatial correlation among the initial colliding pair,

$$t_{22}(\mathbf{p}_1) = - \int d\mathbf{r}_{13} d\mathbf{r}_{23} d\mathbf{p}_2 d\mathbf{p}_3 \mathcal{T}_{12} G_0 [\mathcal{T}_{13} G_0 F_0(\mathbf{r}_{13}) + \mathcal{T}_{23} G_0 F_0(\mathbf{r}_{23})] (1 + P_{12} + P_{13}) \varphi_2 \varphi_3. \quad (3.24)$$

Finally, the expression for $\eta_{KK}^r(\epsilon)$ includes all the contributions from more than two consecutive collisions,

$$\eta_{KK}^r(\epsilon) = \frac{i}{\epsilon 10 m k T} \iint d\mathbf{r}^N d\mathbf{p}^N [\mathbf{p}_1]^{(2)} : \left[\sum_{\alpha, \beta, \gamma} \mathcal{T}_\alpha G_0 \mathcal{T}_\beta G_0 \mathcal{T}_\gamma G_0 + \dots \right] \mathbf{J}_K \rho^{(N)}. \quad (3.25)$$

Approximations are introduced at this stage to simplify this expression. At the lowest order in density, only three or more collisions among the three particles 1, 2 and 3 are retained. The sums of operators that remain in the bracket in Eq. (3.25) is then denoted by

$$\tau(123) = \sum_{\alpha, \beta, \gamma} i \mathcal{T}_\alpha G_0 i \mathcal{T}_\beta G_0 i \mathcal{T}_\gamma G_0 + \dots \quad (3.26)$$

To first order in density, spatial correlations among the three particles are neglected. Within these approximations, the contributions from three or more consecutive collisions are,

$$\begin{aligned} \eta_{KK}^r(\epsilon) &= \frac{-n^3}{\epsilon^2 20 m^2 V k T} \int d\mathbf{r}^3 d\mathbf{p}^3 [\mathbf{p}_1]^{(2)} : \tau(123) (1 + P_{12} + P_{13}) [\mathbf{p}_1]^{(2)} \varphi_1 \varphi_2 \varphi_3 \\ &= \frac{n}{10 m^2 k T} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} \left[-n^2 \epsilon^{-2} t^r(\mathbf{p}_1) \right] [\mathbf{p}_1]^{(2)} \varphi_1 \end{aligned} \quad (3.27)$$

where the operator $t^r(\mathbf{p}_1)$ is defined as,

$$t^r(\mathbf{p}_1) = \frac{1}{2} \int d\mathbf{p}_2 d\mathbf{p}_3 d\mathbf{r}_{13} d\mathbf{r}_{23} \tau(123) (1 + P_{12} + P_{13}) \varphi_2 \varphi_3. \quad (3.28)$$

$\eta_{KK}(\epsilon)$ is obtained by adding Eqs. (3.13), (3.20), (3.22) and (3.27),

$$\eta_{KK}(\epsilon) = \frac{n}{10 m^2 k T} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \mathcal{G}(\epsilon) [\mathbf{p}_1]^{(2)} \varphi_1 + O(n^2) \quad (3.29)$$

with

$$\mathcal{G}(\epsilon) = \frac{1}{\epsilon} - n \left(\frac{\mathfrak{L}_1}{\epsilon^2} + \frac{t_1}{\epsilon} \right) + n^2 \left(\frac{t_{21}}{\epsilon^3} + \frac{t_{22}}{\epsilon^2} - \frac{t^r}{\epsilon^2} \right). \quad (3.30)$$

This is a powers series in the number density whose inverse

$$\mathcal{G}^{-1}(\epsilon) = \epsilon + n \mathfrak{L}_1 + n^2 \left[-t_{22} + (\mathfrak{L}_1 t_1 + t_1 \mathfrak{L}_1) + t^r + \frac{1}{\epsilon} (\mathfrak{L}_1^2 - t_{21}) \right] + \epsilon (n t_1 + n^2 t_1^2) + \dots \quad (3.31)$$

which, in the limit of $\epsilon \rightarrow 0^+$ becomes

$$\mathcal{G}_+^{-1} = \lim_{\epsilon \rightarrow 0^+} \mathcal{G}^{-1}(\epsilon) = n [\mathfrak{L}_{1+} + n (t_{1+} \mathfrak{L}_{1+} + t_+^r + R_1 + R_2)]. \quad (3.32)$$

The operators R_1 and R_2 are defined as,

$$R_1 = \frac{1}{\epsilon}(\mathfrak{L}_{1+}^2 - t_{21+}) \quad R_2 = \mathfrak{L}_{1+}t_{1+} - t_{22+} \quad (3.33)$$

The crucial assumption required is that a function $B_{KK}(\mathbf{p}_1)[\mathbf{p}_1]^{(2)}\varphi_1$, as yet undetermined, exists which satisfies

$$n^{-1}B_{KK}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 = \mathcal{G}_+[\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.34)$$

If such a function exists, the resummation of the divergent series of Eq. (3.30) can be accomplished. An equivalent way of stating Eq. (3.34) is that the operator \mathcal{G}_+^{-1} is well defined and

$$n^{-1}\mathcal{G}_+^{-1}B_{KK}(p_1)[\mathbf{p}_1]^{(2)} = [\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.35)$$

The notation B_{KK} is chosen to indicate the similarity of this function to the B function in the Chapman - Enskog [7, 62] solution of the Boltzmann equation of the shear viscosity. The tensorial properties of the unknown function must be equivalent to $[\mathbf{p}_1]^{(2)}$ since this is the only symmetric traceless second rank tensor that can be constructed from the momentum.

Since \mathcal{G}^{-1} is in the form of a density expansion, it is convenient to also expand $B_{KK}(p_1)$ in powers of density,

$$B_{KK}(p_1) = B^{(0)}(p_1) + nB_{KK}^{(1)}(p_1) + O(n^2). \quad (3.36)$$

Substituting the expansion into Eq. (3.35) and equating powers of density gives rise to a pair of equations,

$$\mathfrak{L}_+(\mathbf{p}_1)B^{(0)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 = [\mathbf{p}_1]^{(2)}\varphi_1, \quad (3.37)$$

and

$$\mathfrak{L}_+(\mathbf{p}_1)B_{KK}^{(1)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 = -t_{1+}[\mathbf{p}_1]^{(2)}\varphi_1 - t_+^r B^{(0)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.38)$$

The contributions of the operators R_1 and R_2 in Eq. (3.38) ultimately cancel each other [51]. $B^{(0)}(p_1)$ and $B_{KK}^{(1)}(p_1)$ are unknown functions which must be determined by solving Eqs. (3.37) and (3.38). Equation (3.34) is then used to substitute these functions into Eq. (3.29) to give an expression for the low density viscosity and its first order density correction from kinetic - kinetic contributions,

$$\begin{aligned} \eta_{KK} &= \frac{1}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} B^{(0)}(p_1) \varphi_1 + \frac{n}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} B_{KK}^{(1)}(p_1) \varphi_1 \\ &= \eta^{(0)} + n\eta_{KK}^{(1)}. \end{aligned} \quad (3.39)$$

$\eta^{(0)}$ gives the purely kinetic momentum transfer, while $\eta_{KK}^{(1)}$ is the kinetic momentum transfer between layers of the flowing gas when the particles moving among the layers are spatially correlated and/or suffering triple collisions.

The other contributions of Eq. (3.4) are obtained in a similar manner. The kinetic - potential term gives a first order density correction. This contribution involves the transfer of potential momentum flux of correlated particles to kinetic momentum flux. Determining this contribution involves solving the equation,

$$\mathfrak{L}_{1+}(\mathbf{p}_1)B_{KV}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 = - \int d\mathbf{p}_2 d\mathbf{r} \mathcal{T}_{12} G_0[\mathbf{r}]^{(2)} \frac{1}{r} \frac{du}{dr} e^{-u/kT} \varphi_1 \varphi_2, \quad (3.40)$$

and substituting $B_{KV}(p_1)$ into the following integral,

$$\eta_{KV} = \frac{n}{10mkT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : B_{KV}(p_1) [\mathbf{p}_1]^{(2)} \varphi_1. \quad (3.41)$$

The potential - kinetic contribution corresponds to the collisional transfer contribution in the Boltzmann equation,

$$\eta_{VK} = \eta_{ct} = - \frac{n}{10mkT} \iint d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{r} [\mathbf{r}]^{(2)} \frac{1}{r} \frac{du}{dr} : G_0 \mathcal{T}_{12} B^{(0)}(p_1) [\mathbf{p}_1]^{(2)} \varphi_1. \quad (3.42)$$

Finally, it can be demonstrated that η_{VV} does not contribute a first order density correction to the viscosity.

It is convenient to define $B^{(1)} = B_{KK}^{(1)} + B_{KV}$ such that the addition of Eqs. (3.38) and (3.40) gives,

$$\begin{aligned} \mathfrak{L}_{1+}(\mathbf{p}_1)B^{(1)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 &= -t_{1+}[\mathbf{p}_1]^{(2)}\varphi_1 - t_+^r B^{(0)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 \\ &\quad - \int d\mathbf{p}_2 d\mathbf{r} \mathcal{T}_{12} G_0 e^{-u/kT} [\mathbf{r}]^{(2)} \frac{1}{r} \frac{du}{dr} \varphi_1 \varphi_2. \end{aligned} \quad (3.43)$$

Kawasaki and Oppenheim show that the right hand side is equivalent to corrections which appear in the Choh - Uhlenbeck approach (designated with a tilde),

$$\mathfrak{L}_{1+}(\mathbf{p}_1)B^{(1)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1 = -\widetilde{\mathcal{M}}(\mathbf{p}_1) - \widetilde{t}_+^r(\mathbf{p}_1)B^{(0)}(p_1)[\mathbf{p}_1]^{(2)}\varphi_1. \quad (3.44)$$

where

$$\widetilde{\mathcal{M}}(\mathbf{p}_1) = m \int d\mathbf{r}_2 d\mathbf{p}_2 \left(\frac{\partial u}{\partial \mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \Omega_{12}[\mathbf{p}\mathbf{r}]^{(2)} \varphi_1 \varphi_2 - B(T)[\mathbf{p}_1]^{(2)} \varphi_1, \quad (3.45)$$

and $\widetilde{t}_+^r(\mathbf{p}_1)$ is defined in Section 3.3.4. $\widetilde{\mathcal{M}}$ is a combination of the kinetic - kinetic term for correlated particles and the kinetic - potential term. This expression includes the Møller operator Ω_{12} , and the second pressure virial coefficient $B(T)$.

With the definition of $B^{(1)}$, the first order density correction has a slightly more compact form,

$$\eta^{(1)} = \frac{1}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : B^{(1)}(p_1) [\mathbf{p}_1]^{(2)} \varphi_1 + \eta_{ct}. \quad (3.46)$$

3.3 Equivalence of the Two Approaches

Kawasaki and Oppenheim's derivation ends at the stage of the previous section. This calculation is limited to repulsive potentials, since for a bound pair, the linearized collision operator \mathfrak{L}_1 is divergent. They show their relations to be equivalent to those of Choh and Uhlenbeck [12], but do not make comparisons with the density corrections of Snider and Curtiss [19]. In this section, the equations of Section 3.2 are solved within certain approximations and the equivalence, or otherwise, of the approaches is studied. To our knowledge, this has not been done previously.

The final form of the first order density corrections of Snider and McCourt [20] is given by their Eqs. (20), (21), and (27). These are the equations to which the Kawasaki and Oppenheim results are compared. In the previous section it was seen

$$\eta = \eta^{(0)} + n\eta^{(1)}, \quad (3.47)$$

where Eq. (3.39) gives the shear viscosity to the zeroth order in density and Eq. (3.46) the first order density correction.

To obtain an explicit expression for the viscosity, $B^{(0)}$ and $B^{(1)}$ must be determined by solving Eqs. (3.37) and (3.44). This is accomplished by expanding $B^{(0)}(p_1)$ in terms of Sonine polynomials in W_1^2 of index 5/2,

$$B^{(0)}(p_1)[\mathbf{p}_1]^{(2)} = \sum_j \mathfrak{b}_j^{(0)} S_{5/2}^{(j)}(W_1^2)[\mathbf{p}_1]^{(2)} \quad (3.48)$$

where $\mathbf{W}_j = \mathbf{p}_j/(2mkT)^{1/2}$ is the dimensionless momentum of particle j . The orthonormality conditions of these polynomials [16] makes them a suitable choice for the expansion. $B^{(1)}[\mathbf{p}_1]^{(2)}$ is similarly expanded in terms of Sonine polynomials,

$$B^{(1)}(p_1)[\mathbf{p}_1]^{(2)} = \sum_j \mathfrak{b}_j^{(1)} S_{5/2}^{(j)}(W_1^2)[\mathbf{p}_1]^{(2)}. \quad (3.49)$$

Keeping the lowest order in the Sonine polynomial expansion, which is the order of approximation of Snider and Curtiss, only the constant first Sonine term $S_{5/2}^{(0)}(W_1^2) = 1$ in these expansions are retained. Therefore

$$B^{(0)}(p_1)[\mathbf{p}_1]^{(2)} \approx \mathfrak{b}_0^{(0)}[\mathbf{p}_1]^{(2)}, \quad (3.50)$$

and similarly

$$B^{(1)}(p_1)[\mathbf{p}_1]^{(2)} \approx \mathfrak{b}_0^{(1)}[\mathbf{p}_1]^{(2)}. \quad (3.51)$$

Consistent with the one-moment approximations for $B^{(0)}$ and $B^{(1)}$, Eqs. (3.37) and (3.44) are dot contracted on the left into $S_{5/2}^{(0)}(W_1^2)[\mathbf{p}_1]^{(2)}/10 = [\mathbf{p}_1]^{(2)}/10$ and integrated with respect to \mathbf{p}_1 , giving

$$\frac{1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \mathfrak{L}_{1+}(\mathbf{p}_1) \mathfrak{b}_0^{(0)} [\mathbf{p}_1]^{(2)} \varphi_1 = \frac{1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} \varphi_1 \quad (3.52)$$

and

$$\begin{aligned} \frac{1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \mathfrak{L}_{1+}(\mathbf{p}_1) \mathfrak{b}_0^{(1)} [\mathbf{p}_1]^{(2)} \varphi_1 &= \frac{-1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \widetilde{t}_+^*(\mathbf{p}_1) \mathfrak{b}_0^{(0)} [\mathbf{p}_1]^{(2)} \varphi_1 \\ &\quad - \frac{1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \widetilde{\mathcal{M}}(\mathbf{p}_1). \end{aligned} \quad (3.53)$$

The factor of $1/10$ leads to a simplification of the numerical factors in later stages. These two equations are solved in the following sections.

Higher moment approximations to the viscosity can be obtained by including, more terms of the expansions in Eqs. (3.48) and (3.49). Equations (3.37) and (3.44) will then have to be contracted into a function which includes more terms of the corresponding series $S_{5/2}^{(j)}(W_1^2)[\mathbf{p}_1]^{(2)}$ and then integrated with respect to \mathbf{p}_1 . The result will be a set of equations for the unknown $\mathfrak{b}_j^{(0)}$ expansion coefficients.

3.3.1 Evaluation of $\mathfrak{b}_0^{(0)}$

The right hand side of Eq. (3.52) is easy to evaluate

$$\frac{1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} \varphi_1 = \frac{(2mkT)^2}{10\pi^{3/2}} \int d\mathbf{W}_1 [\mathbf{W}_1]^{(2)} : [\mathbf{W}_1]^{(2)} e^{-W_1^2} = (mkT)^2. \quad (3.54)$$

Then using the definition of the operator $\mathfrak{L}_{1+}(\mathbf{p}_1)$, Eq. (3.52) becomes,

$$(mkT)^2 = \frac{-4\pi}{10m} \iint d\mathbf{p}_1 d\mathbf{p}_2 \int_0^\infty bdb \mathfrak{b}_0^{(0)} p [\mathbf{p}_1]^{(2)} : \{ [\mathbf{p}'_1]^{(2)} + [\mathbf{p}'_2]^{(2)} - [\mathbf{p}_1]^{(2)} - [\mathbf{p}_2]^{(2)} \} \varphi_1 \varphi_2 \quad (3.55)$$

It is convenient to transform the momentum tensors into relative and center of mass coordinates,

$$[\mathbf{p}_1]^{(2)} = \frac{1}{4} [\mathbf{P}]^{(2)} + [\mathbf{p}]^{(2)} + [\mathbf{Pp}]^{(2)}, \quad (3.56)$$

$$[\mathbf{p}_1]^{(2)} + [\mathbf{p}_2]^{(2)} = \frac{1}{2} [\mathbf{P}]^{(2)} + 2[\mathbf{p}]^{(2)}. \quad (3.57)$$

Making use of the invariance of the center of mass momentum during a collision, $\mathbf{P}' = \mathbf{P}$, Eq. (3.55) becomes,

$$(mkT)^2 = \frac{-8\pi \mathfrak{b}_0^{(0)}}{10m} \int d\mathbf{p} \int_0^\infty bdb p [\mathbf{p}]^{(2)} : \{ [\mathbf{p}']^{(2)} - [\mathbf{p}]^{(2)} \} \varphi(p). \quad (3.58)$$

The integration with respect to \mathbf{P} has been carried out. Introducing the dimensionless relative momentum $\gamma = (p^2/mkT)^{1/2}$ and contracting the tensors gives,

$$(mkT)^2 = -\frac{16\mathbf{b}_0^{(0)}m^2(kT)^{5/2}}{5} \left(\frac{\pi}{m}\right)^{1/2} \int_0^\infty \int_0^\infty d\gamma b d b e^{-\gamma^2} \gamma^7 (\cos^2 \chi - 1) \quad (3.59)$$

where χ is the angle of deflection in a binary collision. The conservation of energy shows the collision does not change the magnitude of the relative momentum and $p' = p$ is used in deriving Eq. (3.59). The $\Omega^{(\ell,s)}$ collisional integrals [7], defined as,

$$\Omega^{(\ell,s)}(T) = \left(\frac{2\pi kT}{\mu}\right)^{1/2} \int_0^\infty \int_0^\infty d\gamma b d b e^{-\gamma^2} \gamma^{2s+3} (1 - \cos^\ell \chi) \quad (3.60)$$

are used to express Eq. (3.59) in compact form,

$$(mkT)^2 = \frac{8\mathbf{b}_0^{(0)}(mkT)^2}{5} \Omega_{L(2,2)} \quad (3.61)$$

μ is the reduced mass of the colliding pair. The value of the expansion coefficient $\mathbf{b}_0^{(0)}$ is obtained from this equation,

$$\mathbf{b}_0^{(0)} = \frac{5}{8\Omega_{L(2,2)}}. \quad (3.62)$$

3.3.2 Evaluation of $\mathbf{b}_0^{(1)}$

From Eq. (3.45),

$$\begin{aligned} \frac{-1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \widetilde{\mathcal{M}}(\mathbf{p}_1) &= \frac{B(T)}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} \varphi_1 \\ &\quad - \frac{m}{10} \iint d\mathbf{r}_2 d\mathbf{p}_2 d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \left(\frac{d\mathbf{u}}{d\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \Omega_{12}[\mathbf{p}\mathbf{r}]^{(2)} \varphi_1 \varphi_2. \end{aligned} \quad (3.63)$$

The first term on the right hand side is easily evaluated and Eq. (3.63) written as,

$$\begin{aligned} \frac{-1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \widetilde{\mathcal{M}}(\mathbf{p}_1) &= B(T)(mkT)^2 \\ &\quad - \frac{m}{10} \iiint d\mathbf{r} d\mathbf{p}_1 d\mathbf{p}_2 [\mathbf{p}_1]^{(2)} : \left(\frac{d\mathbf{u}}{d\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) \Omega_{12}[\mathbf{p}\mathbf{r}]^{(2)} \varphi_1 \varphi_2. \end{aligned} \quad (3.64)$$

The Møller operator does not affect the center of mass momentum, it converts the relative position to the vector \mathbf{r}' defined in Section 2.5.1 and the relative momentum to its precollision value, \mathbf{p}_0 . Integrating over the center of mass momentum then gives,

$$\begin{aligned} \frac{-1}{10} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \widetilde{\mathcal{M}}(\mathbf{p}_1) &= B(T)(mkT)^2 \\ &\quad - \frac{m}{10} \iint d\mathbf{r} d\mathbf{p} [\mathbf{p}]^{(2)} : \left(\frac{d\mathbf{u}}{d\mathbf{r}} \cdot \frac{\partial}{\partial \mathbf{p}} \right) [\mathbf{p}_0 \mathbf{r}']^{(2)} \varphi(p) e^{-\beta u}. \end{aligned} \quad (3.65)$$

The integral on the right is integrated by parts and converted into dimensionless form,

$$\begin{aligned}
& \frac{m}{10} \iint d\mathbf{r} d\mathbf{p} \frac{1}{r} \frac{du}{dr} ([\mathbf{r}\mathbf{p}]^{(2)} + [\mathbf{p}\mathbf{r}]^{(2)}) : [\mathbf{p}_0 \mathbf{r}']^{(2)} \varphi(p) e^{-\beta u} \\
&= \frac{m^2 kT}{10\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{1}{r} \frac{du}{dr} ([\mathbf{r}\boldsymbol{\gamma}]^{(2)} + [\boldsymbol{\gamma}\mathbf{r}]^{(2)}) : [\boldsymbol{\gamma}_0 \mathbf{r}']^{(2)} e^{-\gamma^2} e^{-\beta u} \\
&= \frac{-4\sigma^3}{15\pi^{1/2}} (mkT)^2 F_\eta.
\end{aligned} \tag{3.66}$$

The calculations required to identify F_η are given in Appendix A.

The left hand side of Eq. (3.53) is treated in a manner similar to the left hand side of Eq. (3.52) and in the one moment approximation, only the constant term $\mathbf{b}_0^{(1)}$ is retained. Collecting the terms of Eq. (3.53) gives,

$$\frac{8}{5} (mkT)^2 \mathbf{b}_0^{(1)} \Omega^{(2,2)} = B(T) (mkT)^2 - \frac{4\sigma^3}{15\pi^{1/2}} (mkT)^2 F_\eta. \tag{3.67}$$

The triple collision contribution in Eq. (3.53) has not been included in this expression. It is discussed briefly in Section 3.3.4. The expansion coefficient $\mathbf{b}_0^{(1)}$ is,

$$\mathbf{b}_0^{(1)} = \frac{5}{8\Omega^{(2,2)}} \left[B(T) - \frac{4\sigma^3}{15\pi^{1/2}} F_\eta \right]. \tag{3.68}$$

In solving the generalized Boltzmann equation, the two terms on the right of this equation arise from the non-locality correction terms Δ_2 and Δ_1 in the collision operator respectively. Here they are the result of a combination of the correlated kinetic - kinetic and kinetic - virial time correlation functions.

By comparing the sum of Eqs. (3.62) and (3.68) with the result of Eqs. (20) and (21) of Snider and McCourt,

$$\frac{1}{2} n b_0 = \frac{5}{8\Omega^{(2,2)}} \left[1 + n B(T) - \frac{4\sigma^3 n}{15\pi^{1/2}} F_\eta \right] \tag{3.69}$$

the combination $\mathbf{b}_0^{(0)} + n\mathbf{b}_0^{(1)}$ can be identified as $nb_0/2$. It is to be noted that the perturbative amplitude b_0 is density dependent.

3.3.3 Collisional Transfer Contribution

From Eq. (3.42),

$$\eta_{ct} = \frac{-n}{10mkT} \int d\mathbf{r} \iint d\mathbf{p}_1 d\mathbf{p}_2 \frac{du}{dr} \frac{1}{2r} [\mathbf{r}]^{(2)} : \Omega_{12} \mathbf{b}_0^{(0)} \{ [\mathbf{p}_1]^{(2)} + [\mathbf{p}_2]^{(2)} \} \varphi_1 \varphi_2. \tag{3.70}$$

The momenta are converted to dimensionless center of mass and relative coordinates and then the Møller operator is applied,

$$\eta_{ct} = \frac{-nb_0^{(0)}}{10\pi^3} \iiint d\mathbf{r} d\boldsymbol{\gamma} d\boldsymbol{\mathcal{G}} \frac{du}{dr} \frac{1}{r} [\mathbf{r}]^{(2)} : \{[\boldsymbol{\mathcal{G}}]^{(2)} + [\boldsymbol{\gamma}_0]^{(2)}\} e^{-\gamma^2 - \mathcal{G}^2 - \beta u}. \quad (3.71)$$

The tensors are contracted and integration over dimensionless center of mass momentum, $\boldsymbol{\mathcal{G}}$, carried through,

$$\eta_{ct} = \frac{-nb_0^{(0)}}{10\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{du}{dr} \frac{1}{r} \left\{ [\mathbf{r} \cdot \boldsymbol{\gamma}_0]^2 - \frac{r^2 \gamma_0^2}{3} \right\} e^{-\gamma^2 - \beta u} \quad (3.72)$$

The calculation of Appendix B shows that

$$\eta_{ct} = -nkTb_0^{(0)} \frac{4\pi^{1/2}\sigma^3}{15} N_\eta. \quad (3.73)$$

The corresponding term in Eq. (27) of Snider and McCourt is,

$$\frac{1}{2} nkTb_0 \frac{-4\pi^{1/2}\sigma^3}{15} N_\eta. \quad (3.74)$$

This term originates from the effect of perturbations on the distribution function in the potential part of the pressure tensor. The two corrections agree if $b_0^{(0)}$ is identified as the lowest order density term of $nb_0/2$, which is consistent with the relation from Eq. (3.69).

3.3.4 Triple Collision Contribution

Kawasaki and Oppenheim obtain a contribution to the first order density corrections from three-body collisions which they demonstrate to be equivalent to a similar contribution from Choh and Uhlenbeck. The explicit term in Eq. (3.44), involves the operator

$$\begin{aligned} \widetilde{t}_+^r(\mathbf{p}_1) = & - \iint d\mathbf{x}_2 d\mathbf{x}_3 \theta_{12} \int_0^\infty dt S_{-t}^{(2)}(12) \\ & \times \{(\theta_{13} + \theta_{23})\Omega_{123} - \Omega_{12}[\theta_{13}\Omega_{13} + \theta_{23}\Omega_{23}]\}(1 + P_{12} + P_{13})\varphi_2\varphi_3. \end{aligned} \quad (3.75)$$

Hoffman and Curtiss [22] have studied this correction extensively and shown the relation between their correction and that of Choh and Uhlenbeck. This correction is not discussed further and it is only mentioned that the Hoffman-Curtiss correction, $\eta^{(3M)}$ can be added to the shear viscosity to approximate this correction.

3.3.5 Shear Viscosity

Returning to Eqs. (3.47) for the shear viscosity,

$$\eta = \frac{1}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} b_0^{(0)} \varphi_1 + \frac{n}{10m^2kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : [\mathbf{p}_1]^{(2)} b_0^{(1)} \varphi_1 + n\eta_{ct} \quad (3.76)$$

The first two terms of the right hand side are $kT\mathbf{b}_0^{(0)} + nkT\mathbf{b}_0^{(1)}$. Substituting the values obtained for $\mathbf{b}_0^{(0)}$, $\mathbf{b}_0^{(1)}$ and η_{ct} from the previous sections gives,

$$\eta = \frac{5kT}{8\Omega^{(2,2)}} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta - \frac{4n\pi^{1/2}\sigma^3}{15} N_\eta \right]. \quad (3.77)$$

Comparison with Eq. (27) of Snider and McCourt shows that the two expressions agree exactly.

3.4 Inclusion of Bound Pairs

In this section the first density contribution to the viscosity from the presence of bound pairs is determined within the scope of the Rainwater - Friend theory. In a system with an attractive intermolecular potential formation of bound pairs becomes possible. Accounting for bound pairs by considering the gas to be a nonreactive binary mixture gives rise to density corrections to the shear viscosity which are straightforward to evaluate. The general time correlation function expression for the viscosity of a binary mixture was derived by Mori [63]. This section illustrates that by extending the method which Kawasaki and Oppenheim used to determine the viscosity of a pure gas to a binary mixture of free molecules and bound pairs, an expression identical to the viscosity of binary mixture from the Boltzmann equation approach can be derived. Only contributions from the kinetic part of the flux of the nonreactive mixture are considered. Adding this result to the relations of Section 3.3.5 takes the time correlation formalism for shear viscosity to the level of the Rainwater theory.

The viscosity of a mixture of N_f free (f) and N_b bound (b) molecules is,

$$\eta = \frac{1}{10VkT} \iint d\mathbf{r}^N d\mathbf{p}^N \mathbf{J}_K : G(\epsilon) \mathbf{J}_K \rho^{(N)} \quad (3.78)$$

with the kinetic contribution to the momentum flux \mathbf{J}_K ,

$$\mathbf{J}_K = \sum_{j=1}^{N_f} \frac{[\mathbf{p}_{fj}]^{(2)}}{m_f} + \sum_{\ell=1}^{N_b} \frac{[\mathbf{p}_{b\ell}]^{(2)}}{m_b} = \mathbf{J}_{Kf} + \mathbf{J}_{Kb}. \quad (3.79)$$

The distribution function for an ideal gas mixture consisting of N_f free and N_b bound molecules is

$$\rho^{(N)} = \prod_{j=1}^{N_f} \frac{\varphi(p_{fj})}{V} \prod_{\ell=1}^{N_b} \frac{\varphi(p_{b\ell})}{V}. \quad (3.80)$$

A binary collision expansion for the resolvent of the binary mixture is similar to Eq. (3.7),

$$G = G_0 - i \sum_{\alpha} G_0 \mathcal{T}_{\alpha} G_0 - \sum_{\alpha, \beta}^i G_0 \mathcal{T}_{\alpha} G_0 \mathcal{T}_{\beta} G_0 + i \sum_{\alpha, \beta, \gamma}^i G_0 \mathcal{T}_{\alpha} G_0 \mathcal{T}_{\beta} G_0 \mathcal{T}_{\gamma} G_0 + \dots \quad (3.81)$$

except now the indices of the summations include all possible collision combinations between free and bound species.

3.4.1 Viscosity of a Mixture of Free Molecules and Bound Pairs

An approach similar to Section 3.2 allows the calculation of the viscosity of a binary mixture. The expression obtained is compared to the standard expression for the viscosity of a binary mixture from the Boltzmann equation [7].

Utilizing the binary collision expansion, the analog of Eq. (3.29) for the viscosity of a binary mixture is,

$$\eta_{KK}(\epsilon) = \sum_{\xi, \zeta} \frac{n_\xi}{10kT} \int d\mathbf{p}_\xi \frac{[\mathbf{p}_\xi]^{(2)}}{m_\xi} : \mathcal{G}^{\xi\zeta}(\epsilon) \frac{[\mathbf{p}_\zeta]^{(2)}}{m_\zeta} \varphi(p_\zeta) \quad (3.82)$$

where ξ and ζ denote the molecular species present in the mixture. The sum over species is written explicitly as,

$$\begin{aligned} \eta_{KK}(\epsilon) = & \frac{n_f}{10kT} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \left\{ \mathcal{G}^{ff}(\epsilon) \frac{[\mathbf{p}_f]^{(2)}}{m_f} + \mathcal{G}^{fb}(\epsilon) \frac{[\mathbf{p}_b]^{(2)}}{m_b} \right\} \varphi(p_f) \\ & + \frac{n_b}{10kT} \int d\mathbf{p}_b \frac{[\mathbf{p}_b]^{(2)}}{m_b} : \left\{ \mathcal{G}^{bb}(\epsilon) \frac{[\mathbf{p}_b]^{(2)}}{m_b} + \mathcal{G}^{bf}(\epsilon) \frac{[\mathbf{p}_f]^{(2)}}{m_f} \right\} \varphi(p_b) \end{aligned} \quad (3.83)$$

with the \mathcal{G} operators defined by,

$$\mathcal{G}^{ff}(\epsilon) = \frac{1}{\epsilon} - n_f \frac{1}{\epsilon^2} \mathfrak{L}^{ff} - n_b \frac{1}{\epsilon^2} \mathfrak{L}^{fb} + \dots, \quad (3.84)$$

$$\mathcal{G}^{fb}(\epsilon) = -n_b \frac{1}{\epsilon^2} \mathfrak{L}^{fb} + \dots, \quad (3.85)$$

$$\mathcal{G}^{bb}(\epsilon) = \frac{1}{\epsilon} - n_b \frac{1}{\epsilon^2} \mathfrak{L}^{bb} - n_f \frac{1}{\epsilon^2} \mathfrak{L}^{bf} + \dots, \quad (3.86)$$

$$\mathcal{G}^{bf}(\epsilon) = -n_f \frac{1}{\epsilon^2} \mathfrak{L}^{bf} + \dots \quad (3.87)$$

The form of the $\mathcal{G}^{\xi\zeta}$ operators is obtained by retaining only terms involving up to a single binary collision among uncorrelated particles in the binary collision expansion, Eq. (3.81). The operators have meanings similar to the one component case, with the superscripts indicating the colliding species in the $\mathcal{T}_{\xi\zeta}$ operator. Specifically,

$$\mathfrak{L}^{\xi\xi} = \int d\mathbf{r}_{\xi 2} d\mathbf{p}_{\xi 2} i\mathcal{T}_{\xi 1 \xi 2} (1 + P_{\xi 1 \xi 2}) \varphi(p_{\xi 1}) \quad \text{and} \quad \mathfrak{L}^{\xi\zeta} = \int d\mathbf{r}_\zeta d\mathbf{p}_\zeta i\mathcal{T}_{\xi\zeta} \varphi(p_\zeta). \quad (3.88)$$

Equation (3.83) is thus written,

$$\begin{aligned} \eta_{KK}(\epsilon) = & \frac{n_f}{10kT} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \left[\frac{1}{\epsilon} - n_f \frac{1}{\epsilon^2} \mathfrak{L}^{ff} - n_b \frac{1}{\epsilon^2} \mathfrak{L}^{fb} (1 + P_{bf}) \right] \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi(p_f) \\ & + \frac{n_b}{10kT} \int d\mathbf{p}_b \frac{[\mathbf{p}_b]^{(2)}}{m_b} : \left[\frac{1}{\epsilon} - n_b \frac{1}{\epsilon^2} \mathfrak{L}^{bb} - n_f \frac{1}{\epsilon^2} \mathfrak{L}^{bf} (1 + P_{fb}) \right] \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi(p_b) \end{aligned} \quad (3.89)$$

To simplify the notation, species permutation operators $P_{\xi\zeta}$ are defined which interchange the species labels on the flux functions (but not the Maxwellians) which follow them, for example,

$$P_{bf} \frac{[\mathbf{p}_f]^{(2)}}{m_f} = \frac{[\mathbf{p}_b]^{(2)}}{m_b}. \quad (3.90)$$

The species permutation operators are contrasted with the permutation operators used previously which interchange the labels of molecules of the same species.

Each of the brackets in Eq. (3.89) is a series in powers of $1/\epsilon$ and appears to be divergent. The series are inverted and terms of the lowest order in ϵ and number density n retained as in Eq. (3.30) of Section 3.2. The resumed series are assumed to be finite and give the following set of equations,

$$[n_f^2 \mathfrak{L}_+^{ff} + n_f n_b \mathfrak{L}_+^{fb} (1 + P_{bf})] B_f(p_f) \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi(p_f) = n_f^2 \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi(p_f) \quad (3.91)$$

$$[n_b^2 \mathfrak{L}_+^{bb} + n_b n_f \mathfrak{L}_+^{bf} (1 + P_{fb})] B_b(p_b) \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi(p_b) = n_b^2 \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi(p_b). \quad (3.92)$$

The functions $B_\xi(p_\xi)$ are to be determined by solving these equations.

3.4.2 Solving for the B_ξ 's

The $B_f(p_f)$ and $B_b(p_b)$ functions are expanded in terms of Sonine polynomials $S_{5/2}^{(j)}(W_\xi^2)$ and in a one moment approximation only the constant terms, $\mathfrak{b}_f^{(0)}$ and $\mathfrak{b}_b^{(0)}$ are retained. Eq. (3.91) is then right contracted into $\frac{1}{10} \frac{[\mathbf{p}_f]^{(2)}}{m_f}$ and integrated over \mathbf{p}_f ,

$$\begin{aligned} \frac{n_f^2}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f &= n_f^2 (kT)^2 \\ &= \frac{n_f^2 \mathfrak{b}_f^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathfrak{L}_+^{ff} \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f \\ &\quad + \frac{n_f n_b \mathfrak{b}_f^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathfrak{L}_+^{fb} \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f \\ &\quad + \frac{n_f n_b \mathfrak{b}_b^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathfrak{L}_+^{fb} \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi_f \\ &= (a) + (b) + (c) \end{aligned} \quad (3.93)$$

The first term (a) represents the loss of polarization (non-equilibrium flux) of a free molecule associated with free - free binary collisions. From the definition of the free - free linearized Boltzmann collision operator \mathfrak{L}_+^{ff} ,

$$(a) = \frac{n_f^2 \mathfrak{b}_f^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathfrak{L}_+^{ff} \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f$$

$$\begin{aligned}
&= \frac{-\pi n_f^2 \mathbf{b}_f^{(0)}}{5} \int d\mathbf{p}_{f1} d\mathbf{p}_{f2} \int_0^\infty b db \frac{|\mathbf{p}_{ff}|}{m_f} \frac{[\mathbf{p}_{f1}]^{(2)}}{m_f} : \\
&\quad \left\{ \frac{[\mathbf{p}'_{f1}]^{(2)}}{m_f} + \frac{[\mathbf{p}'_{f2}]^{(2)}}{m_f} - \frac{[\mathbf{p}_{f1}]^{(2)}}{m_f} - \frac{[\mathbf{p}_{f2}]^{(2)}}{m_f} \right\} \varphi_{f1} \varphi_{f2} \quad (3.94)
\end{aligned}$$

The two characteristic free particles of this collision are labeled by the subscripts $f1$ and $f2$ and \mathbf{p}_{ff} is the relative momentum of a pair of free particles. Converting to center of mass and relative coordinates of the free - free pair

$$[\mathbf{p}_{f1}]^{(2)} + [\mathbf{p}_{f2}]^{(2)} = [\mathbf{P}_{ff}]^{(2)} + [\mathbf{p}_{ff}]^{(2)}, \quad (3.95)$$

and integrating over the constant center of mass momentum leads to

$$\begin{aligned}
(a) &= \frac{-4\pi}{5m_f^3} n_f^2 \mathbf{b}_f^{(0)} \int d\mathbf{p}_{ff} b db p_{ff} [\mathbf{p}_{ff}]^{(2)} : \{ [\mathbf{p}'_{ff}]^{(2)} - [\mathbf{p}_{ff}]^{(2)} \} \varphi_f \\
&= n_f^2 \mathbf{b}_f^{(0)} \frac{8(kT)^2 \Omega_{ff}^{(2,2)}}{5} \quad (3.96)
\end{aligned}$$

The middle term, (b) of Eq. (3.93), represents the loss of polarization from a free molecule as a result of a binary collision with a bound pair. This term can be handled in a manner similar to that of (a) namely,

$$\begin{aligned}
(b) &= \frac{n_f n_b \mathbf{b}_f^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathcal{L}_+^{fb} \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f \\
&= \frac{-\pi n_f n_b \mathbf{b}_f^{(0)}}{5} \int d\mathbf{p}_f d\mathbf{p}_b \int_0^\infty b db \frac{|\mathbf{p}_{fb}|}{\mu_{fb}} \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \left\{ \frac{[\mathbf{p}'_f]^{(2)}}{m_f} - \frac{[\mathbf{p}_f]^{(2)}}{m_f} \right\} \varphi_f \varphi_b \quad (3.97)
\end{aligned}$$

The center of mass and relative momentum coordinates of the colliding free and bound pair are,

$$\begin{aligned}
\mathbf{P}_{fb} &= \mathbf{p}_f + \mathbf{p}_b & \mathbf{p}_{fb} &= \frac{m_b}{m_f + m_b} \mathbf{p}_f - \frac{m_f}{m_f + m_b} \mathbf{p}_b \\
\mathbf{p}_f &= \frac{\mu_{fb}}{m_b} \mathbf{P}_{fb} + \mathbf{p}_{fb} & \mathbf{p}_b &= \frac{\mu_{fb}}{m_f} \mathbf{P}_{fb} - \mathbf{p}_{fb} \quad (3.98)
\end{aligned}$$

μ_{fb} is the reduced mass of the free - bound collision. Converting to these new coordinates, gives,

$$\begin{aligned}
(b) &= \frac{-\pi n_f n_b \mathbf{b}_f^{(0)}}{5\mu_{fb}} \int \int_0^\infty b db d\mathbf{p}_{fb} d\mathbf{P}_{fb} p_{fb} \left\{ \frac{\mu_{fb}^2}{m_f m_b^2} [\mathbf{P}_{fb}]^{(2)} + \frac{[\mathbf{p}_{fb}]^{(2)}}{m_f} + \frac{2\mu_{fb}}{m_f m_b} [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)} \right\} : \\
&\quad \times \left\{ \frac{[\mathbf{p}'_{fb}]^{(2)}}{m_f} - \frac{[\mathbf{p}_{fb}]^{(2)}}{m_f} + \frac{2\mu_{fb}}{m_f m_b} ([\mathbf{P}_{fb} \mathbf{p}'_{fb}]^{(2)} - [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)}) \right\} \varphi(p_{fb}) \varphi(P_{fb})
\end{aligned}$$

$$\begin{aligned}
&= \frac{-\pi n_f n_b \mathbf{b}_f^{(0)}}{5m_f^2 \mu_{fb}} \int \int_0^\infty bdb d\mathbf{p}_{fb} p_{fb} [\mathbf{p}_{fb}]^{(2)} : \left\{ [\mathbf{p}'_{fb}]^{(2)} - [\mathbf{p}_{fb}]^{(2)} \right\} \varphi(p_{fb}) \\
&\quad - \frac{4\pi n_f n_b \mathbf{b}_f^{(0)}}{5(m_f + m_b)^2 \mu_{fb}} \int \int_0^\infty bdb d\mathbf{p}_{fb} d\mathbf{P}_{fb} p_{fb} [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)} : \\
&\quad \times \left\{ [\mathbf{P}_{fb} \mathbf{p}'_{fb}]^{(2)} - [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)} \right\} \varphi(p_{fb}) \varphi(P_{fb}). \tag{3.99}
\end{aligned}$$

After contracting and integrating over the center of mass momentum the structure of the omega integrals is recognized,

$$\begin{aligned}
(b) &= \frac{-4\pi^2 n_f n_b \mathbf{b}_f^{(0)}}{5m_f^2 \mu_{fb}} \int \int_0^\infty bdb d\mathbf{p}_{fb} p_{fb}^7 (\cos^2 \chi_{fb} - 1) \varphi(p_{fb}) \\
&\quad - \frac{8\pi^2 n_f n_b \mathbf{b}_f^{(0)}}{3(m_f + m_b)^2 \mu_{fb}} \int \int_0^\infty bdb d\mathbf{p}_{fb} p_{fb}^5 (\cos \chi_{fb} - 1) \varphi(p_{fb}) \\
&= n_f n_b \mathbf{b}_f^{(0)} (kT)^2 \left[\frac{16}{5} \frac{\mu_{fb}^2}{m_f^2} \Omega_{fb}^{(2,2)} + \frac{32}{3} \frac{\mu_{fb}}{m_f + m_b} \Omega_{fb}^{(1,1)} \right]. \tag{3.100}
\end{aligned}$$

Finally, the third term, (c), of Eq. (3.93) gives the transfer of polarization from the bound molecule to the free particle as a result of a free - bound collisions,

$$\begin{aligned}
(c) &= \frac{n_f n_b \mathbf{b}_b^{(0)}}{10} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathcal{L}_+^{fb} \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi_f \\
&= \frac{-\pi n_f n_b \mathbf{b}_b^{(0)}}{5} \int d\mathbf{p}_f d\mathbf{p}_b \int_0^\infty bdb \frac{|\mathbf{p}_{fb}|}{\mu_{fb}} \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \left\{ \frac{[\mathbf{p}'_b]^{(2)}}{m_b} - \frac{[\mathbf{p}_b]^{(2)}}{m_b} \right\} \varphi_f \varphi_b. \tag{3.101}
\end{aligned}$$

Calculations similar to those used in the evaluation of the term (b) show this integral can be simplified to,

$$\begin{aligned}
(c) &= \frac{-\pi n_f n_b \mathbf{b}_b^{(0)}}{5\mu_{fb}} \int \int_0^\infty bdb d\mathbf{p}_{fb} d\mathbf{P}_{fb} p_{fb} \left\{ \frac{\mu_{fb}^2}{m_f m_b^2} [\mathbf{P}_{fb}]^{(2)} + \frac{[\mathbf{p}_{fb}]^{(2)}}{m_f} + \frac{2\mu_{fb}}{m_f m_b} [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)} \right\} : \\
&\quad \times \left\{ \frac{[\mathbf{p}'_{fb}]^{(2)}}{m_b} - \frac{[\mathbf{p}_{fb}]^{(2)}}{m_b} - \frac{2\mu_{fb}}{m_f m_b} ([\mathbf{P}_{fb} \mathbf{p}'_{fb}]^{(2)} - [\mathbf{P}_{fb} \mathbf{p}_{fb}]^{(2)}) \right\} \varphi(p_{fb}) \varphi(P_{fb}) \\
&= n_f n_b \mathbf{b}_b^{(0)} (kT)^2 \left[\frac{16}{5} \frac{\mu_{fb}^2}{m_f^2} \Omega_{fb}^{(2,2)} - \frac{32}{3} \frac{\mu_{fb}}{m_f + m_b} \Omega_{fb}^{(1,1)} \right]. \tag{3.102}
\end{aligned}$$

Terms from (a), (b), and (c) are put together to get a simplified form for Eq. (3.93), namely

$$\begin{aligned}
n_f^2 &= n_f^2 \mathbf{b}_f^{(0)} \frac{8\Omega_{ff}^{(2,2)}}{5} + n_f n_b \mathbf{b}_f^{(0)} \left[\frac{16}{5} \frac{\mu_{fb}^2}{m_f^2} \Omega_{fb}^{(2,2)} + \frac{32}{3} \frac{\mu_{fb}}{m_f + m_b} \Omega_{fb}^{(1,1)} \right] \\
&\quad + n_f n_b \mathbf{b}_b^{(0)} \left[\frac{16}{5} \frac{\mu_{fb}^2}{m_f^2} \Omega_{fb}^{(2,2)} - \frac{32}{3} \frac{\mu_{fb}}{m_f + m_b} \Omega_{fb}^{(1,1)} \right]. \tag{3.103}
\end{aligned}$$

An analogous form is derived from Eq. (3.92),

$$n_b^2 = n_b^2 \mathbf{b}_b^{(0)} \frac{8\Omega_{bb}^{(2,2)}}{5} + n_b n_f \mathbf{b}_f^{(0)} \left[\frac{16}{5} \frac{\mu_{bf}^2}{m_b^2} \Omega_{bf}^{(2,2)} - \frac{32}{3} \frac{\mu_{bf}}{m_f + m_b} \Omega_{bf}^{(1,1)} \right] + n_b n_f \mathbf{b}_b^{(0)} \left[\frac{16}{5} \frac{\mu_{bf}^2}{m_b^2} \Omega_{bf}^{(2,2)} + \frac{32}{3} \frac{\mu_{bf}}{m_f + m_b} \Omega_{bf}^{(1,1)} \right]. \quad (3.104)$$

Equations (3.103) and (3.104) can be written in terms of mole fractions. Using $M = m_f + m_b$ for the total mass of the colliding pair,

$$\begin{aligned} X_f^2 &= \mathbf{b}_f^{(0)} \left[X_f^2 \frac{8\Omega_{ff}^{(2,2)}}{5} + X_f X_b \frac{16}{5} \frac{m_b^2}{M^2} \Omega_{fb}^{(2,2)} + X_f X_b \frac{32}{3} \frac{m_{fb}}{M^2} \Omega_{fb}^{(1,1)} \right] \\ &\quad + \mathbf{b}_f^{(0)} \left[X_f X_b \frac{16}{5} \frac{m_f m_b}{M^2} \Omega_{fb}^{(2,2)} - X_f X_b \frac{32}{3} \frac{m_f m_b}{M^2} \Omega_{fb}^{(1,1)} \right], \\ X_b^2 &= \mathbf{b}_b^{(0)} \left[X_f X_b \frac{16}{5} \frac{m_f m_b}{M^2} \Omega_{bf}^{(2,2)} - X_f X_b \frac{32}{3} \frac{m_f m_b}{M^2} \Omega_{bf}^{(1,1)} \right] \\ &\quad + \mathbf{b}_b^{(0)} \left[X_b^2 \frac{8\Omega_{bb}^{(2,2)}}{5} + X_f X_b \frac{16}{5} \frac{m_f^2}{M^2} \Omega_{bf}^{(2,2)} + X_f X_b \frac{32}{3} \frac{m_f m_b}{M^2} \Omega_{bf}^{(1,1)} \right]. \end{aligned} \quad (3.105)$$

From the identities in Appendix C, the cross sections for the binary mixture shear viscosity H (Greek eta) are identified and the system of equations becomes,

$$\mathbf{b}_f^{(0)} H_{ff} + \mathbf{b}_b^{(0)} H_{fb} = X_f^2 / kT \quad (3.106)$$

$$\mathbf{b}_f^{(0)} H_{bf} + \mathbf{b}_b^{(0)} H_{bb} = X_b^2 / kT \quad (3.107)$$

These are solved for $\mathbf{b}_f^{(0)}$ and $\mathbf{b}_b^{(0)}$ to give,

$$kT \mathbf{b}_f^{(0)} = \frac{X_f^2 H_{bb} - X_b^2 H_{fb}}{H_{ff} H_{bb} - H_{fb} H_{bf}}, \quad kT \mathbf{b}_b^{(0)} = \frac{X_b^2 H_{ff} - X_f^2 H_{bf}}{H_{ff} H_{bb} - H_{fb} H_{bf}}. \quad (3.108)$$

These factors are substituted in Eq. (3.89) to obtain the viscosity of a mixture

$$\begin{aligned} \eta &= \frac{1}{10kT} \int d\mathbf{p}_f \frac{[\mathbf{p}_f]^{(2)}}{m_f} : \mathbf{b}_f^{(0)} \frac{[\mathbf{p}_f]^{(2)}}{m_f} \varphi_f + \frac{1}{10kT} \int d\mathbf{p}_b \frac{[\mathbf{p}_b]^{(2)}}{m_b} : \mathbf{b}_b^{(0)} \frac{[\mathbf{p}_b]^{(2)}}{m_b} \varphi_b \\ &= kT [\mathbf{b}_f^{(0)} + \mathbf{b}_b^{(0)}] = \frac{X_b^2 H_{ff} + X_f^2 H_{bb} - X_f X_b (H_{fb} - H_{bf})}{H_{ff} H_{bb} - H_{fb} H_{bf}}, \end{aligned} \quad (3.109)$$

which is identical to the standard result for the viscosity of a binary mixture. Assumptions similar to those of Stogryn and Hirschfelder can be made to get a first order density correction to the viscosity due to bound pairs.

3.5 Kawasaki and Oppenheim's Modifications Due to Attractive Forces

Attractive forces and the possibility of formation of bound pairs were dealt with by Kawasaki and Oppenheim in a separate article [53] which does not use the binary mixture calculation of the previous section. The treatment formally considers the possibility of reactive collisions which lead to the formation, decomposition or exchange in bound pairs. The potential contribution to the momentum flux allows for these possibilities. Kawasaki and Oppenheim did not attempt to compare their results with previous work on transport coefficients in the presence of bound pairs, in particular the work of Stogryn and Hirschfelder. Within our limited understanding of their work a number of problems exist which are discussed in this section.

The results of their calculations is that the viscosity is expressed as a density expansion

$$\eta = \eta^{(0)} + n\eta^{(1)}. \quad (3.110)$$

The density independent term is the same as in the absence of bound pairs,

$$\eta^{(0)} = \frac{1}{10m^2V_kT} \int d\mathbf{p}_1 [\mathbf{p}_1]^{(2)} : \mathfrak{L}_+^{-1}(\mathbf{p}_1) [\mathbf{p}_1]^{(2)} \varphi_1 \quad (3.111)$$

The first order in density correction is composed of terms analogous to the repulsive potential case,

$$\eta^{(1)} = \eta_{KK1}^{(1)} + \eta_{KKr}^{(1)} + \eta_{KV}^{(1)} + \eta_{VK}^{(1)} + \eta_{VV}^{(1)} \quad (3.112)$$

where

$$\eta_{KK1}^{(1)} \equiv \frac{-1}{10VkT} \int d\mathbf{p}_1 \frac{[\mathbf{p}_1]^{(2)}}{m} : \mathfrak{L}_+^{-1}(\mathbf{p}_1) t_{1+}(\mathbf{p}_1) \frac{[\mathbf{p}_1]^{(2)}}{m} \varphi_1, \quad (3.113)$$

$$\eta_{KKr}^{(1)} \equiv \frac{-1}{10VkT} \int d\mathbf{p}_1 \frac{[\mathbf{p}_1]^{(2)}}{m} : \mathfrak{L}_+^{-1}(\mathbf{p}_1) \hat{t}_+^r(\mathbf{p}_1) \mathfrak{L}_+^{-1}(\mathbf{p}_1) \frac{[\mathbf{p}_1]^{(2)}}{m} \varphi_1, \quad (3.114)$$

$$\eta_{KV}^{(1)} = \eta_{VK}^{(1)} \equiv \frac{1}{10VkT} \int d\mathbf{p}_1 d\mathbf{x}_2 \frac{[\mathbf{p}_1]^{(2)}}{m} : [\Gamma^{-1}(12)\epsilon G_2(12)]_+ [\mathbf{r}_{12}\mathbf{F}_{12}]^{(2)} e^{-\beta u} \Phi(\mathbf{p}^2), \quad (3.115)$$

$$\eta_{VV}^{(1)} \equiv \frac{1}{40VkT} \int d\mathbf{p}_1 d\mathbf{x}_2 [\mathbf{r}_{12}\mathbf{F}_{12}]^{(2)} : [\Gamma^{-1}(12)\epsilon G_2(12)]_+ [\mathbf{r}_{12}\mathbf{F}_{12}]^{(2)} e^{-\beta u(12)} \Phi(\mathbf{p}^2). \quad (3.116)$$

In these equations, $n^{-1}\mathfrak{L}_+^{-1}(\mathbf{p}_1)$ is the binary collision operator or the modified propagator for a free particle which can be considered a measure of the mean free time between collisions for particle 1. The $n^{-1}\Gamma^{-1}(12)$ similarly represents the modified propagator for a pair of interacting particles and can be considered a measure of the mean free time between collisions of the pair 12 with other particles. Explicit expressions for each of the inverse operators are given in Ref. [53].

Eq. (3.114) represents the effects of collisions involving three particles. These particles may all be free, in which case the expression represents a triple collision (this is illustrated in Fig. 6(b) of Ref. [53]), or if two of the particles are bound, it represents a free - bound collision. The contributions from bound - bound collisions are not explicitly discussed. When analyzed, these terms may lead to corrections of the type given in Section 3.4. At lowest gas densities, bound pairs should produce a density correction reflecting the cross section of free - bound collisions which arise solely from kinetic effects. It is this form that is expected to arise from (3.114) when considering the system to be a binary mixture of free and bound species.

Corrections related to potential contributions to the momentum flux for repulsive potentials have been discussed in detail in Section 3.2. For an attractive potential, other than non-locality and collisional transfer corrections, contributions to the viscosity from the formation and decomposition of bound pairs and particle exchange are considered in Eqs. (3.115) and (3.116). Within our understanding of their work, some problems appear to exist with regard to these expressions. In the derivation of the viscosity for repulsive forces, the potential contributions to the momentum flux $[\mathbf{r}_{j\ell}\mathbf{F}_{j\ell}]^{(2)}$ involve forces among separate particles j and ℓ . If the particles j and ℓ are bound together by the force $\mathbf{F}_{j\ell}$, a term of the structure $[\mathbf{r}_{j\ell}\mathbf{F}_{j\ell}]^{(2)}$ no longer contributes to the momentum flux. Therefore, forces in the potential contributions to the momentum flux must only be between separate particles and not internal to a bound pair. In deriving Eqs. (3.115) and (3.116), it was assumed that the pair 12 may constitute a bound pair. In this case it would be incorrect to have the flux function $[\mathbf{r}_{12}\mathbf{F}_{12}]^{(2)}$ as the potential contribution to the momentum flux since it is assumed that the momentum of the bound pair is carried by the motion of its center of mass and the relative motion does not contribute to the flux of momentum in the system.

The rigorous evaluation of the kinetic - virial cross terms in the presence of bound pairs requires a detailed knowledge of the three-particle collisions. The cross sections of various outcomes like bound pair formation and decomposition would be needed in order to evaluate the $\eta_{KV}^{(1)}$ term.

Chapter 4

Complete Binary Collision Approximation for Dilute Gas Transport Coefficients via the Time Correlation Formulation

As stated in Chapter 2, the original motivation for examining the time correlation function formulation of the transport coefficients was to understand the density corrections to the dilute gas transport coefficients, in particular to establish any relation to the viable computational method of Rainwater and Friend [8]. The latter theory is a composite of a number of developments, whereas a derivation from a unified formalism would be desirable. This would also require understanding the role that bound pairs play in gas transport. As a closed equation for the transport coefficient, Eq. (2.29) should be capable of evaluation without recourse to the Boltzmann equation, and in doing so, provide an independent approach to justify or contradict the density corrections obtained by the Boltzmann equation and its generalizations. It appears that most published comparisons between the time correlation function formulation and the results of the Boltzmann equation [34, 45, 47, 50, 64] evaluate the time correlation function using the Boltzmann equation or some generalized kinetic equation. In contrast, Zwanzig [52] uses a binary collision expansion to deduce that the evaluation of Eq. (2.29) requires the solution of a series of integral equations, the lowest order of which is recognized as the linearized Boltzmann equation. But in order to carry out this procedure, Zwanzig had to resum an infinite series in powers of $1/\epsilon$ whose individual terms formally diverge as $\epsilon \rightarrow 0$. As seen in Chapter 3 Kawasaki and Oppenheim [51] extended Zwanzig's method to obtain density corrections to the viscosity coefficient and make contact with the theory of Choh and Uhlenbeck [12]. The method presented here avoids the $1/\epsilon$ expansion by using another technique, also introduced by Zwanzig [65], namely the use of

projection operators.

While examining the density corrections to the dilute gas transport coefficients, it was noticed that the standard treatments that make connection between these disparate formulations (time correlation versus Boltzmann equation) appear to focus on only the first moment approximation to the Boltzmann equation and do not consider the derivation of corrections associated with higher moments (Sonine polynomials) for the accurate calculation of dilute gas transport coefficients. It is the purpose of this chapter to show how these higher moments arise solely from the time correlation formulation. Thus the applications presented in this chapter are limited to gases at low density to deduce expressions for the transport coefficients in terms of kinetic cross sections, while retaining all binary collision effects. The same method of approach is adapted to the inclusion of the necessary multiple moments required for the calculation of the transport coefficients of mixtures. The presentation for mixtures is limited to keeping only one expansion term per species, but it is clear this could be extended to all binary contributions. Many of the techniques shown here are used when expressions for the density corrections to the transport coefficients are derived in later chapters.

In Sec. 4.1 the properties related to the rotational invariance of the resolvent operator and flux functions are discussed. It is shown how these lead to simplifications in the evaluation of the ensemble averages which appear in the time correlation function expressions for the transport coefficients. Section 4.2 gives a brief introduction to projection operators used in this work and demonstrates their idempotency using the results of Sec. 4.1. In Section 4.3 properties of the projection operators are used to carry out a direct resolvent expansion of the time correlation function for a transport coefficient. A result similar to that of Zwanzig [65] is derived. For dilute gases it is clear that a binary collision expansion [60, 61] is needed at some point in this relation. In Section 4.4, the flux function \mathbf{J} of Eq. (2.29) is assumed to be a sum of 1-particle functions, and with the use of a binary collision expansion, an analytic solution is obtained for the low density part of the transport coefficient. In Section 4.5, this solution is interpreted as including the complete set of Sonine polynomials. Section 4.6 reinterprets the formalism of Section 4.4 to derive an expression for the transport coefficient of a system which is a mixture of two species. In that case, for simplicity, only a single moment for each species is considered. The chapter ends with a discussion. Most of the material in this chapter has appeared in a previous publication [66].

4.1 Rotational Invariance of the Resolvent Matrix Elements

From Eq. (2.29) it is recalled that matrix elements of the resolvent with respect to the flux vectors must be determined in order to evaluate the transport coefficients,

$$\sigma = \lim_{z \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \odot \frac{1}{z - \mathcal{L}} \mathbf{J} \rangle\rangle. \quad (4.1)$$

In the absence of external fields, the resolvent operator is rotationally invariant and its form does not change when the coordinate system is rotated. This rotational invariance leads to the simplification of subsequent calculations. To make use of these simplifications, a number of concepts and some notation are introduced in this section.

The continuous group of all rotations in three-dimensional space, $SO(3)$, has an infinite number of irreducible representations, corresponding to the infinite number of elements and classes which it possesses. These irreducible representations have *weights* $0, 1, 2, 3, \dots, \alpha, \dots$ corresponding to their tensorial rank, and *dimension* $1, 3, 5, \dots, 2\alpha + 1, \dots$, corresponding to the number of independent elements in each representation. Thus for example, the infinite set of vectors ($\alpha = 1$) which have $2\alpha + 1 = 3$ independent components, form an irreducible representation of the three-dimensional rotation group. The dimension of the irreducible representation should be distinguished from the three spatial dimensions x, y and z which are common to all irreducible representations. If the operation of rotation in the three-dimensional space is represented by a matrix \hat{D} , the rotational invariance of the resolvent operator implies,

$$\hat{D} \frac{1}{z - \mathcal{L}} \hat{D}^{-1} = \frac{1}{z - \mathcal{L}}. \quad (4.2)$$

The rotational invariance of the resolvent allows the use of a generalized version of the Wigner - Eckart theorem [67, 68]: When acting on \mathbf{J} , a symmetric traceless tensor of rank ℓ , the rotationally invariant operator $1/(z - \mathcal{L})$ produces a tensor \mathbf{T} ,

$$\frac{1}{z - \mathcal{L}} \mathbf{J} = \mathbf{T} \quad (4.3)$$

of the same rank as \mathbf{J} , which belongs to the same irreducible representation. That is, if a component of \mathbf{J} transforms under a rotation R according to

$$\mathbf{J}_\rho = \sum_\sigma \mathfrak{D}(R)_{\rho\sigma}^{(\alpha)} \mathbf{J}_\sigma, \quad (4.4)$$

where the $\mathfrak{D}(R)_{\rho\sigma}^{(\alpha)}$ are matrices for the irreducible representation of weight α of the rotation R , then the components of \mathbf{T} also satisfy

$$\mathbf{T}_\rho = \sum_\sigma \mathfrak{D}(R)_{\rho\sigma}^{(\alpha)} \mathbf{T}_\sigma. \quad (4.5)$$

It follows that if \mathbf{J} is a three-dimensional Cartesian vector, then so is \mathbf{T} and if \mathbf{J} is a symmetric traceless second rank tensor, then so is \mathbf{T} .

The canonical distribution function $\rho^{(N)}$ is rotationally invariant in the absence of external fields and as a result, the inner product $\langle\langle \mathbf{J}(z - \mathcal{L})^{-1} \mathbf{J} \rangle\rangle = \langle\langle \mathbf{J} | \mathbf{T} \rangle\rangle$ is an isotropic tensor of rank 2α . This isotropic, rotationally invariant tensor must be proportional to $\mathbf{E}^{(\alpha)}$, the rotationally invariant tensor of rank 2α which acts as the Cartesian identity in the $2\alpha + 1$ irreducible representation of the three-dimensional rotation group of \mathbf{J} ,

$$\langle\langle \mathbf{J} | \mathbf{T} \rangle\rangle = a \mathbf{E}^{(\alpha)}, \quad (4.6)$$

with some scalar a , which is determined by magnitude and directional properties of \mathbf{J} and \mathbf{T} . The rotationally invariant 2α rank tensor $\mathbf{E}^{(\alpha)}$ acts like an identity for the irreducible representation. As such, it is useful to impose upon it the condition of idempotency,

$$\mathbf{E}^{(\alpha)} \odot \mathbf{E}^{(\alpha)} = \mathbf{E}^{(\alpha)}. \quad (4.7)$$

The idempotency property is required when constructing projection operators in the next section. It is now appropriate to consider in greater detail the two cases that are encountered in this thesis.

The flux functions studied in this thesis are the heat flux vector which belongs to the irreducible representation of dimension 3 of the $SO(3)$ group and the symmetric traceless second rank transverse momentum flux tensor which belongs to the irreducible representation of dimension 5. The detailed form of the corresponding identity tensors $\mathbf{E}^{(1)}$ and $\mathbf{E}^{(2)}$ are studied below.

For a vectorial flux function, $\alpha = 1$ and the second rank rotationally invariant tensor $\mathbf{E}^{(1)}$ must be a multiple of \mathbf{U} , the unit rotationally invariant second rank tensor [69],

$$\mathbf{U} \equiv \sum_{ij} \hat{\mathbf{i}} \hat{\mathbf{j}} \delta_{ij} = \hat{\mathbf{x}} \hat{\mathbf{x}} + \hat{\mathbf{y}} \hat{\mathbf{y}} + \hat{\mathbf{z}} \hat{\mathbf{z}}. \quad (4.8)$$

For a three-dimensional space, the i and j indices, and unit vectors $\hat{\mathbf{i}}$ and $\hat{\mathbf{j}}$ are summed over the x , y , and z directions. A schematic geometric representation of the summation is suggested by the shape of the symbol \mathbf{U} [70]. The two “branches” of the symbol \mathbf{U} represent the number of indices or in other words, the rank of the tensor. The connectedness of the branches at the bottom shows that the indices must be identical, and in this manner indicates the presence of the Kronecker delta function. A summation over three spatial dimensions is implied.

For vector flux functions \mathbf{J} , the inner product $\langle\langle \mathbf{J} | \mathbf{T} \rangle\rangle$ is a scalar multiple of the second rank rotationally invariant identity tensor,

$$\langle\langle \mathbf{J} | \mathbf{T} \rangle\rangle = a \mathbf{U}. \quad (4.9)$$

To obtain the scalar multiple a , both sides are double contracted onto \mathbf{U} ,

$$a\mathbf{U}:\mathbf{U} = \mathbf{U}:\langle\langle\mathbf{J}|\mathbf{T}\rangle\rangle \quad (4.10)$$

which gives,

$$a = \frac{\langle\langle\mathbf{J}:\mathbf{T}\rangle\rangle}{3}. \quad (4.11)$$

This follows from $\mathbf{U}:\mathbf{U} = 3$ and $\mathbf{U}:\mathbf{AB} = \mathbf{A}\cdot\mathbf{B}$. Using the schematic representation described above, the branch of the \mathbf{U} closest to the contraction is dotted into the vector closest to it (\mathbf{A}), and the farthest branch of \mathbf{U} is contracted onto the next vector (\mathbf{B}). Since the indices on the two branches are identical, the result is the dot product of the two original vectors.

For a symmetric traceless second rank tensorial flux function \mathbf{J} like the transverse momentum flux in shear viscosity, the identity $\mathbf{E}^{(2)}$ is a fourth rank isotropic Cartesian identity tensor. This tensor must be a linear combination of the three rotationally invariant fourth rank tensors [69]. These isotropic tensors are given in terms of delta functions,

$$\mathbb{UU} \equiv \sum_{ijkl} \hat{\mathbf{i}}\hat{\mathbf{j}}\hat{\mathbf{k}}\hat{\mathbf{l}} \delta_{ij}\delta_{kl} = (\hat{\mathbf{x}}\hat{\mathbf{x}} + \hat{\mathbf{y}}\hat{\mathbf{y}} + \hat{\mathbf{z}}\hat{\mathbf{z}})(\hat{\mathbf{x}}\hat{\mathbf{x}} + \hat{\mathbf{y}}\hat{\mathbf{y}} + \hat{\mathbf{z}}\hat{\mathbf{z}}), \quad (4.12)$$

$$\mathbb{W} \equiv \sum_{ijkl} \hat{\mathbf{i}}\hat{\mathbf{j}}\hat{\mathbf{k}}\hat{\mathbf{l}} \delta_{ik}\delta_{jl}, \quad (4.13)$$

$$\mathbb{U} \equiv \sum_{ijkl} \hat{\mathbf{i}}\hat{\mathbf{j}}\hat{\mathbf{k}}\hat{\mathbf{l}} \delta_{il}\delta_{jk} = \hat{\mathbf{x}}\mathbb{U}\hat{\mathbf{x}} + \hat{\mathbf{y}}\mathbb{U}\hat{\mathbf{y}} + \hat{\mathbf{z}}\mathbb{U}\hat{\mathbf{z}}. \quad (4.14)$$

The schematic representation introduced previously is also useful in this case. The four branches indicate that the tensors have four indices and are thus of fourth rank, and the connectivity at the bottom of the branches indicates the specific combination of indices which are identical. In three-dimensional space, the indices are summed over the three spatial directions x , y , and z .

$\mathbf{E}^{(2)}$ must be a linear combination of these three tensors and can be expressed as

$$\mathbf{E}^{(2)} = a\mathbb{UU} + b(\mathbb{W} + \mathbb{U}). \quad (4.15)$$

In Appendix D the coefficients chosen to make $\mathbf{E}^{(2)}$ idempotent are determined to be

$$\mathbf{E}^{(2)} = \frac{1}{2}(\mathbb{W} + \mathbb{U}) - \frac{1}{3}\mathbb{UU}. \quad (4.16)$$

For the momentum flux tensor \mathbf{J} , $\langle\langle\mathbf{J}|\mathbf{T}\rangle\rangle$ is a multiple of $\mathbf{E}^{(2)}$,

$$\langle\langle\mathbf{J}|\mathbf{T}\rangle\rangle = a\mathbf{E}^{(2)}. \quad (4.17)$$

Contraction of both sides of Eq. (4.17) into $\mathbf{E}^{(2)}$ allows the identification of the scalar multiple a ,

$$a\mathbf{E}^{(2)} \overset{4}{\odot} \mathbf{E}^{(2)} = \mathbf{E}^{(2)} \overset{4}{\odot} \langle\langle\mathbf{J}|\mathbf{T}\rangle\rangle \implies a = \frac{\langle\langle\mathbf{J}:\mathbf{T}\rangle\rangle}{5}. \quad (4.18)$$

4.2 Projection Operators

In the context of irreversible statistical mechanics, projection operators were first introduced by Nakajima [71] and Zwanzig [72]. Starting with the Liouville equation Zwanzig derived a generalized master equation using projection operators [65, 73]. More recent applications of projection operators have been reviewed by Hynes and Deutsch [74] and Grabert [75].

The nature of the calculation involved in determining the matrix element of the resolvent operator suggests the use of a projection operator. A complete set of orthonormal N -particle basis functions $\{\Psi_j(\mathbf{r}^N, \mathbf{p}^N)\}$ can be constructed of which \mathbf{J} is a member,

$$\mathbf{J} = \Psi_0(\mathbf{r}^N, \mathbf{p}^N) \quad (4.19)$$

The Ψ_j basis functions have tensorial properties identical to \mathbf{J} . In general, they are not sums of individual particle functions and involve correlations among particles in a complicated manner. The resolvent produces a linear combination of these basis vectors in N -particle space,

$$\frac{i}{z - \mathcal{L}} \mathbf{J} = \frac{i}{z - \mathcal{L}} \Psi_0 = \sum_j a_j \Psi_j, \quad (4.20)$$

but this linear combination is projected back onto Ψ_0 when calculating the matrix element,

$$\langle\langle \mathbf{J} \oslash \frac{i}{z - \mathcal{L}} \mathbf{J} \rangle\rangle = \langle\langle \Psi_0 \oslash \sum_j a_j \Psi_j \rangle\rangle = a_0(n, T). \quad (4.21)$$

It is seen that a direct calculation of the result of the operation of resolvent on the flux function \mathbf{J} is computationally quite wasteful, since only that part of the complete evolution which remains in the \mathbf{J} subspace has a nonvanishing contribution in the final result. By projecting the resolvent onto the subspace of the flux function \mathbf{J} , the extra calculations can be avoided. This projection and its consequences are introduced in the next section.

Any projection operator must possess the condition of idempotency, i.e.,

$$\mathcal{P}^2 = \mathcal{P}. \quad (4.22)$$

For a flux function \mathbf{J} of tensorial rank α , the projection operator is

$$\mathcal{P} = A|\mathbf{J}\rangle\rangle \oslash \langle\langle \mathbf{J}|. \quad (4.23)$$

The condition of idempotency requires that,

$$\mathcal{P}^2 = A^2|\mathbf{J}\rangle\rangle \oslash \langle\langle \mathbf{J}|\mathbf{J}\rangle\rangle \oslash \langle\langle \mathbf{J}| = \mathcal{P} = A|\mathbf{J}\rangle\rangle \oslash \langle\langle \mathbf{J}|. \quad (4.24)$$

Determining the constant A requires the evaluation of $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle$. If there are no external fields in the system, $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle$ is a rotational invariant, and in particular, a scalar multiple of $\mathbf{E}^{(\alpha)}$, the rotationally invariant tensor of rank 2α which acts as the Cartesian identity tensor in the $2\alpha+1$ -dimensional representation of the rotational group in three spatial dimensions. Proper normalization factors can always be chosen for the flux function \mathbf{J} such that $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle = N\mathbf{E}^{(\alpha)}$.

For a vectorial flux function (tensor of first rank), if $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle$ is to be rotationally invariant, it must be a scalar multiple of the only possible second rank rotationally invariant tensor \mathbf{U} [69],

$$\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle = N\mathbf{U}. \quad (4.25)$$

Thus in Eq. (4.24),

$$A^2 |\mathbf{J}\rangle\rangle \cdot \langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle \cdot \langle\langle \mathbf{J} | = A^2 N |\mathbf{J}\rangle\rangle \cdot \mathbf{U} \cdot \langle\langle \mathbf{J} | = A |\mathbf{J}\rangle\rangle \cdot \langle\langle \mathbf{J} |, \quad (4.26)$$

and so $A = 1/N$.

For a tensorial flux function \mathbf{J} which is a symmetric traceless tensor of second rank, verification of the idempotency property of Eq. (4.24), requires recognizing that $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle = N\mathbf{E}^{(2)}$. The calculations are otherwise analogous to that given for a vector flux function.

4.3 Projection Operator - Resolvent Relations

The thermal average bracket $\langle\langle \mid \rangle\rangle$ involves the “bra” and “ket” defined either in quantum or classical mechanics as

$$\begin{aligned} \langle\langle \mathbf{X} | &\equiv \int d\mathbf{x}^N \mathbf{X} \equiv \text{Tr}_{1\dots N} \mathbf{X} & | \mathbf{Y} \rangle\rangle &\equiv \mathbf{Y} f^{(N)} \equiv \frac{1}{2} [\mathbf{Y}, \rho^{(N)}]_+ \\ \langle\langle \mathbf{X} | \mathbf{Y} \rangle\rangle &\equiv \int d\mathbf{x}^N \mathbf{X} \mathbf{Y} f^{(N)} \equiv \frac{1}{2} \text{Tr}_{1\dots N} \mathbf{X} [\mathbf{Y}, \rho^{(N)}]_+, \end{aligned} \quad (4.27)$$

where, if only translational degrees of freedom are involved, a phase space element is $d\mathbf{x}^N = d\mathbf{p}^N d\mathbf{r}^N$, while in quantum mechanics, the noncommutation of an observable \mathbf{Y} and the equilibrium density operator $\rho^{(N)}$ requires, for example, the introduction of the anticommutator to preserve hermiticity. Obvious generalizations are required if there are internal states and/or the molecular system is a mixture. It is the classical terminology and language that are used here, but the classical formalism can be immediately transcribed into a quantum formalism. The bracket acts as a scalar product of two phase space functions so that a vector space language can, and is, used in the rest of the chapter. The “bra” and “ket” tensors are seen to be asymmetric with respect to the N -particle distribution function $f^{(N)}$. Different positionings of the distribution function are possible, but the above inclusion of $f^{(N)}$ in the

“ket” is the most convenient. Due to the asymmetric distribution of the distribution function, even though the bracket combination is finite, the individual “bra” and “ket” tensors are not components of a Hilbert space.

While $\mathbf{J}(t)$ changes as it evolves with time, only its component along the phase space \mathbf{J} direction is of importance for the calculation of σ . This is equivalent to determining the matrix element of the resolvent that is diagonal in \mathbf{J} . The generalization of Zwanzig’s [65] projection operator is the projection operator \mathcal{P} onto the $2\alpha+1$ dimensional subspace spanned by the components of \mathbf{J}

$$\mathcal{P} = A |\mathbf{J}\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} |. \quad (4.28)$$

The normalization constant A is introduced to make the projection operator idempotent

$$\mathcal{P}^2 = A^2 |\mathbf{J}\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} | \mathbf{J}\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} | = A |\mathbf{J}\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} | = \mathcal{P}. \quad (4.29)$$

On the assumption that the equilibrium density operator (distribution function) is rotationally invariant, and that the flux operator \mathbf{J} has no preference for any particular direction in space, it follows that $\langle\langle \mathbf{J} | \mathbf{J}\rangle\rangle$ is a 2α rank tensor which must be a rotational invariant. $\langle\langle \mathbf{J} | \mathbf{J}\rangle\rangle$ is thus a scalar multiple of $\mathbf{E}^{(\alpha)}$, the rotationally invariant tensor of rank 2α that acts as the Cartesian tensor identity for the $2\alpha + 1$ dimensional irreducible representation of the three dimensional rotation group [36, 76]. Thus

$$\langle\langle \mathbf{J} | \mathbf{J}\rangle\rangle = a \mathbf{E}^{(\alpha)} \quad (4.30)$$

with a proportionality constant a determined by taking the contraction of both sides of Eq. (4.30) with $\mathbf{E}^{(\alpha)}$ to show that

$$a = \frac{\langle\langle \mathbf{J} \overset{\alpha}{\odot} | \mathbf{J}\rangle\rangle}{2\alpha + 1} \quad (4.31)$$

and by substituting Eq. (4.30) into Eq. (4.29),

$$A = \frac{2\alpha + 1}{\langle\langle \mathbf{J} \overset{\alpha}{\odot} | \mathbf{J}\rangle\rangle}. \quad (4.32)$$

The general expression for a transport coefficient is given in Eq. (2.29). The right flux function begins in the \mathbf{J} subspace. The resolvent changes both the magnitude and direction of this “vector” in the function space, but the dot product projects the resultant vector back onto the \mathbf{J} subspace. Since \mathcal{P} projects onto the subspace of functions determined by the components of \mathbf{J} , it follows that the transport coefficient can be written

$$\sigma = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \overset{\alpha}{\odot} | \mathcal{P} \frac{1}{i\epsilon - \mathcal{L}} \mathcal{P} \mathbf{J}\rangle\rangle, \quad (4.33)$$

involving the projection of the resolvent operator. This can be expanded in terms of the resolvent of the projected Liouville operator according to (for convenience and possible generalization, this is expressed in terms of $z = i\epsilon$)

$$\begin{aligned}
\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} &= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} [z - \mathcal{L} + (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P}) + \mathcal{P}\mathcal{L}(1 - \mathcal{P}) + (1 - \mathcal{P})\mathcal{L}\mathcal{P}] \frac{1}{z - \mathcal{L}} \mathcal{P} \\
&= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P} + \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \frac{1}{z - \mathcal{L}} \mathcal{P} \\
&= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P} \\
&\quad + \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P}.
\end{aligned} \tag{4.34}$$

The first term describes the evolution within the \mathbf{J} subspace while the second term describes the influence of the rest of the function space on the subspace determined by \mathbf{J} (the subspace complimentary to \mathbf{J}). Solving for the projected resolvent gives

$$\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} = \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P} - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} (1 - \mathcal{P})\mathcal{L}\mathcal{P}} \tag{4.35}$$

Since the \mathbf{J} 's for the transport coefficients belong to irreducible representations of the rotation group with time independent normalization a , the projected Liouville operator $\mathcal{P}\mathcal{L}\mathcal{P} = 0$. The proof [65] states that from the Liouville equation, $\langle\langle \mathbf{J} | \mathcal{L} | \mathbf{J} \rangle\rangle$ can be written as $\langle\langle \mathbf{J} | \dot{\mathbf{J}} \rangle\rangle$, which is proportional to $d\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle / dt$. Since the equilibrium ensemble is constant with time, so is $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle$, its time derivative vanishes, $\mathcal{P}\mathcal{L}\mathcal{P} = 0$ and Eq. (4.35) is simplified to

$$\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} = \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}}. \tag{4.36}$$

With this expression for the projected resolvent, the transport coefficient expression, Eq. (4.33), becomes

$$\begin{aligned}
\sigma &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}} | \mathbf{J} \rangle\rangle \\
&= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \overset{\alpha}{\odot} | \mathbf{X} \rangle\rangle
\end{aligned} \tag{4.37}$$

where $|\mathbf{X}\rangle\rangle$ is defined by

$$|\mathbf{X}\rangle\rangle = \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}} |\mathbf{J}\rangle\rangle. \tag{4.38}$$

Inverting this defining relation and using the $\epsilon \rightarrow 0$ limit, it is seen that

$$|\mathbf{J}\rangle\rangle = -\mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P} |\mathbf{X}\rangle\rangle. \tag{4.39}$$

The phase space inner product of this equation with $\langle\langle \mathbf{J} |$ implies that

$$\mathbf{E}^{(\alpha)} = -A \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle \overset{\alpha}{\odot} A \langle\langle \mathbf{J} | \mathbf{X} \rangle\rangle, \quad (4.40)$$

where Eq. (4.30) has been used. Since both brackets on the right in this expression are 2α rank rotationally invariant tensors, they are each a scalar multiple of $\mathbf{E}^{(\alpha)}$. Manipulations similar to those stated in Eqs. (4.30) and (4.31) give

$$1 = \frac{-A}{2\alpha + 1} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \mathcal{L} \frac{1}{z - (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle \frac{AV\sigma}{iB}, \quad (4.41)$$

which results in an expression for the transport coefficient in the form

$$\frac{1}{\sigma} = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{A^2 V}{(2\alpha + 1)B} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \mathcal{L} \frac{i}{z - (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle. \quad (4.42)$$

It can be noted that the above manipulations have led to an operator combination that has the structure of an N -particle transition operator. The Liouville operator in this expression is projected onto the subspace complimentary to \mathbf{J} . The $\epsilon \rightarrow 0$ limit of a transition operator has well understood convergence properties. Physically, the study of general time evolution in the system, Eq. (4.33) has been reduced to the study of collision events.

Zwanzig [65] simplified this to the equivalent form

$$\frac{1}{\sigma} = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{A^2 V}{(2\alpha + 1)B} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \mathcal{L} \frac{i}{z - (1 - \mathcal{P}) \mathcal{L}} \mathcal{L} | \mathbf{J} \rangle\rangle. \quad (4.43)$$

His derivation involved the generalized Master equation with the consequent identification of the transport coefficient as the inverse of the Laplace transform of the memory kernel of that equation.

4.4 One Particle Properties at Low Density

For a low density gas, the measured physical properties are all associated with individual molecular attributes. In particular, transport is due solely to the kinetic motion of the individual molecules, as distinct from transport associated with the intermolecular potential, which becomes significant at higher densities, see Chapters 6 and 7. Collisions disrupt these free kinetic motions, giving rise to the transfer of flux from one molecule to another. This interrupts the transport and gives rise to the resistance to flow of the fluid (viscosity), finite transfer of energy (thermal conductivity), etc. In such cases: 1) the phase function \mathbf{J} is a sum of one particle properties; 2) the equilibrium averaging involves a distribution function

$f^{(N)}$ which is a product of one particle Boltzmann factors; 3) the intermolecular potential for the system is pairwise additive so that the Liouville operator has kinetic and potential contributions

$$\mathcal{L} = \sum_j \mathcal{K}_j + \sum_{j < \ell} \mathcal{V}_{j\ell} = -i \sum_j \frac{\mathbf{p}_j}{m} \cdot \frac{\partial}{\partial \mathbf{r}_j} + i \sum_{k < \ell} \frac{\partial u_{k\ell}}{\partial \mathbf{r}_{k\ell}} \cdot \frac{\partial}{\partial \mathbf{p}_{k\ell}}; \quad (4.44)$$

and 4) termolecular collisions are to be ignored. It is the combination of these four restrictions that are used to derive otherwise exact expressions for the transport coefficients involving only binary collisions.

In later sections the general formalism developed here is specialized, first to identify how all higher Sonine polynomial terms of the Chapman-Cowling solution of the Boltzmann equation arise from the time correlation formalism. This shows how the binary collision expressions derived here are the same as those obtained by exactly solving the Boltzmann equation. Second, the formalism is adapted to show how the Boltzmann equation expressions for mixtures arise from the time correlation function formalism. It does not appear that either of these detailed connections have been made previously for the general case.

On the basis that any physical observable is associated with individual molecular attributes, it follows that the flux \mathbf{J} is an additive property of the individual molecules in the system,

$$\mathbf{J} \equiv \sum_{j=1}^N \mathbf{J}_{Kj}, \quad (4.45)$$

whose contribution, \mathbf{J}_{Kj} , from molecule j is a function only of that molecule's momentum, \mathbf{p}_j . For convenience of notation it is assumed that \mathbf{J}_{Kj} is normalized so that

$$\langle\langle \mathbf{J}_{K1} | \mathbf{J}_{K1} \rangle\rangle = \mathbf{E}^{(\alpha)}, \quad \text{equivalently} \quad \langle\langle \mathbf{J}_{K1} \overset{\alpha}{\odot} | \mathbf{J}_{K1} \rangle\rangle = 2\alpha + 1. \quad (4.46)$$

Provided the distribution function for the gas

$$f^{(N)} = \prod_{j=1}^N \frac{\varphi_j}{V}, \quad (4.47)$$

is a product of one particle distribution functions which are normalized

$$\int d\mathbf{x}_j \frac{\varphi_j}{V} = 1, \quad (4.48)$$

then the inner product of Eq. (4.31) is $N(2\alpha + 1)$ and the normalization factor for the projector of Eq. (4.28) becomes $A = 1/N$.

Equation (4.42) for the transport coefficient can then be written

$$\frac{1}{\sigma} = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{V}{BN(2\alpha + 1)} \langle\langle \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle$$

$$\begin{aligned}
&= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{(N-1)V}{BN(2\alpha+1)} \langle\langle \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathcal{V}_{12} \frac{i}{z - (1-\mathcal{P})\mathcal{L}(1-\mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle \\
&\equiv \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{(N-1)V}{BN(2\alpha+1)} \int d\mathbf{x}_1 \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathbf{B}_1^{(N)}, \tag{4.49}
\end{aligned}$$

on the basis, first that \mathbf{J} is a sum with all particles contributing equally, and second, that only the potential part of \mathcal{L} has any effect on \mathbf{J}_{K1} , with particle 2 being a typical particle interacting with particle 1. In the following a closed expression for the vector valued function

$$\mathbf{B}_1^{(N)} \equiv \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} f^{(N)}, \tag{4.50}$$

is calculated. The shorthand notation $\mathcal{L}_{\mathcal{P}} \equiv (1-\mathcal{P})\mathcal{L}(1-\mathcal{P})$ has been introduced for convenience.

Since, in Eq. (4.50) for $\mathbf{B}_1^{(N)}$, the pair 12 is interacting, it is appropriate to identify this interaction with a binary collision between this particular pair of particles. This can be accomplished by introducing the resolvent for the pair evolution operator $\mathcal{L}_{12} \equiv \sum_i \mathcal{K}_i + \mathcal{V}_{12}$. This is the Liouville operator of an N -particle system where only the 12 pair are interacting. After reorganization, $\mathbf{B}_1^{(N)}$ can be written in the form

$$\begin{aligned}
\mathbf{B}_1^{(N)} &= \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} [z - \mathcal{L}_{\mathcal{P}} + (1-\mathcal{P})\mathcal{L}(1-\mathcal{P}) - \mathcal{L}_{12}] \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} f^{(N)} \\
&= \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L} \mathbf{J} f^{(N)} \\
&\quad + \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[\sum_{k < \ell} \mathcal{V}_{k\ell} - \mathcal{P} \mathcal{L} \right] \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} f^{(N)}. \tag{4.51}
\end{aligned}$$

This is a generalization of Watson's [60] binary collision expansion. Since the two left-most operators in the integrals of this equation, $\mathcal{V}_{12}(z - \mathcal{L}_{12})^{-1}$, involve only particles 1 and 2, and these in a symmetrical manner, the integration over all the other particles $3 \cdots N$ can be carried out before getting to these operators. Moreover, the equations can be simplified by emphasizing only the behaviour of one particle, chosen as that labeled by 1, with particle 2 taken into account by the introduction of the permutation operator P_{12} . Further simplification is obtained by introducing the 2-particle transition operator

$$\mathcal{T}_{12} \equiv \mathcal{V}_{12} + \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} = \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (z - \mathcal{K}_{12}) \tag{4.52}$$

and the reduced pair distribution function, $f_{12}^{(2)} = \int d\mathbf{x}^{(N-2)} f^{(N)} = \varphi_1 \varphi_2 / V^2$. In terms of these quantities, the first term in $\mathbf{B}_1^{(N)}$ is

$$\begin{aligned}
\int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L} \mathbf{J} f^{(N)} &= \int d\mathbf{x}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} (1 + P_{12}) \mathbf{J}_{K1} f_{12}^{(2)} \\
&= \int d\mathbf{x}_2 i \mathcal{T}_{12} (1 + P_{12}) \mathbf{J}_{K1} \frac{\varphi_1 \varphi_2}{V^2} = \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_{K1}, \tag{4.53}
\end{aligned}$$

where the binary (linearized Boltzmann) collision operator, \mathcal{R}_1 is defined as

$$\mathcal{R}_1 \equiv \frac{n}{\varphi_1} \int d\mathbf{x}_2 i\mathcal{T}_{12}(1 + P_{12})\varphi_1\varphi_2. \quad (4.54)$$

Technically, terms involving a third particle, such as $\int d\mathbf{x}_3 \mathcal{V}_{13}(\mathbf{J}_{K1} + \mathbf{J}_{K3})\varphi_1\varphi_2\varphi_3$ arise in simplifying the integral on the left hand side of Eq. (4.53). It is argued that the potential between particles 1 and 3 that is incorporated in the Liouville operator \mathcal{L} (more specifically \mathcal{V}_{13}) depends only on the relative position \mathbf{r}_{13} and the integral over the position of particle 3 can be converted to that relative position whose integration then gives 0. Similarly, the definition of \mathcal{T}_{12} involves a separate \mathcal{V}_{12} factor that does not appear on the right hand side first in the line of Eq. (4.53) but whose integration over the position of particle 2 gives a null value,

$$\int d\mathbf{x}_2 \mathcal{V}_{12}(1 + P_{12})\mathbf{J}_{K1}f_{12}^{(2)} = 0. \quad (4.55)$$

This same procedure is not valid for the term that has been kept because of other \mathbf{r}_{12} dependent terms.

The remaining terms in $\mathbf{B}_1^{(N)}$ are handled in a similar manner,

$$\begin{aligned} & \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[\sum_{k < \ell} \mathcal{V}_{k\ell} - \mathcal{P}\mathcal{L} \right] \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L}\mathbf{J}f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{T}_{12} \frac{i}{z - \mathcal{K}_{12}} (1 + P_{12}) \left[(N-2) \int d\mathbf{x}^{(N-2)} \mathcal{V}_{13} \right. \\ & \quad \left. - \mathbf{J}_{K1} \frac{f_{12}^{(2)}}{N} \overset{\alpha}{\odot} \int d\mathbf{x}^N \mathbf{J}\mathcal{L} \right] \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L}\mathbf{J}f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{T}_{12} \frac{i}{z - \mathcal{K}_{12}} (1 + P_{12}) \left[(N-2) \int d\mathbf{x}^{(N-2)} \right. \\ & \quad \left. - \mathbf{J}_{K1} f_{12}^{(2)} (N-1) \overset{\alpha}{\odot} \int d\mathbf{x}^N \mathbf{J}_{K1} \right] \mathcal{V}_{13} \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L}\mathbf{J}f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{T}_{12} \frac{i}{z} (1 + P_{12}) \left[(N-2)\mathbf{B}_{12}^{(N)} - f_{12}^{(2)} \mathbf{J}_{K1} (N-1) \overset{\alpha}{\odot} \int d\mathbf{x}_1 \mathbf{J}_{K1} \mathbf{B}_1^{(N)} \right] (-i) \quad (4.56) \end{aligned}$$

with a reasonably obvious definition for $\mathbf{B}_{12}^{(N)}$, which is discussed further below. The last term of Eq. (4.56) can be simplified by the use of the projection operator

$$\mathcal{P}_0 \equiv \varphi_1 \mathbf{J}_{K1} \overset{\alpha}{\odot} \int d\mathbf{p}_1 \mathbf{J}_{K1}. \quad (4.57)$$

This is a projection onto the one particle subspace determined by \mathbf{J}_{K1} in the momentum space of particle 1, in contrast to \mathcal{P} which is projector onto an N -particle subspace. On collecting the various expressions, $\mathbf{B}_1^{(N)}$ satisfies the equation

$$\mathbf{B}_1^{(N)} = \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_{K1} - \frac{i}{z} \int d\mathbf{x}_2 i\mathcal{T}_{12}(1 + P_{12}) \left[(N-2)\mathbf{B}_{12}^{(N)} - \frac{N-1}{V^2} \varphi_2 \mathcal{P}_0 \int d\mathbf{r}_1 \mathbf{B}_1^{(N)} \right]. \quad (4.58)$$

The function $\mathbf{B}_{12}^{(N)}$ can be simplified with the following approximations

$$\begin{aligned}\mathbf{B}_{12}^{(N)} &= \int d\mathbf{x}^{(N-2)} \mathcal{V}_{13} \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J} f^{(N)} \\ &\approx \frac{\varphi_2}{V} \int d\mathbf{x}^{(N-2)} \mathcal{V}_{13} \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J} f^{(N-1)} \\ &= \frac{\varphi_2}{V} \mathbf{B}_1^{(N-1)} \approx \frac{\varphi_2}{V} \mathbf{B}_1^{(N)}.\end{aligned}\quad (4.59)$$

The first approximation is based on the idea that this term inherently involves the interaction (collision) between particles 1 and 3 with particle 2 entering only indirectly as a spectator for this collision. On the basis that only binary collisions are to be retained, it is thus appropriate to ignore any interaction with particle 2, thus its distribution function can be passed through the remaining combination of resolvent and Liouville operators. The remaining integral correctly involves only $N - 1$ particles, which is the second equality. It is a consequence of these approximations that termolecular collisions are eliminated. Finally, if N is very large, the $\mathbf{B}_1^{(N-1)}$ function is essentially the same as $\mathbf{B}_1^{(N)}$, the second approximation. Consistent with this independence of N , the system size labeling on \mathbf{B}_1 is dropped in the remainder of this paper. Another simplification of the same type is $(N - 1)/V \approx (N - 2)/V \approx n$. Since the system is homogeneous, \mathbf{B}_1 is independent of the position of particle 1, and it follows that $\int d\mathbf{r}_1 \mathbf{B}_1 = V \mathbf{B}_1$ and Eq. (4.58) becomes a closed equation for \mathbf{B}_1 , specifically

$$\mathbf{B}_1 = \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_{K1} - \frac{i\varphi_1}{z} \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_1. \quad (4.60)$$

The object is now to solve this equation. As a closed equation for a one particle function, there is no need to retain the particle label, so this is dropped in the further development. These manipulations show the motivation for defining the \mathbf{B}_1 in Eq. (4.49). A similar closed equation can not be obtained directly for $1/\sigma$.

Since Eq. (4.60) contains both the full \mathbf{B} and its projected part $(1 - \mathcal{P}_0) \mathbf{B}$, it is appropriate to first solve for the $(1 - \mathcal{P}_0)$ part of \mathbf{B} . Left multiplying Eq. (4.60) by $(1 - \mathcal{P}_0)$ gives

$$(1 - \mathcal{P}_0) \mathbf{B} = (1 - \mathcal{P}_0) \frac{\varphi}{VN} \mathcal{R} \mathbf{J}_K - \frac{i}{z} (1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \mathbf{B}, \quad (4.61)$$

which can be solved for $(1 - \mathcal{P}_0) \mathbf{B}$,

$$(1 - \mathcal{P}_0) \mathbf{B} = \frac{z}{z + i(1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \frac{\varphi}{VN} \mathcal{R} \mathbf{J}_K. \quad (4.62)$$

Substituting this back into Eq. (4.60), taking the tensor contraction with \mathbf{J}_K , and integrating over the momentum of particle 1 gives

$$\int d\mathbf{p} \mathbf{J}_K \overset{\circ}{\circ} \mathbf{B} = \frac{1}{VN} \left[\int d\mathbf{p} \mathbf{J}_K \overset{\circ}{\circ} \varphi \mathcal{R} \mathbf{J}_K \right]$$

$$\begin{aligned}
& -\frac{i}{z} \int d\mathbf{p} \mathbf{J}_K \odot^\alpha \varphi \mathcal{R} \frac{1}{\varphi z + i(1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \varphi \mathcal{R} \mathbf{J}_K \Big] \\
& = \frac{1}{VN} [(2\alpha + 1) \mathcal{R}_{0,0} \\
& \quad - \int d\mathbf{p} \mathbf{J}_K \odot^\alpha \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \frac{1}{(1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \varphi \mathcal{R} \mathbf{J}_K] . \quad (4.63)
\end{aligned}$$

The operator inverse can be evaluated if an appropriate complete orthonormal basis $\{\mathbf{O}_j\}$ of 1-particle functions is introduced. This basis must be restricted to functions orthogonal to the collisional invariants, equivalently to the eigenvectors of the collision operator \mathcal{R} whose eigenvalues are zero. Furthermore, for convenience, the basis should have $\mathbf{J}_K = \mathbf{O}_0(\mathbf{p})$ as a particular member of the basis and all members should belong to the same $(2\alpha + 1)$ dimensional irreducible representation of the 3-dimensional rotation group, with orthonormalization determined by

$$\int d\mathbf{p} \mathbf{O}_j(\mathbf{p}) \varphi \mathbf{O}_\ell(\mathbf{p}) = \delta_{j\ell} \mathbf{E}^{(\alpha)}. \quad (4.64)$$

Matrix elements of \mathcal{R} , after taking their rotational invariance into account, are usually expressed in terms of kinetic cross sections \mathfrak{S} [77, 78, 79], namely

$$\int d\mathbf{p} \mathbf{O}_j \varphi \mathcal{R} \mathbf{O}_\ell \equiv \mathcal{R}_{j,\ell} \mathbf{E}^{(\alpha)} = n \langle v \rangle \mathfrak{S}_{j,\ell} \mathbf{E}^{(\alpha)}, \quad (4.65)$$

wherein $\langle v \rangle$ is the average relative speed of the pair of colliding particles. The projector $1 - \mathcal{P}_0$ then merely selects out the $\mathbf{O}_j \neq \mathbf{O}_0$ elements of the basis, with the consequence that

$$\begin{aligned}
\int d\mathbf{p} \mathbf{J}_K \odot^\alpha \mathbf{B} &= \frac{2\alpha + 1}{VN} \left[\mathcal{R}_{0,0} - \sum_{j,\ell \neq 0} \mathcal{R}_{0,j} \left(\frac{1}{\mathcal{R}} \right)_{j,\ell} \mathcal{R}_{\ell,0} \right] \\
&= \frac{(2\alpha + 1) \langle v \rangle}{V^2} \left[\mathfrak{S}_{0,0} - \sum_{j,\ell \neq 0} \mathfrak{S}_{0,j} \left(\frac{1}{\mathfrak{S}} \right)_{j,\ell} \mathfrak{S}_{\ell,0} \right]. \quad (4.66)
\end{aligned}$$

Finally, the transport coefficient is determined by taking the appropriate limit of this expression, namely

$$\frac{1}{\sigma} = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{V^2}{(2\alpha + 1)B} \int d\mathbf{p} \mathbf{J}_K \odot^\alpha \mathbf{B} = \frac{\langle v \rangle}{B} \left[\mathfrak{S}_{0,0} - \sum_{j,\ell \neq 0} \mathfrak{S}_{0,j} \left(\frac{1}{\mathfrak{S}} \right)_{j,\ell} \mathfrak{S}_{\ell,0} \right]. \quad (4.67)$$

The result usually presented (see for example Ref. [52]) as the evaluation of a dilute gas transport coefficient according to the time correlation function method is the first term in Eq. (4.67), i.e., the $\mathfrak{S}_{0,0}$ term. Here it is seen how correction terms to this standard approximation arise within the binary collision approximation of the time correlation function.

4.5 The Complete Sonine Expansion

In solving the Boltzmann equation for the purpose of calculating transport coefficients, the distribution function is expanded about local equilibrium and after eliminating the time derivatives, a linear equation is obtained for the perturbation of the distribution function from local equilibrium, ϕ (Eq. (2.10) gives this form along with the first order in density generalizations). The inhomogeneous term in this equation is, for each of the viscosity, thermal conductivity and (for mixtures) diffusion coefficient, the respective flux of momentum, energy and species mass. For a given transport property, the linear (Chapman Enskog) equation [7, 62, 79] can be expressed in the present notation as

$$\mathbf{J}_K = \mathcal{R}\phi \quad (4.68)$$

and the transport coefficient is given by

$$\sigma = \frac{nB}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_K \overset{\alpha}{\odot} \phi \varphi, \quad (4.69)$$

with the factor nB chosen to agree with the normalization of Eq. (2.29). There are solvability and uniqueness conditions that must be satisfied, the only one of importance for the present discussion being the uniqueness conditions, namely that the perturbation ϕ must be orthogonal to any (collisional) summational invariant ψ ,

$$\int d\mathbf{p} \phi \psi \varphi = 0, \quad (4.70)$$

these being the mass, momentum and energy.

The solution of the Chapman Enskog Eq. (4.68) can be calculated in a number of different ways. A first approximation is to assume $\phi = b\mathbf{J}_K$ is proportional to \mathbf{J}_K . In that case, a matrix element of Eq. (4.68) with \mathbf{J}_K gives

$$b = 1/n\langle v \rangle \mathfrak{S}_{0,0} \quad (4.71)$$

and the transport coefficient

$$\sigma = B/\langle v \rangle \mathfrak{S}_{0,0}, \quad (4.72)$$

compares with the first term in Eq. (4.67). An exact solution can be obtained by making a complete expansion of ϕ and taking appropriate matrix elements with all the basis elements. A more formal method is to introduce the inverse operator \mathcal{R}^{-1} (subject to the orthogonality condition) and formally write the transport coefficient as

$$\sigma = \frac{nB}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_K \overset{\alpha}{\odot} \varphi \left(\frac{1}{\mathcal{R}} \right) \mathbf{J}_K. \quad (4.73)$$

Introduction of a complete orthonormal basis set allows the inverse operator to be calculated. The classic orthogonal basis used in solving the Boltzmann equation are functions consisting of a product of the appropriate tensor in reduced momentum $\mathbf{W} \equiv \mathbf{p}/\sqrt{2mkT}$ and a Sonine (equivalently associated Laguerre) polynomial in W^2 . The normalized version of this is [77],

$$\mathbf{L}^{\alpha s}(\mathbf{W}) \equiv \sqrt{\frac{\sqrt{\pi}(2\alpha+1)!\Gamma(s+1)}{2^{\alpha+1}(\alpha!)^2\Gamma(s+\alpha+3/2)}} L_s^{\alpha+1/2}(W^2) [\mathbf{W}]^{(\alpha)}, \quad (4.74)$$

where $[\mathbf{W}]^{(\alpha)}$ is the symmetric traceless tensor of rank α (and belonging to an irreducible representation of the 3-dimensional rotation group). For the shear viscosity and diffusion, the flux function $\mathbf{J}_K = \mathbf{L}^{\alpha 0}$ corresponds to $s = 0$ whereas for the thermal conductivity, $\mathbf{J}_K = \mathbf{L}^{11}$. For future reference, the matrix elements of the collision operator \mathcal{R} with this basis set define the kinetic cross sections $\mathfrak{S}(\frac{\alpha s}{\alpha s'})$,

$$n\langle v \rangle \mathfrak{S}(\frac{\alpha s}{\alpha s'}) = \langle \langle \mathbf{L}^{\alpha s} | \mathcal{R} | \mathbf{L}^{\alpha s'} \rangle \rangle. \quad (4.75)$$

The standard method [7] of solving Eq. (4.68) calculates the matrix inverse and expresses the above matrix element as the ratio of two determinants. In contrast, if the matrix representation of \mathcal{R} is divided into parts associated with and without \mathbf{J}_K , this can be most efficiently accomplished with the use of the projector \mathcal{P}_0 introduced in the last section. Since it is the projected element of the inverse operator that appears in the transport coefficient, the analog of Eq. (4.35) is

$$\mathcal{P}_0 \frac{1}{\mathcal{R}} \mathcal{P}_0 = \frac{1}{\mathcal{P}_0 \mathcal{R} \mathcal{P}_0 - \mathcal{P}_0 \mathcal{R} \frac{1}{(1-\mathcal{P}_0) \mathcal{R} (1-\mathcal{P}_0)} \mathcal{R} \mathcal{P}_0} \mathcal{P}_0. \quad (4.76)$$

As the $\{0,0\}$ matrix element of this inverse operator, the transport coefficient is then given by

$$\frac{1}{\sigma} = \frac{1}{nB} \left[\mathcal{R}_{0,0} - \sum_{j,\ell \neq 0} \mathcal{R}_{0,j} \left(\frac{1}{\mathcal{R}} \right)_{j,\ell} \mathcal{R}_{\ell,0} \right] \quad (4.77)$$

which, when converted to kinetic cross sections is identical to Eq. (4.67).

The above formalism has inherently assumed that the molecules have only translational states. In case the molecules have internal states, the flux operators in general will involve the internal states and the complete set of functions must span the internal states as well as the translational states. It is then necessary to include a trace over the (quantum) internal states as well as the integration over the position and momentum. To correctly formulate this mix of classical and quantum descriptions the distribution function must be replaced by a quantity which is simultaneously a Wigner function [80] for the translational states and a

density operator in the internal states. A further complexity is that a complete set of internal state operators includes operators that do not commute with the internal state hamiltonian. When acting on such an operator \mathbf{O} , the z parameter in the definition, Eq. (4.52), of the collision superoperator \mathcal{T} requires $z = \omega + i\epsilon$ to have its real part equal to the eigenvalue ω of \mathcal{K} when acting on \mathbf{O} (that is, ω is the difference of energies of the ket and bra Dirac states of \mathbf{O}). This work does not address such questions. But except when treating transport properties in the presence of a field, it has been argued that terms that are off diagonal in the eigenstates of the internal state hamiltonian are rapidly phase randomized [81]. As such, the set of operators used for expansion can be limited to those that commute with the internal state hamiltonian. With this constraint, the formal development is the same as above, except that the basis elements must span this diagonal-in-internal-state-energy part of the space of operators on internal states.

4.6 Transport Coefficients of a Binary Mixture

The collisions between molecules of the same species behave very differently from collisions between different species, thus it is not sufficient to use an average of the transport coefficients of the separate individual species in a mixture, but rather it is necessary to take into account how they influence each other. It is thus necessary, even at the lowest order of approximation, to include a separate flux function for each of the species. This section discusses the simplest case of a nonreacting ideal gas binary mixture, each species having a single basis function (that is, ignoring the role of higher Sonine polynomials or other dependences on rotational, electronic, etc. internal states). The method of formulation is to directly adapt the general treatment of Section III by considering the two species, labeled a and b , as being equivalent to two different hypothetical internal states of a molecule, with of course the mass now dependent on the internal state.

The integration over molecular states now must include a summation over the species, using here a generic label s ,

$$\int d\mathbf{x} = \sum_s \iint d\mathbf{p} d\mathbf{r}, \quad (4.78)$$

as well as the integration over translational degrees of freedom of the corresponding species (ignoring the possible presence of other internal states). Corresponding to this, the one particle distribution function (density operator) for a typical molecule has the structure

$$\frac{\varphi}{V} = \sum_s \chi_s X_s \frac{\varphi_s}{V}, \quad (4.79)$$

involving the identification state χ_s of species s , the normalized species distribution function φ_s/V and its mole fraction X_s . For an ideal gas mixture, the higher order distribution functions can be considered as products of the one particle distribution functions, compare Eq. (4.47), ignoring the constraint that only $X_a N$ of the total N molecules can be of species a . To make the properties of the mixture clearer, it is useful to introduce a two dimensional species vector space, so that the species projection operators become

$$\chi_a \Longleftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi_b \Longleftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \varphi \Longleftrightarrow \begin{pmatrix} X_a \varphi_a \\ X_b \varphi_b \end{pmatrix}. \quad (4.80)$$

Finally, the flux operator also has contributions from both species, thus

$$\mathbf{J}_K = \sum_s \wp_s \mathbf{J}_{Ks}, \quad (4.81)$$

where \wp_s are the projectors onto their respective species, namely

$$\wp_a \Longleftrightarrow \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \wp_b \Longleftrightarrow \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (4.82)$$

The technique of introducing a vector space and reformulating the solution as a matrix problem is used a number of times in the following chapters. It simplifies the calculations whenever there is more than one type of component in the flux vector (in the present case, kinetic fluxes of species a and b).

The analogous trace over molecular states becomes the row vector

$$\frac{1}{V} \text{Tr} \mathbf{J}_K = \sum_s \int d\mathbf{p} \mathbf{J}_{Ks} \chi_s^\dagger \Longleftrightarrow \int d\mathbf{p} (\mathbf{J}_{Ka} \quad \mathbf{J}_{Kb}). \quad (4.83)$$

Equations (4.49) and (4.63) can be directly adapted to the calculation of a mixture transport coefficient, but now the projector \mathcal{P}_0 onto the flux function \mathbf{J} becomes the two dimensional matrix with components

$$(\mathcal{P}_0)_{ss'} = (\varphi \mathbf{J}_K \overset{\alpha}{\odot} \int d\mathbf{p} \mathbf{J}_K)_{ss'} = \chi_s X_s \varphi_s \mathbf{J}_{Ks} \overset{\alpha}{\odot} \int d\mathbf{p} \mathbf{J}_{Ks'} \chi_{s'}^\dagger, \quad (4.84)$$

or in matrix form

$$\mathcal{P}_0 \Longleftrightarrow \begin{pmatrix} X_a \varphi_a \mathbf{J}_{Ka} \\ X_b \varphi_b \mathbf{J}_{Kb} \end{pmatrix} \overset{\alpha}{\odot} \int d\mathbf{p} (\mathbf{J}_{Ka} \quad \mathbf{J}_{Kb}). \quad (4.85)$$

There are analogous species flux projectors

$$\mathcal{P}_s \Longleftrightarrow \varphi_s \mathbf{J}_{Ks} \overset{\alpha}{\odot} \int d\mathbf{p} \mathbf{J}_{Ks} \begin{pmatrix} \delta_{a,s} & 0 \\ 0 & \delta_{b,s} \end{pmatrix}. \quad (4.86)$$

Within the constraint of having two species and only the flux operators \mathbf{J}_{Ks} for these species, the identity is equivalent to $\mathcal{P}_a + \mathcal{P}_b$, so that the projector $1 - \mathcal{P}_0$ is

$$1 - \mathcal{P}_0 \Longleftrightarrow \begin{pmatrix} X_b \mathcal{P}_a & -(\mathcal{P}_0)_{ab} \\ -(\mathcal{P}_0)_{ba} & X_a \mathcal{P}_b \end{pmatrix} = \zeta \overset{\alpha}{\odot} \xi^\dagger. \quad (4.87)$$

The factorization is recognized as a consequence of the essential factorization of $(\mathcal{P}_0)_{ss'}$, with the two dimensional vectors defined as

$$\zeta \Longleftrightarrow \begin{pmatrix} \varphi_a \mathbf{J}_{Ka} \\ -\varphi_b \mathbf{J}_{Kb} \end{pmatrix} \quad \xi \Longleftrightarrow \int d\mathbf{p} \begin{pmatrix} X_b \mathbf{J}_{Ka} \\ -X_a \mathbf{J}_{Kb} \end{pmatrix}. \quad (4.88)$$

Equation (4.87) represents, of course, the projection onto the particular vector ζ in the two-dimensional space of species flux.

A transport coefficient of a one particle property is given by Eq. (4.49) with the integral evaluated by Eq. (4.63). The latter depends on the evaluation of an inverse of a projected collision operator. Since in the present case this projection is one dimensional, it follows that

$$\left[(1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \right]^{-1} = \frac{1}{\text{Den}} \zeta \overset{\alpha}{\odot} \xi^\dagger \quad (4.89)$$

in which the denominator is

$$\text{Den} = \frac{1}{2\alpha + 1} \xi^\dagger \overset{\alpha}{\odot} \varphi \mathcal{R} \frac{1}{\varphi} \zeta = X_b \mathcal{R}_{a,a} + X_a \mathcal{R}_{b,b} - X_a \mathcal{R}_{a,b} - X_b \mathcal{R}_{b,a}. \quad (4.90)$$

This involves the collision matrix elements

$$\begin{aligned} \mathcal{R}_{a,a} &= \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_{Ka} \overset{\alpha}{\odot} \varphi_a \mathcal{R} \mathbf{J}_{Ka} \\ &= n X_a \langle v \rangle_a \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| \begin{smallmatrix} a \\ a \end{smallmatrix} \right)_{aa} + n X_b \langle v \rangle_{ab} \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| \begin{smallmatrix} a \\ a \end{smallmatrix} \right)_{ab} \end{aligned} \quad (4.91)$$

and

$$\mathcal{R}_{a,b} = \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_{Ka} \overset{\alpha}{\odot} \varphi_a \mathcal{R} \mathbf{J}_{Kb} = n X_b \langle v \rangle_{ab} \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| \begin{smallmatrix} a \\ b \end{smallmatrix} \right)_{ab}, \quad (4.92)$$

together with the analogs obtained by interchanging species a and b . Note that when the flux operators are associated with the same species, there are two types of terms, one in which the binary collision is between molecules of the same species and another when the collision partner is a molecule of the other species. The “telephone” notation of the cross sections involves a classification of the irreducible representation for the translational (here α) and internal state (here 0) motions, the species carrying the flux function and which pair of molecules are colliding, see Refs. [78, 79].

Equation (4.63) requires the evaluation of the inner product

$$\begin{aligned} & \int d\mathbf{p} \mathbf{J}_K \overset{\alpha}{\odot} \varphi \mathcal{R} \frac{1}{\varphi} \zeta \overset{\alpha}{\odot} \xi^\dagger \varphi \mathcal{R} \mathbf{J}_K \\ &= \int d\mathbf{p} \begin{pmatrix} \mathbf{J}_{Ka} & \mathbf{J}_{Kb} \end{pmatrix} \overset{\alpha}{\odot} \varphi \mathcal{R} \begin{pmatrix} \mathbf{J}_{Ka}/X_a \\ -\mathbf{J}_{Kb}/X_b \end{pmatrix} \overset{\alpha}{\odot} \int d\mathbf{p} \begin{pmatrix} X_b \mathbf{J}_{Ka} & -X_a \mathbf{J}_{Kb} \end{pmatrix} \varphi \mathcal{R} \begin{pmatrix} \mathbf{J}_{Ka} \\ \mathbf{J}_{Kb} \end{pmatrix} \\ &= (2\alpha + 1) \left[\mathcal{R}_{a,a} - \frac{X_a}{X_b} \mathcal{R}_{a,b} + \frac{X_b}{X_a} \mathcal{R}_{b,a} - \mathcal{R}_{b,b} \right] X_a X_b [\mathcal{R}_{a,a} + \mathcal{R}_{a,b} - \mathcal{R}_{b,a} - \mathcal{R}_{b,b}] \\ &= (2\alpha + 1) X_a X_b [\mathcal{R}_{a,a} + \mathcal{R}_{a,b} - \mathcal{R}_{b,a} - \mathcal{R}_{b,b}]^2. \end{aligned} \quad (4.93)$$

The last equality depends on the symmetry of the Boltzmann collision integral

$$X_a \mathcal{R}_{a,b} = X_b \mathcal{R}_{b,a}. \quad (4.94)$$

Also required is the matrix element

$$\mathcal{R}_{0,0} = \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_K \odot^\alpha \varphi \mathcal{R} \mathbf{J}_K = X_a \mathcal{R}_{a,a} + X_a \mathcal{R}_{a,b} + X_b \mathcal{R}_{b,a} + X_b \mathcal{R}_{b,b} \quad (4.95)$$

Putting these results into Eqs. (4.49) and (4.63), together with simplifying the result by an extensive use of the symmetry of Eq. (4.94), the mixture transport coefficient becomes

$$\frac{\sigma}{nB} = \frac{X_b \mathcal{R}_{a,a} + X_a \mathcal{R}_{b,b} - X_a \mathcal{R}_{a,b} - X_b \mathcal{R}_{b,a}}{\mathcal{R}_{a,a} \mathcal{R}_{b,b} - \mathcal{R}_{a,b} \mathcal{R}_{b,a}}. \quad (4.96)$$

This expression is exactly the same as that obtained from the Boltzmann equation, as found for example in McCourt, et al. [79] for binary mixtures where it is expressed in terms of kinetic cross sections.

4.7 Discussion

The original motivation for this work was to obtain expressions for the density corrections of the transport coefficients. As an analogous problem, it was asked how corrections to the lowest order approximation to the Boltzmann equation could be derived from the time correlation formalism. Naturally the density corrections require keeping the fluxes associated with collisional transfer, but in the low density limit, the effect of such terms in \mathbf{J} , and the effects of spatial correlation of the particles may be neglected. Even the restricted cases considered here illustrate the elaborate coupling of terms that may arise when evaluating Eq. (2.29) to find corrections to the lowest order expressions for the gas transport coefficients. But the method introduced here deduces from the time correlation function formulation, expressions for the transport coefficients that immediately include the higher ordered Sonine polynomials and the analogous expressions for mixtures. Both derivations appear to be novel.

The formalism given is completely general and can be used in the low density limit for any of the applications stated in the introduction. It only involves the assumption that \mathbf{J} is a sum of one particle properties and the restriction to binary collisions. The implementation of the latter is the set of approximations made in Eq. (4.59). The meaning of the binary collision operator \mathcal{R} is different for each case, but the formalism is otherwise the same.

For a \mathbf{J} which includes two particle phase space functions, or for cases where the spatial correlations of particles can no longer be neglected, the manipulations presented in this

chapter must be changed. The nature of some of the expansions are, however, the same in these cases, and by adaptation of the formalism, a density expansion for the transport coefficients can be obtained. This method of approach is again general and is illustrated for viscosity and thermal conductivity in the following chapters.

Chapter 5

Bound-Free Gas Transport Coefficients via the Time Correlation Formulation based on an Atomic Picture

5.1 Introduction

Bound pairs contribute to the first order density corrections of dilute gas transport coefficients. These effects arise primarily through the difference between atom-atom, atom-diatom and diatom-diatom cross sections, as well as the difference in the gas density (equivalently the pressure) due to the dimerization. For the thermal conductivity in particular, the energy carried by a dimer is clearly different from that of two free atoms, so bound dimers must be taken into account for this reason as well. Another direct energy effect is the possible shift in the atom-dimer ratio as the gas changes temperature. These effects were first considered by Nernst [82] and revisited in a modern setting by Stogryn and Hirschfelder [83]. The latter used the mixture equations for the transport coefficients to treat the differing collisional effects, while accounting for internal states via an Eucken method [84]. This method has been adopted by Rainwater and coworkers [8] as part of their program for fitting experimental moderately dense gas transport coefficient data. While this (molecular) method is intuitively correct from a chemical viewpoint, it does not recognize that a bound pair is truly just a pair of atoms (with of course a special chemical interaction), having the consequence that all properties of the gas should be derivable from the same fundamental formalism expressed in terms of the atoms. It is this atomic picture that is emphasized in this work, which is aimed at showing how the differing collisional effects can be obtained from a unified atomic picture.

An atomic picture has been used by Kawasaki and Oppenheim [53] in the time correlation function formalism to derive density corrections for a system with an attractive potential. The results were also used [59] to obtain kinetic equations for the time evolution of the distribution function of the gas with bound pairs. To our knowledge, these expressions have not been used to obtain numerical values for the contribution of the bound pairs to the first order density correction to the transport coefficients, nor have they been compared to the corresponding formal mixture expressions which are standardly used in applications. More recently, a coupled set of Boltzmann type kinetic equations for the time evolution of the bound pairs and the free molecules has been derived and the resultant equations solved to obtain the bound state contribution to the density corrections [25]. These derivations are at times complex, and it is difficult to assess the effect of the approximations made in the derivation on the final result. The alternative of starting with the time correlation function expressions for the transport coefficients [31, 32] can provide support for, or arguments against, the approximation methods inherent in the kinetic equations type approach. Unfortunately, the evaluation of the time correlation function also involves an assessment of how to carry out its expansion and to select which terms are important. Since the two methods are inherently different in detail, provided they result in the same estimation of a transport coefficient, they supplement each other's validity. In Chapter 4, the explicit starting point was an expression for a transport coefficient in terms of a time correlation function using a projected Liouville operator. That expression is rigorously equivalent to the standard expression of Green and Kubo. In that chapter, the time correlation function expression for a transport coefficient was evaluated in the dilute gas limit, in a manner that did not formally reduce to solving the Boltzmann equation, but whose resulting expression is the same as that standardly calculated by the Boltzmann equation method [7, 62]. In the present chapter the N -particle (atomic) density operator is written in a way [86] which emphasizes both unbound (free) atoms and bound pairs of atoms (dimers). The final expression for a transport coefficient in the presence of bound pairs is identical to that of a molecular mixture of atoms and dimers as derived from the Boltzmann equation. While this is to be expected, it is the unifying connection between atomic and molecular pictures that has been attained.

The density operator for an N -particle system having $2D$ particles bound in pairs [86] is reviewed in Section 5.2. In Sec. 5.3, the methods of Chapter 4 are used to deduce an expression for the transport coefficient of such a system from the time correlation function formalism. Kawasaki and Oppenheim [53] used what amounts to an atomic picture in the time correlation function formalism to obtain first order density corrections to the shear viscosity coefficient in the presence of bound pairs. The relation of their work to this pre-

sentation is discussed in Sec. 5.4. The chapter ends with a discussion. The material of this chapter is to appear in a future publication [87].

5.2 Distribution Functions for an N -Particle System with Unbound Particles and Bound Pairs

For an equilibrium system of particles with a sufficiently attractive intermolecular potential, there is a fraction that are bound together as pairs (often referred to here as dimers). The number of bound pairs D , more accurately the dimer density n_D , is determined by an equilibrium constant

$$\frac{n_D}{n_M^2} = K_b = \frac{q_D}{V} \left(\frac{V}{q_M} \right)^2 \quad (5.1)$$

and the unbound (free or monomer) density n_M . The equilibrium constant can be calculated in terms of the molecular partition functions q_D , q_M and the volume V . The partition functions are of course dependent on the temperature T as well as the volume V . It is also assumed that the chemical binding is such that the valence forces are saturated after pair binding so that the binding of three and/or more particles is disallowed. While the equilibrium constant can be related to the second virial coefficient, see e. g. Ref. [83], and thus interpreted as a nonideality of the N -particle system, this connection is not addressed here and the system containing bound pairs is treated as an ideal gas mixture. The inclusion of gas nonideality corrections to the transport coefficient expressions is the object of the next two chapters.

The canonical distribution for an N -particle quantum system in a volume V , having only pairwise interactions can be expanded in terms of Ursell operators [21]. If in this expansion only those terms are retained which have one and two particle Ursell operators, then this corresponds to a gas having only pair correlations, an approximation used by Snider [88] for examining the density corrections to the Boltzmann equation. Furthermore, if only the bound state part of the 2-particle Ursell operator is retained, then one has a mathematical expression which represents all particles as being free (1-particle Ursell operator) or bound in pairs. On the basis that for a large system, the number of bound pairs is very well determined, it is appropriate to restrict the sum over all products of Ursell operators to those terms which correspond to the number of bound pairs and free particles as determined by chemical equilibrium, Eq. (5.1). The resulting distribution then consists of a sum of terms, each of which has M free particles (monomers) and D bound pairs (dimers), with

$$N = M + 2D. \quad (5.2)$$

It is crucial to recognize that it is not known which pairs are bound, so that the resulting density operator must include all possible permutations of particle labels between being free and bound. The form of this density operator first appeared [86] when a kinetic theory for the formation and decay of bound pairs was presented. Explicitly it is

$$\rho^{(N)} = g(N, M, D)^{-1} \sum_{\mu, \delta} \prod_{j \in \mu} \frac{\rho_{fj}}{M} \prod_{k\ell \in \delta} \frac{\rho_{bk\ell}}{D}, \quad (5.3)$$

with

$$g(N, M, D) = \frac{N!}{M!D!2^D} \quad (5.4)$$

being the number of ways N atoms can be distributed into a set μ of M monomers, and a set δ of D dimers. In Eq. (5.3), ρ_{fj} is the density operator for a free particle j , normalized to the number of free particles

$$\text{Tr}_j \rho_{fj} = M, \quad (5.5)$$

and $\rho_{bk\ell}$ is the bound pair density operator of particles $k\ell$, normalized to the number of dimers,

$$\text{Tr}_{k\ell} \rho_{bk\ell} = D. \quad (5.6)$$

When approximately evaluating the time correlation function in the following section it is useful to select out one particle for special treatment. In particular, identifying the possible states for particle 1,

$$\begin{aligned} \rho^{(N)} &= \left(\frac{g(N, M, D)}{g(N-1, M-1, D)} \right)^{-1} \left(\frac{\rho_{f1}}{M} \right) \rho^{(N-1)} \\ &\quad + \left(\frac{g(N, M, D)}{g(N-2, M, D-1)} \right)^{-1} \sum_j \left(\frac{\rho_{b1j}}{D} \right) \rho^{(N-2)} \\ &= \frac{1}{N} \rho_{f1} \rho^{(N-1)} + \frac{2}{N(N-1)} \sum_j \rho_{b1j} \rho^{(N-2)}, \end{aligned} \quad (5.7)$$

with it being understood that $\rho^{(N-1)}$ is for the particles $2, \dots, N$ and $\rho^{(N-2)}$ is associated with the corresponding particles $2, \dots, j-1, j+1, \dots, N$. Note that particle 1 may be either free or part of a bound pair, with its partner in binding being any other particle in the system.

This discussion emphasizes the particle aspects of the monomer dimer mixture since a dimer is just a special state of a pair of particles. But when determining, for example the pressure, it is the number of freely moving units $M + D$ that strike the walls of the container that is of importance, namely the molecular point of view. Relevant to this, the mole fractions of monomers and dimers are $X_f \equiv M/(M + D)$ and $X_b \equiv D/(M + D)$. These quantities arise naturally in the following.

5.3 Transport Coefficients for a System With Bound Pairs

As seen previously [31, 32] a transport coefficient σ can be expressed as the limit of the Laplace transform of the time correlation function of the flux \mathbf{J} of the corresponding physical property,

$$\sigma = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha + 1)V} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \frac{1}{z - \mathcal{L}} \mathbf{J} \rangle\rangle. \quad (5.8)$$

Here B is a factor appropriate for the particular transport coefficient and the introduction of the volume factor V recognizes the difference between the extensivity of a flux and the intensivity of a transport coefficient. The bracket designates a canonical thermal average for an N -particle system of volume V while $\overset{\alpha}{\odot}$ is a tensorial contraction of order α which depends on the tensorial properties of \mathbf{J} . Finally, $z = i\epsilon$ and \mathcal{L} is the N -particle Liouville superoperator. As in Chapter 4, a quantum language is generally used in the following except when classical mechanics can make a significant simplification. In particular, the product of noncommuting operators for physical observables have not been considered with any care and should, where necessary, be replaced by their anticommutator average, see Eq. (4.27). Dynamical effects associated with the commutator with some hamiltonian occur only through their appearance as superoperators. All equations can be interpreted classically and easily translated into a classical formalism if that is desired.

It was shown in Section 4.3 that, with the introduction of an idempotent projection operator,

$$\mathcal{P} = A | \mathbf{J} \rangle \rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} |, \quad (5.9)$$

the expression for the transport coefficient could be written as,

$$\frac{1}{\sigma} = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{A^2 V}{(2\alpha + 1)B} \langle\langle \mathbf{J} \overset{\alpha}{\odot} \mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} | \mathbf{J} \rangle\rangle, \quad (5.10)$$

with the constant A , determined by the condition of idempotency, given by

$$A = \frac{2\alpha + 1}{\langle\langle \mathbf{J} \overset{\alpha}{\odot} | \mathbf{J} \rangle\rangle}. \quad (5.11)$$

This relation assumes that \mathbf{J} belongs to a specific irreducible representation of the three-dimensional rotation group and that $\langle\langle \mathbf{J} | \mathbf{J} \rangle\rangle$ and \mathcal{L} are rotational invariants. In particular, the present treatment is restricted to (electric and/or magnetic) field independent transport coefficients.

The general expression for a transport coefficient, Eq. (5.10), is valid for all densities and all chemical situations. In Chapter 4 this was specialized in two ways, both for gases at low

density. First it was considered that all particles were the same and free, corresponding to the $D = 0$ case discussed in Section 5.2. A complete treatment of the low density situation was carried out for this case. Second, the individual particles were assigned a species label and the properties of a binary mixture were worked out. The latter treatment was further simplified by limiting the operator space to having only one (flux) observable for each species. Clearly that restriction could be easily removed, but with the inherent addition of more involved algebra. In the present chapter, particles are allowed to form pair bound states. At low gas density the N -particle density operator is approximated by Eq. (5.3) and it is further assumed that the flux operator for a bound pair is equal to the sum of the flux operators for the atoms making up the bound pair. The method of expansion results in a pair of coupled equations, one for each species. As a special case, these equations are further simplified by assuming that only one observable is important for each of the free and bound pairs. In this way, as is to be expected, the resulting expression for a transport coefficient has the same structure as the mixture formula of Section 4.6. But the present method of derivation of this result emphasizes the atomic structure of the diatomics and shows how molecular transport coefficients can be obtained from an atomic description, at least at low density and where only the translational kinetic contributions to a molecular flux are of importance.

The flux function \mathbf{J} in Eq. (5.10) is the sum of kinetic and potential parts. The kinetic part of a flux function is a sum of one particle functions of the momenta of each of the particles in the system while the potential part of the flux depends in general on both the coordinates and the momenta of two (or possibly more) particles in the system. In the present work on the transport properties of a dilute gas it is assumed that the potential contributions are negligible compared to the kinetic part and thus ignored from further consideration. The flux function \mathbf{J} is thus taken as having the form

$$\mathbf{J} = \sum_j \mathbf{J}_{Kj} \quad (5.12)$$

where \mathbf{J}_{Kj} is the kinetic contribution of particle j and is exclusively a function of momentum. The flux function is, for convenience assumed to be normalized such that,

$$\langle\langle \mathbf{J} \overset{\alpha}{\odot} \mathbf{J} \rangle\rangle = \text{Tr}_1 \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathbf{J}_{K1} \rho_{f1} + \text{Tr}_{12} \mathbf{J}_{K12} \overset{\alpha}{\odot} \mathbf{J}_{K12} \rho_{b12} = (2\alpha + 1)(M + D). \quad (5.13)$$

Essentially this follows from Eq. (5.7) with the notion that only the translational motion of either a free atom or a bound pair contributes, 1 for each of the $2\alpha + 1$ components of \mathbf{J} . The factor $M + D$ is the count of the number of freely translating molecules. While $\mathbf{J}_{K12} \equiv \mathbf{J}_{K1} + \mathbf{J}_{K2}$ is formally the kinetic flux operator for a diatomic, the relative motion of the atoms in the diatom should be essentially fixed and thus not contribute to the flux.

In this approximation only the center of mass motion of the bound pair contributes to the kinetic flux. If (as is the case for thermal conductivity), the internal motion of the bound pair contributes significantly to the flux of the property under study, a correction to the above expression needs to be introduced. The expression for the normalization constant A follows from Eq. (5.13) according to

$$A = \frac{1}{M + D}. \quad (5.14)$$

This is a generalization of the value of $1/N$ which was obtained in Section 4.4 for a system consisting of only monomers.

With these restrictions, and the further restriction that the potential is pairwise additive, Eq. (5.10) can be expressed in a form that emphasizes the flux operator for a typical particle interacting with a second typical particle, namely

$$\begin{aligned} \frac{(M + D)^2(2\alpha + 1)B}{V\sigma} &= N(N - 1) \langle\langle \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_p} \mathcal{L}\mathbf{J} \rangle\rangle \\ &= N(N - 1) \langle\langle \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}} \left[1 - \mathcal{P}\mathcal{L} \frac{1}{z - \mathcal{L}_p} \right] \mathcal{L}\mathbf{J} \rangle\rangle \\ &= N(N - 1) \text{Tr}_{1\dots N} \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}} \\ &\quad \times \left[\mathcal{L}\mathbf{J}\rho^{(N)} - \mathbf{J}\rho^{(N)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J}\mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L}\mathbf{J} \rangle\rangle \right]. \end{aligned} \quad (5.15)$$

The last forms of this equation involve expanding the resolvent of the projected Liouville operator in terms of the unprojected Liouville operator for the subsequent identification of whether the selected particle is free or part of a bound pair. Neglecting the possibility of chemical recombination and decay, once a particle is identified as being free or part of a bound pair, it is required to remain so identified as far as the Liouville operator is concerned. This essentially eliminates the possibility of chemical reaction. Within this perspective, particles 1 and 2 have a special meaning in Eq. (5.15), so the appropriate form for Eq. (5.7) to select out the state of particle 1 is,

$$\rho^{(N)} = \frac{\rho_{f1}}{N} \rho^{(N-1)} + \frac{2}{N(N - 1)} \left(\rho_{b12} + \sum_{j>2} \rho_{b1j} \right) \rho^{(N-2)}. \quad (5.16)$$

The term with ρ_{b12} is subsequently neglected when used in Eq. (5.15) since this term would be associated with internal motion because the potential superoperator \mathcal{V}_{12} is for the same pair of particles. As a consequence, the transport coefficient is the sum of two contributions, one from free particles and the other from bound pairs, namely

$$\frac{(M + D)^2(2\alpha + 1)B}{V\sigma} = \text{Tr}_1 \mathbf{J}_{K1} \overset{\alpha}{\odot} \mathbf{B}_{f1} + \text{Tr}_{13} \mathbf{J}_{K13} \overset{\alpha}{\odot} \mathbf{B}_{b13}, \quad (5.17)$$

where

$$\mathbf{B}_{f1} \equiv (N-1) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho^{(N-1)} - \mathbf{J} \rho_{f1} \rho^{(N-1)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \quad (5.18)$$

and

$$\mathbf{B}_{b13} \equiv (N-2) \text{Tr}_{2,4\dots N} \mathcal{V}_{(13)2} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{b13} \rho^{(N-2)} - \mathbf{J} \rho_{b13} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right]. \quad (5.19)$$

The interaction of a dimer with another atom has been given the shortened label $\mathcal{V}_{(13)2} \equiv \mathcal{V}_{12} + \mathcal{V}_{32}$. Note that the \mathbf{B}_j 's have the same tensorial properties as the \mathbf{J}_{Kj} 's. These \mathbf{B}_j 's are akin to quantities which have been named reduced time correlation functions [47]. The objective of the following subsections is to derive a pair of closed equations for \mathbf{B}_f and \mathbf{B}_b , which can subsequently be solved for this pair of quantities.

5.3.1 Free Atom Contributions

The $\rho^{(N-1)}$ in Eq. (5.18) can be further decomposed in analogy with Eq. (5.7), but now selecting out the possible state of particle 2. The result allows the effects of monomer-monomer, monomer-dimer and dimer-dimer collisions to be separately identified so that \mathbf{B}_{f1} can be written in the form

$$\mathbf{B}_{f1} = \mathbf{B}_{f1f} + \mathbf{B}_{f1b}, \quad (5.20)$$

with

$$\mathbf{B}_{f1f} = \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} - \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \quad (5.21)$$

and

$$\mathbf{B}_{f1b} = \text{Tr}_{2\dots N} \mathcal{V}_{1(23)} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} - \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right]. \quad (5.22)$$

In the second equation, the symmetry between the two particles in a bound state has been used to write the potential superoperator in a form suitable for a monomer-dimer collision. The resolvents in each of the above expressions involve the Liouville superoperator \mathcal{L} of the entire N -particle system. These need to be expanded for each case in a manner appropriate for the respective two molecule collision.

For a collision between two free molecules, the resolvent $(z - \mathcal{L})^{-1}$ is expanded in terms of the resolvent for the pair of molecules

$$\frac{i}{z - \mathcal{L}} = \frac{i}{z - \mathcal{L}_{12}} \left[1 + \sum_{j>2} \left(\mathcal{V}_{1j} + \mathcal{V}_{2j} + \sum_{2<j<\ell} \mathcal{V}_{j\ell} \right) \frac{1}{z - \mathcal{L}} \right]. \quad (5.23)$$

Note that the 2-particle Liouville superoperator is to contain the kinetic superoperators for *all* the N -particles, so that \mathcal{L} and \mathcal{L}_{12} differ only by a combination of potential superoperators. Since the trace in Eq. (5.21) is over all particles except 1, and noting that particle 2 plays a special role via the presence of \mathcal{V}_{12} , the contributions in Eq. (5.23) from all $\mathcal{V}_{j\ell}$ for $j, \ell > 2$ vanish. Thus it follows that Eq. (5.21) can be rewritten and approximated according to

$$\begin{aligned}
\mathbf{B}_{f1f} &= \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[1 + \sum_{j>2} (\mathcal{V}_{1j} + \mathcal{V}_{2j}) \frac{1}{z - \mathcal{L}} \right] \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} - \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \\
&\approx \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[\mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{f1} \rho_{f2} \right. \\
&\quad \left. - (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{f1} \rho_{f2} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \\
&\quad + \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \rho_{f2} (N - 2) \text{Tr}_{3\dots N} \mathcal{V}_{13} \frac{1}{z - \mathcal{L}} \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho^{(N-2)} - \mathbf{J} \rho_{f1} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right], \tag{5.24}
\end{aligned}$$

involving the particle permutation operator P_{12} . The approximation indicated in the second form of this quantity is in the treatment of the terms involving the product of resolvents. Essentially it involves treating the interaction partner, particle 2, in a manner different from the other particles in the gas. In a dilute gas, the opportunity for the two particles to recollide or for three or more (unbound) particles to be simultaneously interacting is very small, so the approximation is to implement the idea that, if particle 2 is to be involved in a collision with particle 1, it will not have been involved in any previous collision with particle 1. This is accomplished by “promoting” its density operator, ρ_{f2} , through various Liouville and resolvent operators, thus

$$\begin{aligned}
&\text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) (N - 2) \mathcal{V}_{13} \frac{1}{z - \mathcal{L}} \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} - \mathbf{J} \rho_{f1} \rho_{f2} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \\
&\approx \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \rho_{f2} (N - 2) \text{Tr}_{3\dots N} \mathcal{V}_{13} \frac{1}{z - \mathcal{L}} \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho^{(N-2)} - \mathbf{J} \rho_{f1} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right]. \tag{5.25}
\end{aligned}$$

While this has been discussed in slightly more detail in Chapter 4, it is clear that an expansion based on this “promotion” procedure could be carried out, with this as the leading term and correction terms added as the difference between the exact expression and this leading term.

The correction term would then account for all the recollision and multiple collision events, while the leading term that is kept here is associated with particle 1 successively colliding with a number of (different) particles.

With the further approximation that all reference to particle 2 is ignored to the right of the trace over particles 3 to N , this trace can be recognized as the appropriate \mathbf{B}_{f1} with particle 2 missing, namely

$$\begin{aligned} \mathbf{B}_{f1}^{(N-1)} &\equiv \text{Tr}_{3\dots N} \mathcal{V}_{13} \frac{1}{z - \mathcal{L}^{(N-1)}} \left[\mathcal{L}^{(N-1)} \mathbf{J}^{(N-1)} \rho_{f1} \rho^{(N-2)} \right. \\ &\quad \left. - \mathbf{J}^{(N-1)} \rho_{f1} \rho^{(N-2)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \rangle\rangle \right] \approx \mathbf{B}_{f1}^{(N)} \equiv \mathbf{B}_{f1}. \end{aligned} \quad (5.26)$$

The last approximation, which is appropriate for large N , ignores the difference between $N - 1$ and N particles. As a consequence, \mathbf{B}_{f1f} can be approximated by

$$\begin{aligned} \mathbf{B}_{f1f} &= \rho_{f1} \mathcal{R}_1^{ff} \left[\mathbf{J}_{K1} + \frac{i}{z} \mathbf{J}_{K1} A \overset{\alpha}{\odot} (\text{Tr}_1 \mathbf{J}_{K1} \mathbf{B}_{f1} + \text{Tr}_{13} \mathbf{J}_{K13} \mathbf{B}_{b13}) - \frac{i}{z \rho_{f1}} \mathbf{B}_{f1} \right] \\ &= \rho_{f1} \mathcal{R}_1^{ff} \left[\mathbf{J}_{K1} - \frac{i}{z \rho_{f1}} \mathbf{B}_{f1} + \frac{iAM}{z \rho_{f1}} \mathcal{P}_{ff} \mathbf{B}_{f1} + \frac{iAM}{z \rho_{f1}} \mathcal{P}_{fb} \mathbf{B}_{b13} \right]. \end{aligned} \quad (5.27)$$

Here \mathcal{R}_1^{ff} is a z -parameterized binary collision superoperator describing the binary collision of particle 1 with another free particle [89],

$$\mathcal{R}_1^{ff} \equiv \frac{1}{\rho_{f1}} \text{Tr}_2 i \mathcal{T}_{12}(z) \rho_{f1} \rho_{f2} (1 + P_{12}). \quad (5.28)$$

The z -parameterized transition superoperator [90]

$$\mathcal{T}_{12}(z) \equiv \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (z - \mathcal{K}_{12}) = \mathcal{V}_{12} + \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} \quad (5.29)$$

can be expressed in several ways. In the limit $z = i\epsilon \rightarrow 0$, the transition superoperator converges to the abstract transition superoperator \mathcal{T}_{12} provided it acts on a function of momentum only, and \mathcal{R}^{ff} converges to the linearized binary relaxation superoperator associated with the Boltzmann equation. \mathcal{P}_{ff} is the projection superoperator onto the subspace of the flux operator for a free particle, here labeled as particle 1,

$$\mathcal{P}_{ff} \equiv \mathbf{J}_{K1} \frac{\rho_{f1}}{M} \overset{\alpha}{\odot} \text{Tr}_1 \mathbf{J}_{K1}, \quad (5.30)$$

being identical to the \mathcal{P}_0 introduced in Eq. (4.57). \mathcal{P}_{fb} is the transfer superoperator

$$\mathcal{P}_{fb} \equiv \mathbf{J}_{K1} \frac{\rho_{f1}}{M} \overset{\alpha}{\odot} \text{Tr}_{13} \mathbf{J}_{K13}, \quad (5.31)$$

describing the transfer of the polarization (nonequilibrium flux) from a bound pair to a free monomer. Finally it should be remarked that the identification in Eq. (5.27) of the unprojected \mathbf{B}_{f1} term assumes that the system is large so that in the definition of \mathbf{B}_{f1} , it does not matter if $N - 1$ or $N - 2$ particles need to be considered. Note that Eq. (5.27) reduces to Eq. (4.60) if there are no bound pairs. It is important to note that \mathbf{B}_{f1f} has been expressed in terms of the original \mathbf{B}_f and \mathbf{B}_b functions. This indicates that a closed set of equations for the latter two quantities may be possible.

Similar calculations are used for the free-bound term \mathbf{B}_{f1b} , except that the N -particle resolvent is expanded in such a way as to emphasize the dynamics of the three particles associated with the collision of free particle 1 with bound pair 23,

$$\begin{aligned}
\mathbf{B}_{f1b} &= \text{Tr}_{2\dots N} \mathcal{V}_{1(23)} \frac{i}{z - \mathcal{L}_{123}} \left[1 + \sum_{j>3} (\mathcal{V}_{1j} + \mathcal{V}_{2j} + \mathcal{V}_{3j}) \frac{1}{z - \mathcal{L}} \right] \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} - \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} A \overset{\alpha}{\odot} \left\langle \left\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \right\rangle \right\rangle \right] \\
&= \text{Tr}_{23} \mathcal{V}_{1(23)} \frac{i}{z - \mathcal{L}_{123}} \left[\mathcal{V}_{1(23)} (\mathbf{J}_{K1} + \mathbf{J}_{K23}) \rho_{f1} \rho_{b23} \right. \\
&\quad \left. - (\mathbf{J}_{K1} + \mathbf{J}_{K23}) \rho_{f1} \rho_{b23} A \overset{\alpha}{\odot} \left\langle \left\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \right\rangle \right\rangle \right] \\
&\quad + \text{Tr}_{23} \mathcal{V}_{1(23)} \frac{i}{z - \mathcal{L}_{123}} (N - 3) \text{Tr}_{4\dots N} \left(\mathcal{V}_{14} + \mathcal{V}_{(23)4} \right) \frac{1}{z - \mathcal{L}} \\
&\quad \times \left[\mathcal{L} \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} - \mathbf{J} \rho_{f1} \rho_{b23} \rho^{(N-3)} A \overset{\alpha}{\odot} \left\langle \left\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{J} \right\rangle \right\rangle \right]. \quad (5.32)
\end{aligned}$$

On the basis that only binary collisions are to be retained, so that neither three or more molecular collisions are of importance, nor are recollisions, it is appropriate to promote either ρ_{b23} or ρ_{f1} to the left of the trace $\text{Tr}_{4\dots N}$ according to whether the $\mathcal{V}_{(23)4}$ or the \mathcal{V}_{14} term is being considered. In each case the appropriate binary collision operator can be identified and the result written as

$$\begin{aligned}
\mathbf{B}_{f1b} &\approx \rho_{f1} \mathcal{R}_1^{fb} \left[\mathbf{J}_{K1} + \mathbf{J}_{K23} + \frac{iAM}{z\rho_{f1}} (\mathcal{P}_{ff} \mathbf{B}_{f1} + \mathcal{P}_{fb} \mathbf{B}_{b23}) \right. \\
&\quad \left. + \frac{iAD}{z\rho_{b23}} (\mathcal{P}_{bb} \mathbf{B}_{b23} + \mathcal{P}_{bf} \mathbf{B}_{f1}) - \frac{i}{z} \left(\frac{1}{\rho_{f1}} \mathbf{B}_{f1} + \frac{1}{\rho_{b23}} \mathbf{B}_{b23} \right) \right] \quad (5.33)
\end{aligned}$$

where the free-bound binary collision operator,

$$\mathcal{R}_1^{fb} \equiv \frac{1}{\rho_{f1}} \text{Tr}_{23} \mathcal{V}_{1(23)} \frac{i}{z - \mathcal{L}_{123}} (z - \mathcal{K}_{1(23)}) \rho_{f1} \rho_{b23}, \quad (5.34)$$

the projection superoperator onto the flux of a bound pair,

$$\mathcal{P}_{bb} \equiv \frac{\rho_{b23}}{D} \mathbf{J}_{K23} \overset{\alpha}{\odot} \text{Tr}_{23} \mathbf{J}_{K23}, \quad (5.35)$$

and the transfer superoperator

$$\mathcal{P}_{bf} \equiv \frac{\rho_{b23}}{D} \mathbf{J}_{K23} \overset{\alpha}{\odot} \text{Tr}_1 \mathbf{J}_{K1}, \quad (5.36)$$

have definitions analogous to those given in Eqs. (5.28-5.31).

Eqs. (5.27) and (5.33) can be combined to obtain an equation for the free molecules. Dropping the labels on the particles, since now only a single free particle and/or bound pair appears in these quantities, the equation for free molecules is

$$\begin{aligned} \mathbf{B}_f = & \rho_f (\mathcal{R}^{ff} + \mathcal{R}^{fb}) \mathbf{J}_{Kf} + \rho_f \mathcal{R}^{fb} \mathbf{J}_{Kb} \\ & + \rho_f \left[-(\mathcal{R}^{ff} + \mathcal{R}^{fb}) \frac{i}{z\rho_f} (1 - X_f \mathcal{P}_{ff}) + \mathcal{R}^{fb} \frac{i}{z\rho_b} X_b \mathcal{P}_{bf} \right] \mathbf{B}_f \\ & + \rho_f \left[(\mathcal{R}^{ff} + \mathcal{R}^{fb}) \frac{i}{z\rho_f} X_f \mathcal{P}_{fb} - \mathcal{R}^{fb} \frac{i}{z\rho_b} (1 - X_b \mathcal{P}_{bb}) \right] \mathbf{B}_b. \end{aligned} \quad (5.37)$$

It is to be noted that this is an equation that involves only two operators, namely \mathbf{B}_f and \mathbf{B}_b , rather than requiring separate treatment for each of the possible four collision types, specifically for a free particle, the operators \mathbf{B}_{f1f} , \mathbf{B}_{f1b} , and analogous quantities for a bound pair. The analog of Eq. (5.37) for a bound pair is now considered.

5.3.2 Bound Pair Contributions

The bound pair contribution to $1/\sigma$ is determined by the \mathbf{B}_{b13} of Eq. (5.19). Its evaluation is treated in a manner analogous to the free particle contribution. First is the decomposition of $\rho^{(N-2)}$ so as to identify whether the bound pair (13) collides in a binary collision with a free particle or with another bound pair. This leads to an automatic separation of \mathbf{B}_{b13} into a pair of terms

$$\mathbf{B}_{b13} = \mathbf{B}_{b13f} + \mathbf{B}_{b13b}, \quad (5.38)$$

where

$$\mathbf{B}_{b13f} = \text{Tr}_{2,4\dots N} \mathcal{V}_{(13)2} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{b13} \rho_{f2} \rho^{(N-3)} - \mathbf{J} \rho_{b13} \rho_{f2} \rho^{(N-3)} A \overset{\alpha}{\odot} \left\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} \right\rangle \right] \quad (5.39)$$

and

$$\mathbf{B}_{b13b} = \text{Tr}_{2,4\dots N} \mathcal{V}_{(13)(24)} \frac{i}{z - \mathcal{L}} \left[\mathcal{L} \mathbf{J} \rho_{b13} \rho_{b24} \rho^{(N-4)} - \mathbf{J} \rho_{b13} \rho_{b24} \rho^{(N-4)} A \overset{\alpha}{\odot} \left\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} \right\rangle \right]. \quad (5.40)$$

The bound-bound term \mathbf{B}_{b13b} has the simpler structure, being by nature the analog of \mathbf{B}_{f1f} . Its expansion in terms of a 4-particle resolvent and subsequent identification of binary collisions is

$$\begin{aligned}\mathbf{B}_{b13b} &= \text{Tr}_{2,4\dots N} \mathcal{V}_{(13)(24)} \frac{i}{z - \mathcal{L}_{1234}} \left[1 + \sum_{j>4} (\mathcal{V}_{1j} + \mathcal{V}_{2j} + \mathcal{V}_{3j} + \mathcal{V}_{4j}) \frac{1}{z - \mathcal{L}} \right] \\ &\quad \times \left[\mathcal{L} \mathbf{J} \rho_{b13} \rho_{b24} \rho^{(N-4)} - \mathbf{J} \rho_{b13} \rho_{b24} \rho^{(N-4)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J} \rangle\rangle \right] \\ &\approx \rho_{b13} \mathcal{R}_{(13)}^{bb} \left[\mathbf{J}_{K13} + \frac{iAD}{z \rho_{b13}} (\mathcal{P}_{bf} \mathbf{B}_{f1} + \mathcal{P}_{bb} \mathbf{B}_{b13}) - \frac{i}{z \rho_{b13}} \mathbf{B}_{b13} \right],\end{aligned}\quad (5.41)$$

where the bound-bound collision superoperator is

$$\mathcal{R}_{(13)}^{bb} \equiv \frac{1}{\rho_{b13}} \text{Tr}_{24} \mathcal{V}_{(13)(24)} \frac{i}{z - \mathcal{L}_{1234}} (z - \mathcal{K}_{(13)(24)}) \rho_{b13} \rho_{b24} (1 + P_{(13)(24)}), \quad (5.42)$$

involving the dimer permutation superoperator $P_{(13)(24)}$. This reduces in the limit $z = i\epsilon \rightarrow 0$ to the corresponding linearized collision superoperator of the Boltzmann equation, provided it is restricted to act only on functions of momentum. Finally, the bound-free term \mathbf{B}_{b13f} , can be approximated by the restriction to binary collisions to

$$\begin{aligned}\mathbf{B}_{b13f} &= \text{Tr}_{2,4\dots N} \mathcal{V}_{(13)2} \frac{i}{z - \mathcal{L}_{123}} \left[1 + \sum_{j>3} (\mathcal{V}_{1j} + \mathcal{V}_{2j} + \mathcal{V}_{3j}) \frac{1}{z - \mathcal{L}} \right] \\ &\quad \times \left[\mathcal{L} \mathbf{J} \rho_{b13} \rho_{f2} \rho^{(N-3)} - \mathbf{J} \rho_{b13} \rho_{f2} \rho^{(N-3)} A \overset{\alpha}{\odot} \langle\langle \mathbf{J} \mathcal{L} \frac{1}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J} \rangle\rangle \right] \\ &\approx \rho_{b13} \mathcal{R}_{(13)}^{bf} \left[\mathbf{J}_{K13} + \mathbf{J}_{K2} + \frac{iAD}{z \rho_{b13}} (\mathcal{P}_{bb} \mathbf{B}_{b13} + \mathcal{P}_{bf} \mathbf{B}_{f2}) \right. \\ &\quad \left. + \frac{iAM}{z \rho_{f2}} (\mathcal{P}_{ff} \mathbf{B}_{f2} + \mathcal{P}_{fb} \mathbf{B}_{b23}) - \frac{i}{z} \left(\frac{1}{\rho_{f2}} \mathbf{B}_{f2} + \frac{1}{\rho_{b13}} \mathbf{B}_{b13} \right) \right],\end{aligned}\quad (5.43)$$

where

$$\mathcal{R}_{(13)}^{bf} \equiv \frac{1}{\rho_{b13}} \text{Tr}_2 \mathcal{V}_{(13)2} \frac{i}{z - \mathcal{L}_{123}} (z - \mathcal{K}_{(13)2}) \rho_{b13} \rho_{f2}. \quad (5.44)$$

The same remarks can be made for this collision superoperator as for the former. In all simplifications involving the identification of a binary collision, there is a “promotion” of a density operator through a Liouville superoperator and resolvent to become identified with the collision superoperator, on the basis that, if a free particle or bound pair collides with the non-traced over molecule, that free particle or bound pair cannot have been previously involved in a collision that affects the non-traced over particle. It is this major assumption about the nature of recollisions, specifically the lack of any recollisions, that defines the independence of binary collision events and is the analog of Boltzmann’s Stosszahlansatz for the evaluation of a time correlation function in the dilute gas regime.

Combining the above two quantities associated with bound-bound and bound-free collisions results in an equation for the bound pair contribution to $1/\sigma$, namely

$$\begin{aligned} \mathbf{B}_b = & \rho_b \mathcal{R}^{bf} \mathbf{J}_{Kf} + \rho_b (\mathcal{R}^{bb} + \mathcal{R}^{bf}) \mathbf{J}_{Kb} \\ & + \rho_b \left[(\mathcal{R}^{bf} + \mathcal{R}^{bb}) \frac{i}{z\rho_b} X_b \mathcal{P}_{bf} - \mathcal{R}^{bf} \frac{i}{z\rho_f} (1 - X_f \mathcal{P}_{ff}) \right] \mathbf{B}_f \\ & + \rho_b \left[-(\mathcal{R}^{bf} + \mathcal{R}^{bb}) \frac{i}{z\rho_b} (1 - X_b \mathcal{P}_{bb}) + \mathcal{R}^{bf} \frac{i}{z\rho_f} X_f \mathcal{P}_{fb} \right] \mathbf{B}_b. \end{aligned} \quad (5.45)$$

As for the free particle contribution, there is no longer any need for a detailed labeling of the particles. It is sufficient to retain only whether a typical free particle or bound pair is involved. Except for the inhomogeneous terms involving \mathbf{J}_{Kf} and \mathbf{J}_{Kb} , this equation involves only the two operators \mathbf{B}_f and \mathbf{B}_b . It remains to solve the coupled pair of equations (5.37) and (5.45) for \mathbf{B}_f and \mathbf{B}_b .

5.3.3 Solving for \mathbf{B}_f and \mathbf{B}_b

The objective is to solve the two equations (5.37) and (5.45) so as to calculate the transport coefficient via Eq. (5.17). These two equations can be written in matrix form

$$\begin{pmatrix} M_{ff} & M_{fb} \\ M_{bf} & M_{bb} \end{pmatrix} \begin{pmatrix} \mathbf{B}_f \\ \mathbf{B}_b \end{pmatrix} = \begin{pmatrix} \mathbf{Y}_f \\ \mathbf{Y}_b \end{pmatrix} \quad (5.46)$$

with somewhat obvious identifications of the M and \mathbf{Y} components. But it is noticed that each matrix element is actually a superoperator, so inverting the matrix to obtain a solution involves inverting a matrix of superoperators. A formal solution can be written down, either in matrix form while recognizing that the matrix elements do not commute, as well as the inherent operator difference (space of operators for a free particle versus the space of operators for a bound pair) between the first and second index of the matrix, or algebraically

$$\begin{aligned} \mathbf{B}_f &= \frac{1}{M_{ff} - M_{fb} M_{bb}^{-1} M_{bf}} (\mathbf{Y}_f - M_{fb} M_{bb}^{-1} \mathbf{Y}_b) \\ \mathbf{B}_b &= \frac{1}{M_{bb} - M_{bf} M_{ff}^{-1} M_{fb}} (\mathbf{Y}_b - M_{bf} M_{ff}^{-1} \mathbf{Y}_f) \end{aligned} \quad (5.47)$$

The simplest approximation for the evaluation of these operator equations is to restrict each species to have a single flux function, namely the appropriate \mathbf{J}_{Kj} . This “two moment” approximation is equivalent to the assumption that the \mathbf{B}_j are proportional to the corresponding \mathbf{J}_{Kj} , specifically

$$\mathbf{B}_j \approx \rho_j \mathbf{J}_{Kj} b_j \quad (5.48)$$

with expansion coefficients b_j . On taking matrix elements of Eqs. (5.37) and (5.45) with respect to the \mathbf{J} 's, these coupled superoperator equations become a pair of coupled scalar equations.

In terms of the two moment approximation, the matrix elements of the $M_{j\ell}$ superoperators become equivalent to the scalars

$$\begin{aligned} m_{ff} &\equiv \frac{1}{2\alpha+1} \text{Tr}_f \mathbf{J}_{Kf} \overset{\alpha}{\odot} M_{ff} \rho_f \mathbf{J}_{Kf} = 1 + \frac{i}{z} (X_b \mathcal{R}_{ff} - X_f \mathcal{R}_{fb}) \\ m_{fb} &\equiv \frac{1}{2\alpha+1} \text{Tr}_f \mathbf{J}_{Kf} \overset{\alpha}{\odot} M_{fb} \rho_b \mathbf{J}_{Kb} = \frac{i}{z} (X_f \mathcal{R}_{fb} - X_b \mathcal{R}_{ff}) \\ m_{bf} &\equiv \frac{1}{2\alpha+1} \text{Tr}_b \mathbf{J}_{Kb} \overset{\alpha}{\odot} M_{bf} \rho_f \mathbf{J}_{Kf} = \frac{i}{z} (X_b \mathcal{R}_{bf} - X_f \mathcal{R}_{bb}) \\ m_{bb} &\equiv \frac{1}{2\alpha+1} \text{Tr}_b \mathbf{J}_{Kb} \overset{\alpha}{\odot} M_{bb} \rho_b \mathbf{J}_{Kb} = 1 + \frac{i}{z} (X_f \mathcal{R}_{bb} - X_b \mathcal{R}_{bf}) \end{aligned} \quad (5.49)$$

wherein it is noticed that the collision superoperator matrix elements only appear in certain combinations, namely

$$\begin{aligned} \mathcal{R}_{jj} &\equiv \frac{1}{(2\alpha+1)N_j} \text{Tr}_j \mathbf{J}_{Kj} \rho_j \overset{\alpha}{\odot} (\mathcal{R}^{jj} + \mathcal{R}^{j\ell}) \mathbf{J}_{Kj} \\ &= n_j \langle v \rangle_j \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| j \right)_{jj} + n_\ell \langle v \rangle_{j\ell} \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| j \right)_{j\ell} \end{aligned} \quad (5.50)$$

and

$$\mathcal{R}_{j\ell} \equiv \frac{1}{(2\alpha+1)N_j} \text{Tr}_j \mathbf{J}_{Kj} \rho_j \overset{\alpha}{\odot} \mathcal{R}^{j\ell} \mathbf{J}_{K\ell} = n_\ell \langle v \rangle_{j\ell} \mathfrak{S} \left(\begin{smallmatrix} \alpha 0 \\ \alpha 0 \end{smallmatrix} \middle| j \right)_{j\ell}. \quad (5.51)$$

In these equations, N_j is either M or D , according to whichever is appropriate, and the notation for mixture kinetic cross sections has been indicated so as to make connection with the standard gas kinetic theory based on the Boltzmann equation [79]. The $\mathcal{R}_{j\ell}$ notation for the matrix elements of the binary collision operators was introduced in Eqs. (4.91) and (4.92). In the two moment approximation and taking into account the normalization properties of the \mathbf{J}_{Kf} and \mathbf{J}_{Kb} functions, the projectors \mathcal{P}_{ff} , \mathcal{P}_{bb} act as the respective identities, but a transfer operator has the detailed effect

$$\mathcal{P}_{j\ell} \rho_\ell \mathbf{J}_{K\ell} = \frac{n_\ell}{n_j} \mathbf{J}_{Kj} \rho_j, \quad (5.52)$$

having a density ratio introduced as well as the desired transfer of polarization from one species to the other as a result of the relative concentration of each species.

There remains the evaluation of the \mathbf{Y}_j and the b_j within the two moment approximation. Clearly the \mathbf{Y}_j matrix elements are

$$\begin{aligned} y_f &\equiv \frac{1}{2\alpha+1} \text{Tr}_f \mathbf{J}_{Kf} \mathbf{Y}_f = \mathcal{R}_{ff} + \mathcal{R}_{fb}, \\ y_b &\equiv \frac{1}{2\alpha+1} \text{Tr}_b \mathbf{J}_{Kb} \mathbf{Y}_b = \mathcal{R}_{bf} + \mathcal{R}_{bb}. \end{aligned} \quad (5.53)$$

The two moment solution is the scalar analog of Eqs. (5.47). For b_f this is

$$\begin{aligned}
b_f &= \frac{1}{m_{ff} - m_{fb}m_{bb}^{-1}m_{bf}} (y_f - m_{fb}m_{bb}^{-1}y_b) \\
&= \frac{\mathcal{R}_{ff} + \mathcal{R}_{fb} + \frac{i}{z}(\mathcal{R}_{ff}\mathcal{R}_{bb} - \mathcal{R}_{fb}\mathcal{R}_{bf})}{1 + \frac{i}{z}[X_b(\mathcal{R}_{ff} - \mathcal{R}_{bf}) + X_f(\mathcal{R}_{bb} - \mathcal{R}_{fb})]} \\
&\xrightarrow{z \rightarrow 0} \frac{\mathcal{R}_{ff}\mathcal{R}_{bb} - \mathcal{R}_{fb}\mathcal{R}_{bf}}{X_b(\mathcal{R}_{ff} - \mathcal{R}_{bf}) + X_f(\mathcal{R}_{bb} - \mathcal{R}_{fb})}
\end{aligned} \tag{5.54}$$

and an analogous equation for b_b by interchanging indices. Finally the transport coefficient is

$$\begin{aligned}
\frac{n^2 B}{\sigma} &= n_f b_f + n_b b_b \\
&= \frac{(n_f + n_b)(\mathcal{R}_{ff}\mathcal{R}_{bb} - \mathcal{R}_{fb}\mathcal{R}_{bf})}{X_b(\mathcal{R}_{ff} - \mathcal{R}_{bf}) + X_f(\mathcal{R}_{bb} - \mathcal{R}_{fb})}.
\end{aligned} \tag{5.55}$$

This is the standard result of the lowest order approximation for the transport coefficient of a mixture derived from the Boltzmann equation [7], and is also in agreement with the transport coefficient for a mixture derived previously via the time correlation function approach in Sections 3.4 and 4.6. It should be noted that this expression arises solely from the kinetic contributions to the flux function \mathbf{J} .

5.4 The Kawasaki - Oppenheim Treatment of Bound States

Aspects of the Kawasaki and Oppenheim treatment of systems with attractive potentials and bound states were discussed in Sec. 3.5. Further discussion with reference to the work of this chapter follows.

From the time correlation function formalism Kawasaki and Oppenheim [53] derived first order density corrections to the shear viscosity of a gas with an attractive intermolecular potential. Their work is based on an atomic picture with no explicit emphasis on bound pairs in the classical distribution function used for calculating the thermal averages. They make no connection to the standard expression for the viscosity of a mixture so it is difficult to compare the final expressions obtained here with their results. Within our limited understanding of their treatment, we try to make some comparison between their approach and the present treatment.

Kawasaki and Oppenheim carry out a generalization of Zwanzig's binary collision expansion [52] of the full resolvent $1/(z - \mathcal{L})$ for the N -particle system. This produces an infinite

series in the divergent parameter $1/\epsilon$, which is subsequently resummed (assuming that such a resummation is valid) before taking the limit $\epsilon \rightarrow 0$. Since the resummation is carried out on the resolvent, the result is an operator inverse whose action on the flux function is obtained only by successively solving integral equations, each of which is of the form of the linearized Boltzmann equation. Hamer and Oppenheim [59] reexpress the integral equations derived by them in terms of kinetic equations as they might appear in gas kinetic theory. In contrast, the present approach formally avoids any such infinite series, and within the two moment approximation of Eq. (5.48), there is no need to solve an integral equation. In that way, the present procedure is directly computational. If a more accurate evaluation of a transport coefficient is desired, then matrix inversions are required. The present approach does however involve terms which are of order $1/\epsilon$, so again the set of equations must be solved (or more appropriately reorganized) before the $\epsilon \rightarrow 0$ limit is taken. But now this involves only the inversion of a 2×2 matrix rather than an infinite series resummation.

The first order density corrections derived by Kawasaki and Oppenheim include contributions from both kinetic and potential parts of the momentum flux and account for both the presence of bound states and collision nonlocalities. But their treatment is to first order in the density of the atoms rather than to first order in the density of the molecules. In this way their results are limited to having a small mole fraction of dimers. Moreover, their bound state contributions have only been explicitly stated for the cross effects between the kinetic and potential fluxes whereas the present treatment is based entirely on kinetic flux contributions and does not address the effects of either potential contributions or collision nonlocalities. It is puzzling why their three particle collision contribution in the purely kinetic flux term has not been further decomposed to explicitly include bound free collision contributions to the viscosity. Correctly there are potential and collision nonlocality contributions to the transport coefficients, but at low *molecular* density, the dominant contributions should be of purely kinetic origin. This is what is obtained here and discussed in the kinetic theory literature [7]. The inclusion of potential, collision nonlocality and termolecular collision contributions via the present approach requires a careful separation of bound and unbound motion. The emphasis of the present chapter is in understanding how to completely include bound pairs at low density.

Kawasaki and Oppenheim's approach is phrased in classical mechanics, and consistent with that, their definition of a bound state is in terms of whether the isolated pair should stay forever within each other's force range. They also note the possible importance of unbound states whose lifetimes are long compared to the mean free time of particles in the gas. While the role of states with finite but long lives can be important, and difficult to know how

to efficiently approximate, the mathematical consequences of being bound or unbound are significant. The quantum case is especially clear with the spectrum of the (pair) Hamiltonian H_{12} for *relative* motion being either discrete and negative, $\varepsilon_b < 0$, or continuous and positive, \mathbf{p}^2/m , neglecting the possibility of internal motions for the individual particles. [The reduced mass of the pair is $m/2$.] The corresponding states are complete in the sense that any (pair particle) state $|\Psi\rangle$ can be expressed as a linear combination of them

$$|\Psi\rangle = \sum_b |b\rangle \langle b|\Psi\rangle + \int d\mathbf{p} |\psi_{\mathbf{p}}\rangle \langle \psi_{\mathbf{p}}|\Psi\rangle, \quad (5.56)$$

where $|b\rangle$ is the *bound* state and $|\psi_{\mathbf{p}}\rangle$ is a scattering state associated with incoming relative momentum \mathbf{p} , all with appropriate normalization. It is the consequent structure of the resolvent $1/(z - \mathcal{L}_{12})$ for the pair that is of importance in calculating the transport coefficients. Restricted to relative motion (for simplicity of presentation), the action of this resolvent superoperator on an arbitrary operator O is

$$\begin{aligned} \frac{1}{z - \mathcal{L}_{12}} O &= \sum_{b,b'} |b\rangle \frac{O_{bb'}}{z - \varepsilon_b + \varepsilon_{b'}} \langle b'| + \sum_b \int d\mathbf{p}' |b\rangle \frac{O_{b\mathbf{p}'}}{z - \varepsilon_b + \mathbf{p}'^2/m} \langle \psi_{\mathbf{p}'}| \\ &\quad + \sum_{b'} \int d\mathbf{p} |\psi_{\mathbf{p}}\rangle \frac{O_{\mathbf{p}b'}}{z - \mathbf{p}^2/m + \varepsilon_{b'}} \langle b'| \\ &\quad + \iint d\mathbf{p} d\mathbf{p}' |\psi_{\mathbf{p}}\rangle \frac{O_{\mathbf{p}\mathbf{p}'}}{z - \mathbf{p}^2/m + \mathbf{p}'^2/m} \langle \psi_{\mathbf{p}'}|. \end{aligned} \quad (5.57)$$

It is only the first term with both ket and bra states bound that has isolated poles. These occur at the energy differences (frequencies) between the bound states. This is the analog of the discussion in Appendix A of Ref. [53]. All such singularities need to be avoided, or if they occur, then (in transport coefficient calculations) there should be a resummation procedure that leads to a finite result. The method used in the present work is to never expand in terms of the pair Liouville resolvent when the corresponding bound state is present. Rather it was chosen to immediately go to three or four particle resolvents, to describe how the bound state collides with a free particle or another bound pair, see Eqs. (5.41) and (5.43).

5.5 Discussion

To account for bound pairs in the time correlation function formalism, the density operator used in calculating the ensemble average of the flux function must reflect the presence of bound pairs. This can take the form of a mixture of two species, as done in Chapter 4, but such an approach does not reflect the atomic makeup of the bound pairs. In contrast, the present treatment includes just those parts of the pair Ursell operator that correspond to the

pair being bound. This "atomic" picture of the free and bound pairs gives, see Eq. (5.55), the same low density transport coefficient as obtained in Section 4.6 from the "molecular" picture of a mixture, or by solving the Boltzmann equation [7] for the pair of species.

The method presented here for the reduction of the time correlation function, correctly its Laplace transform, to an expression in terms of binary collision cross sections depends on the introduction of several procedures, most of which were used in Chapter 4. First is the introduction of the projection operator \mathcal{P} . This has the advantage of eliminating the infinite series expansions in $1/\epsilon$ and gives an equation for $1/\sigma$ in terms of the matrix element of an N -particle transition superoperator, Eq. (5.10), which is simplified for the dilute gas case to looking for the effect on a single particle, Eq. (5.15). Second is the binary collision expansion. This was straightforward in Chapter 4 where all particles are free, but here it requires first expanding the resolvent for $\mathcal{L}_\mathcal{P}$ in terms of the resolvent for \mathcal{L} so as to be able to recognize which pair of molecules are colliding, Eq. (5.15). It was the discovery of this obvious third procedure which allowed the various free and bound state collision processes to be identified. Fourth is the structure of the N -particle density operator, Eq. (5.7), so as to recognize the various states for particle 1. It is at this stage that the appropriate binary collision expansion is made, with either 2, 3 or 4-particle Liouville resolvents being introduced according to the nature of the binary collision. Finally there is the assumption of "promotion", whereby the density operator for the collision partner is moved through potential and resolvent terms so as to identify an isolated binary collision operator. This allows the trace over all N particles to be separated into that associated with the binary collision and the remainder. Its validity is based on the notion that molecules are independent before colliding and its use rules out the possible contribution of termolecular, etc. collisions and recollisions. But it is this separation into isolated binary collisions that allows the remaining pieces to be related to the primitive quantities and so to close the pair of equations and provide a formal expression of the transport coefficient in terms of binary collision cross sections.

Chapter 6

Moderately Dense Gas Shear Viscosity Coefficient via the Time Correlation Formulation

6.1 Introduction

In moderately dense gases, the viscosity is associated with both kinetic and potential contributions to the momentum flux. In this chapter the effect of both of these contributions on the viscosity coefficient are studied. As in Chapters 4 and 5, the first step is to determine proper projection operators. A key point for the development of this approach was the realization that the total momentum flux requires two separate projection operators, one for each of the kinetic and potential components of the momentum flux. This is required because these two flux components have different convergence properties and must be treated in distinct manners. At these densities, it is also necessary to include spatial correlations due to the intermolecular potential in the equilibrium N -particle distribution function of the system. The properties of the reduced distribution functions with the inclusion of spatial correlations are reviewed in Section 6.2. In this chapter, it is assumed that the intermolecular forces are repulsive in nature. This prevents the formation of bound states and makes the integrals over binary collision operators finite. In this respect, the scope of this work is similar to that of Snider and Curtiss [19], along with the added corrections of Hoffman and Curtiss [22]. The expressions for the first order density corrections that they obtain are stated for reference. In Section 6.3 the projection operators for the viscosity in the presence of potential contributions to the momentum flux are introduced. These projection operators involve separate projections onto the kinetic and potential components of the N -particle phase space of the system. In this section and Section 6.4 the calculation of the viscosity coefficient is formulated as a matrix inversion problem and the forms of the matrix elements that need

to be calculated are given. These matrix elements are explicitly calculated in Section 6.5. The N -particle resolvents in the general expressions are simplified with a binary collision expansion and expressions for the matrix elements in terms of integrals over collision parameters of a binary collision are derived. Contributions from matrix elements give rise to forms which are consistent with the Snider and McCourt corrections along with the additional Hoffman and Curtiss correction, and a density correction related to three particle collisions. The corrections are put together in Section 6.6 where it is demonstrated that within a comparable set of approximations, the present theory gives density corrections consistent with those of the generalized Boltzmann equation. The chapter concludes with a discussion. The appendices provide details of a number of the identifications made throughout the work.

6.2 Distribution Function for the N -Particle System and Shear Viscosity

The N -particle distribution function of the system is assumed to be normalized to unity,

$$\text{Tr}_{1\dots N}\rho^{(N)} = 1. \quad (6.1)$$

The normalization convention chosen for reduced distribution functions is

$$\rho^{(s)} = \frac{N!}{(N-s)!} \text{Tr}_{s+1\dots N}\rho^{(N)}. \quad (6.2)$$

The one-particle and two-particle reduced distribution functions are of interest and can be determined to various levels of approximation. The one-particle reduced distribution function is given as,

$$\rho_i^{(1)} = Ne^{-\beta H_i^{(1)}}/Q_1 = n\varphi_i \quad (6.3)$$

with $Q_1 = V/\Lambda^3$ as the one-particle partition function and $\Lambda \equiv h/\sqrt{2\pi mkT}$ as the thermal de Broglie wavelength. The normalized Maxwellian momentum distribution is $\varphi_i = \Lambda^3 e^{-\beta H_i^{(1)}}$. From Eq. (6.2), $\rho_i^{(1)}$ is normalized to the number of particles in the system,

$$\text{Tr}_i \rho_i^{(1)} = N = nV. \quad (6.4)$$

To lowest order in density, the two-particle reduced distribution function is,

$$\rho_{12}^{(2)} = \rho_1^{(1)}\rho_2^{(1)} + n^2\Lambda^6 U_{12}^{(2)} \quad (6.5)$$

expressed in terms of the 2-particle Ursell function,

$$U_{jk}^{(2)} = e^{-\beta H_{jk}^{(2)}} - e^{-\beta(H_j^{(1)}+H_k^{(1)})}. \quad (6.6)$$

This simplifies to,

$$\begin{aligned}\rho_{12}^{(2)} &= n^2 \varphi_1 \varphi_2 + n^2 \Lambda^6 U_{12}^{(2)} \\ &\approx \left[n^2 + n^2 \left(e^{-\beta u_{12}} - 1 \right) \right] \varphi_1 \varphi_2 \approx n^2 \varphi_1 \varphi_2 e^{-\beta u_{12}}.\end{aligned}\quad (6.7)$$

The next term in the density expansion of $\rho_{12}^{(2)}$ is required on several occasions. This term written as,

$$\rho_{12}^{(2)} = n^2 \varphi_1 \varphi_2 e^{-\beta u_{12}} Y_{[0]}(\mathbf{r}_{12}) \quad (6.8)$$

where $Y_{[0]}(\mathbf{r}_{12})$ is defined as

$$Y_{[0]}(\mathbf{r}_{12}) = 1 + n \int d\mathbf{r}_3 \left(e^{-\beta u_{13}} - 1 \right) \left(e^{-\beta u_{23}} - 1 \right) + O(n^2). \quad (6.9)$$

The Snider and Curtiss expression for the viscosity coefficient is,

$$\eta = \frac{1}{2} n k T b_0 \left[1 - \frac{4n\pi^{1/2}\sigma^3}{15} N_\eta + \frac{2n^2\sigma^4}{15} (\pi m k T)^{1/2} (H_\eta - R_\eta) \right], \quad (6.10)$$

where

$$b_0 = \frac{5}{4n\Omega^{(2,2)}} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta \right]. \quad (6.11)$$

Along with the Hoffman - Curtiss correction, the viscosity up to first order in density is of the following form,

$$\eta = \frac{5kT}{8\Omega^{(2,2)}} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta - \frac{4\pi^{1/2}}{15} n\sigma^3 N_\eta - \frac{n}{8\pi^2} \frac{R}{\Omega^{(2,2)*}} \right]. \quad (6.12)$$

The quantities in this expression were seen in Chapter 2 to be integrals over the collision parameters, and are thus stated in the most simple form for a general potential. It is the object of the present chapter to obtain a comparable expression for the first order density corrections from the time correlation function formula using the projection operator approach.

6.3 Projection Operators for Shear Viscosity

The thermal average “bra” and “ket” vector notation was introduced in Chapter 4. The notation used is quantum mechanical in nature, but in the following, explicit calculations are only done using classical mechanics. Thus the trace represents an integration over phase space and the notation $\rho^{(s)}$, usually reserved for the reduced density operator, is used for the distribution function. This allows the relations to be transcribed into a quantum formalism with ease.

For a dense gas, the transverse momentum flux tensor \mathbf{J} defined in Eq. (2.23), has both a kinetic and a potential part so that the phase function ket and bra are specifically

$$|\mathbf{J}\rangle\rangle = \left\{ \sum_j \frac{1}{m} [\mathbf{p}_j \mathbf{p}_j]^{(2)} - \sum_{j<\ell} \frac{du(r_{j\ell})}{dr_{j\ell}} \frac{1}{r_{j\ell}} [\mathbf{r}_{j\ell} \mathbf{r}_{j\ell}]^{(2)} \right\} \rho^{(N)}(\mathbf{r}^N, \mathbf{p}^N) \quad (6.13)$$

$$\langle\langle \mathbf{J} | = \iint d\mathbf{r}^N d\mathbf{p}^N \left\{ \sum_j \frac{1}{m} [\mathbf{p}_j \mathbf{p}_j]^{(2)} - \sum_{j<\ell} \frac{du(r_{j\ell})}{dr_{j\ell}} \frac{1}{r_{j\ell}} [\mathbf{r}_{j\ell} \mathbf{r}_{j\ell}]^{(2)} \right\} \quad (6.14)$$

Other than the momentum flux, the ket includes the N -particle distribution function and the bra includes an integration over N -particle phase space. The momentum and potential contributions denoted by the subscript K (kinetic) and V (potential) need to be treated separately. It is convenient to define the normalized components

$$\begin{aligned} \mathbf{J}_K &\equiv \sum_j \sqrt{2} [\mathbf{W}_j]^{(2)} \\ \mathbf{J}_V &\equiv \frac{-1}{A_V} \sum_{j<\ell} \frac{du(r_{j\ell})}{dr_{j\ell}} \frac{1}{r_{j\ell}} [\mathbf{r}_{j\ell}]^{(2)} \end{aligned} \quad (6.15)$$

chosen so that

$$\langle\langle \mathbf{J}_K | \mathbf{J}_K \rangle\rangle = \langle\langle \mathbf{J}_V | \mathbf{J}_V \rangle\rangle = N \mathbf{E}^{(2)}. \quad (6.16)$$

Here $\mathbf{W}_j = \mathbf{p}_j / \sqrt{2mkT}$ is the dimensionless momentum of particle j and $\mathbf{E}^{(2)}$ is the rotationally invariant tensor of rank four which acts as the Cartesian tensor identity for the five dimensional irreducible representation of rotation group $SO(3)$. The latter equalities follow from the rotational properties of the fluxes in the system (in the absence of external fields) along with the projector property of $\mathbf{E}^{(2)}$ discussed in Sec. 4.1. The numerical factors in Eqs. (6.15) are chosen in a manner so as to satisfy the normalization conditions. Thus by four-fold contraction into $\mathbf{E}^{(2)}$ it is seen that,

$$5N = \langle\langle \mathbf{J}_K : \mathbf{J}_K \rangle\rangle = \frac{2N}{\pi^{3/2}} \int d\mathbf{W}_1 [\mathbf{W}_1]^{(2)} : [\mathbf{W}_1]^{(2)} e^{-W_1^2} = \frac{4N}{3\pi^{3/2}} \int d\mathbf{W}_1 W_1^4 e^{-W_1^2} = 5N. \quad (6.17)$$

The normalization constant A_V is also determined from Eq. (6.16), by a four-fold contraction of both sides of the equation into $\mathbf{E}^{(2)}$,

$$\begin{aligned} 5N A_V^2 &= \frac{N(N-1)}{2} \iint d\mathbf{r}^N d\mathbf{p}^N \left(\frac{du_{12}}{dr_{12}} \right)^2 \frac{2}{3} r_{12}^2 \rho^{(N)} \\ &= \frac{4N(N-1)\pi}{3V} \int dr \left(\frac{du}{dr} \right)^2 r^4 g(r) \\ &\equiv 5N n \Gamma_\eta, \end{aligned} \quad (6.18)$$

where $g(r)$ is the radial distribution function. The normalization factor $A_V = \sqrt{n\Gamma_\eta}$ is seen to be,

$$\Gamma_\eta = \frac{4\pi}{15} \int dr \left(\frac{du}{dr} \right)^2 r^4 g(r). \quad (6.19)$$

Integration by parts, along with the use of the lowest order in density approximation for the radial distribution function, $g(r) = e^{-\beta u}$ relates this integral to the shear modulus at infinite frequency, G_∞ derived by Zwanzig and Mountain [91],

$$G_\infty = nkT + \frac{2\pi n^2}{15} \int_0^\infty dr e^{-\beta u} \frac{d}{dr} \left[r^4 \frac{du}{dr} \right]. \quad (6.20)$$

The kinetic and potential components of the momentum are also orthogonal,

$$\langle\langle \mathbf{J}_K | \mathbf{J}_V \rangle\rangle = \langle\langle \mathbf{J}_V | \mathbf{J}_K \rangle\rangle = 0. \quad (6.21)$$

In terms of these orthonormal components, the total momentum flux operator is,

$$\mathbf{J} = \sqrt{2}kT\mathbf{J}_K + A_V\mathbf{J}_V. \quad (6.22)$$

The subspace of the momentum flux is thus subdivided into kinetic and potential components. As is explained below, it is necessary to define separate projectors onto the kinetic and potential fluxes,

$$\begin{aligned} \mathcal{P}_K &= \frac{1}{N} |\mathbf{J}_K\rangle\rangle : \langle\langle \mathbf{J}_K | \\ \mathcal{P}_V &= \frac{1}{N} |\mathbf{J}_V\rangle\rangle : \langle\langle \mathbf{J}_V | \end{aligned} \quad (6.23)$$

with multiplication properties

$$\mathcal{P}_K\mathcal{P}_K = \mathcal{P}_K; \quad \mathcal{P}_V\mathcal{P}_V = \mathcal{P}_V; \quad \mathcal{P}_K\mathcal{P}_V = \mathcal{P}_V\mathcal{P}_K = 0. \quad (6.24)$$

The combined projector $\mathcal{P} \equiv \mathcal{P}_K + \mathcal{P}_V$, is also idempotent

$$\mathcal{P}\mathcal{P} = \mathcal{P} \quad (6.25)$$

and has the property that

$$\begin{aligned} \mathcal{P}|\mathbf{J}\rangle\rangle &= \mathcal{P}_K|\mathbf{J}\rangle\rangle + \mathcal{P}_V|\mathbf{J}\rangle\rangle \\ &= \sqrt{2}kT\mathcal{P}_K|\mathbf{J}_K\rangle\rangle + A_V\mathcal{P}_V|\mathbf{J}_V\rangle\rangle \\ &= \sqrt{2}kT|\mathbf{J}_K\rangle\rangle + A_V|\mathbf{J}_V\rangle\rangle \\ &= |\mathbf{J}\rangle\rangle, \end{aligned} \quad (6.26)$$

essentially because $|J\rangle\rangle$ is an element in the 2-dimensional operator space associated with \mathcal{P} , cf. Eq. (6.22).

The standard form of the viscosity coefficient in time correlation function theory is,

$$\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{B}{5V} \langle\langle J | \frac{i}{z - \mathcal{L}} J \rangle\rangle, \quad (6.27)$$

where $z \equiv i\epsilon$ and $B = 1/(2kT)$. From the properties of the projector \mathcal{P} , it is possible to insert \mathcal{P} both before and after the resolvent in this expression since only the part of the resolvent in the \mathcal{P} -space is needed in order to determine the transport coefficient. This has the advantage that by operator manipulations the projected resolvent can be calculated in terms of a related memory kernel, namely

$$\mathcal{P} \frac{i}{z - \mathcal{L}} \mathcal{P} = \frac{\mathcal{P}}{-iz + i\mathcal{P}\mathcal{L}\mathcal{P} + \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} (1 - \mathcal{P})\mathcal{L}\mathcal{P}}, \quad (6.28)$$

see Eq. (4.35). Moreover, it is easily proven that $\mathcal{P}\mathcal{L}\mathcal{P} = 0$, so that in the limit $z \rightarrow 0$, the projected resolvent is just the inverse of the memory kernel. Since the memory kernel is a direct product of a 2×2 matrix and the tensorial identity $\mathbf{E}^{(2)}$ of the 5-dimensional irreducible representation of the rotation group, the inverse must be carried out as a matrix. For this purpose it is convenient to introduce the 2-dimensional vector notation

$$|J_K\rangle\rangle \iff \begin{pmatrix} \sqrt{N} \\ 0 \end{pmatrix}; \quad |J_V\rangle\rangle \iff \begin{pmatrix} 0 \\ \sqrt{N} \end{pmatrix} \quad (6.29)$$

and the analogous row vectors

$$\langle\langle J_K| \iff (\sqrt{N} \ 0); \quad \langle\langle J_V| \iff (0 \ \sqrt{N}). \quad (6.30)$$

In this representation the total flux operator is represented according to

$$\begin{aligned} |J\rangle\rangle &\iff \sqrt{N} \begin{pmatrix} \sqrt{2kT} \\ A_V \end{pmatrix}, \\ \langle\langle J| &\iff \sqrt{N} (\sqrt{2kT} \ A_V). \end{aligned} \quad (6.31)$$

By using the two dimensional vector form of the projection operators, the memory kernel is represented by the 2×2 matrix

$$\mathcal{P}\mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P} \iff \frac{1}{N} \begin{pmatrix} \mathbb{M}_{KK} & \mathbb{M}_{KV} \\ \mathbb{M}_{VK} & \mathbb{M}_{VV} \end{pmatrix} \quad (6.32)$$

in which

$$\mathbb{M}_{\Theta\Phi} \equiv \frac{1}{5} \langle\langle J_\Theta | \overset{\alpha}{\odot} \mathcal{L} \frac{i}{z - \mathcal{L}_\mathcal{P}} \mathcal{L} J_\Phi \rangle\rangle, \quad (6.33)$$

and Θ and Φ represent kinetic (K) or potential (V) components. As in previous chapters, $\mathcal{L}_{\mathcal{P}} = (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})$. The inverse of this matrix is straightforward to determine,

$$\mathcal{P} \frac{i}{z - \mathcal{L}} \mathcal{P} \iff \frac{N}{\mathbb{M}_{KK}\mathbb{M}_{VV} - \mathbb{M}_{KV}\mathbb{M}_{VK}} \begin{pmatrix} \mathbb{M}_{VV} & -\mathbb{M}_{KV} \\ -\mathbb{M}_{VK} & \mathbb{M}_{KK} \end{pmatrix}. \quad (6.34)$$

The viscosity coefficient η is thus given in terms of the components of the memory kernel by

$$\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{N^2 B}{V} \frac{\left\{ (\sqrt{2}kT \quad A_V) \begin{pmatrix} \mathbb{M}_{VV} & -\mathbb{M}_{KV} \\ -\mathbb{M}_{VK} & \mathbb{M}_{KK} \end{pmatrix} \begin{pmatrix} \sqrt{2}kT \\ A_V \end{pmatrix} \right\}}{\mathbb{M}_{KK}\mathbb{M}_{VV} - \mathbb{M}_{KV}\mathbb{M}_{VK}} \quad (6.35)$$

where the factor of 5 is canceled by the trace of the identity $\mathbf{E}^{(2)}$ and all matrix elements are scalars. It remains to calculate these four matrix elements of the memory kernel.

Equation (6.35) appears complicated and it is appropriate to ask why the transport coefficient is treated with a 2-dimensional basis, Eq. (6.31), instead of with a simpler one-dimensional basis $|J\rangle$ with the corresponding projector,

$$\mathcal{P}_{\text{total}} \equiv A|J\rangle\langle J|. \quad (6.36)$$

Such a projector was investigated, but the subsequent calculations seemed to run into convergence problems that could not be eliminated. This seemed to indicate that in the calculation of the transport coefficient, the kinetic and potential components of the flux $|J\rangle$ should not be treated in the same manner. The 2-dimensional approach allows the kinetic and potential subspaces to be weighted differently, appropriate for their fundamentally different natures.

6.4 Reduction to Projected Liouville Superoperators

Two types of terms arise in the calculation of the viscosity coefficient, Eq. (6.27). These have the interesting property that while

$$\mathbb{Z}_{KK} \equiv \langle\langle J_K | \frac{i}{z - \mathcal{L}} J_K \rangle\rangle \quad (6.37)$$

leads to a binary collision expansion which is divergent, and so should be treated as in Chapter 4, the corresponding series for

$$\mathbb{Z}_{VV} \equiv \langle\langle J_V | \frac{i}{z - \mathcal{L}} J_V \rangle\rangle \quad (6.38)$$

is convergent. As a consequence of this differing behaviour, it is useful to expand the projected Liouville resolvent in the \mathbb{M} -matrix elements in terms of the resolvent of the kinetic

or potential projected Liouville superoperator. The $\mathbb{M}_{\Theta\Phi}$ involve the projected Liouville superoperator $\mathcal{L}_{\mathcal{P}} \equiv (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})$. In this case the projected Liouville superoperators

$$\mathcal{L}_K \equiv (1 - \mathcal{P}_K)\mathcal{L}(1 - \mathcal{P}_K), \quad (6.39)$$

$$\mathcal{L}_V \equiv (1 - \mathcal{P}_V)\mathcal{L}(1 - \mathcal{P}_V) \quad (6.40)$$

are the appropriate memory evolution superoperators if there was, respectively, only purely kinetic or potential fluxes. It is chosen to do the expansion according to associating the projection with the first index Θ of the matrix element,

$$\begin{aligned} \frac{1}{z - \mathcal{L}_{\mathcal{P}}} &= \frac{1}{z - \mathcal{L}_{\Theta}} [z - \mathcal{L}_{\mathcal{P}} + \mathcal{L}_{\mathcal{P}} - \mathcal{L}_{\Theta}] \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \\ &= \frac{1}{z - \mathcal{L}_{\Theta}} \left[1 - (\mathcal{L}\mathcal{P}_{\Theta} + \mathcal{P}_{\Theta}\mathcal{L}) \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \right]. \end{aligned} \quad (6.41)$$

The final equality uses $\mathcal{P}_{\Theta}\mathcal{L}\mathcal{P}_{\Phi} = 0$ for all combinations of Θ and Φ .

\mathbb{M}_{KK} then has the expansion

$$\begin{aligned} \mathbb{M}_{KK} &= \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \left[1 - (\mathcal{L}\mathcal{P}_V + \mathcal{P}_V\mathcal{L}) \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \right] \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rangle\rangle + \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_V \rangle\rangle \frac{i}{5N} \langle\langle \mathbf{J}_V : | \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &\quad + \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle \frac{i}{5N} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &\equiv \mathbb{K}_{KK} + \mathbb{K}_{KV} \frac{i}{N} \mathbb{M}_{VK}^R + \mathbb{K}_{KV}^L \frac{i}{N} \mathbb{M}_{VK}. \end{aligned} \quad (6.42)$$

The notation $\mathbb{K}_{\Theta\Phi}$ indicates that the Liouville superoperator in the resolvent is projected onto the $(1 - \mathcal{P}_K)$ subspace, and the two subscripts indicate the particular elements over which it is calculated. The L or R superscript indicates that the matrix element in question has only one Liouville superoperator appearing respectively on the left or the right of the projected resolvent.

The \mathbb{M}_{VK}^R matrix element vanishes. By the definition of \mathbb{M}_{VK}^R ,

$$\begin{aligned} 5\mathbb{M}_{VK}^R &= \langle\langle \mathbf{J}_V : | \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \langle\langle \mathbf{J}_V : | \frac{i}{z - \mathcal{L}_V} \left[1 - (\mathcal{L}\mathcal{P}_K + \mathcal{P}_K\mathcal{L}) \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \right] \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{i}{z} \langle\langle \mathbf{J}_V : | \mathcal{L} \mathbf{J}_K \rangle\rangle - \frac{i}{z} \langle\langle \mathbf{J}_V : | \mathcal{L} \mathbf{J}_K \rangle\rangle \frac{1}{5N} \langle\langle \mathbf{J}_K : | \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &\quad - \frac{i}{z} \langle\langle \mathbf{J}_V : | \mathbf{J}_K \rangle\rangle \frac{1}{5N} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{1}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= 0. \end{aligned} \quad (6.43)$$

This uses the facts that $\mathbf{J}_V \mathcal{L}_V = 0$ and the matrix elements $\langle\langle \mathbf{J}_V : | \mathbf{J}_K \rangle\rangle$ and $\langle\langle \mathbf{J}_V : | \mathcal{L} \mathbf{J}_K \rangle\rangle$ vanish. The resolvent $1/(z - \mathcal{L}_P)$ in \mathbb{M}_{VK}^R was expanded in terms of the resolvent projected onto the $(1 - \mathcal{P}_V)$ subspace which is associated with the first index of the matrix element.

\mathbb{M}_{VK} has the expansion

$$\begin{aligned}
\mathbb{M}_{VK} &= \frac{1}{5} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&= \frac{1}{5} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} \left[1 - (\mathcal{L} \mathcal{P}_K + \mathcal{P}_K \mathcal{L}) \frac{1}{z - \mathcal{L}_P} \right] \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&= \frac{1}{5} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_K \rangle\rangle + \frac{1}{5} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_K \rangle\rangle \frac{i}{5N} \langle\langle \mathbf{J}_K : | \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&\quad + \frac{1}{5} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathbf{J}_K \rangle\rangle \frac{i}{5N} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&\equiv \mathbb{V}_{VK} + \mathbb{V}_{VK} \frac{i}{N} \mathbb{M}_{KK}^R + \mathbb{V}_{VK}^L \frac{i}{N} \mathbb{M}_{KK}.
\end{aligned} \tag{6.44}$$

Clearly the quantities \mathbb{M}_{KK} and \mathbb{M}_{VK} are coupled. By an exactly parallel argument to that of Eq. (6.43), the \mathbb{M}_{KK}^R element is

$$\begin{aligned}
5\mathbb{M}_{KK}^R &= \langle\langle \mathbf{J}_K : | \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&= \langle\langle \mathbf{J}_K : | \frac{i}{z - \mathcal{L}_K} \left[1 - (\mathcal{L} \mathcal{P}_V + \mathcal{P}_V \mathcal{L}) \frac{1}{z - \mathcal{L}_P} \right] \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&= \frac{i}{z} \langle\langle \mathbf{J}_K : | \mathcal{L} \mathbf{J}_K \rangle\rangle - \frac{i}{z} \langle\langle \mathbf{J}_K : | \mathcal{L} \mathbf{J}_V \rangle\rangle \frac{1}{5N} \langle\langle \mathbf{J}_V : | \frac{1}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&\quad - \frac{i}{z} \langle\langle \mathbf{J}_K : | \mathbf{J}_V \rangle\rangle \frac{1}{5N} \langle\langle \mathbf{J}_V : | \mathcal{L} \frac{1}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_K \rangle\rangle \\
&= 0.
\end{aligned} \tag{6.45}$$

On this basis, the \mathbb{M} -matrix elements are expressed in terms of matrix elements of the subspace projected resolvents according to

$$\mathbb{M}_{KK} = \frac{\mathbb{K}_{KK} + \frac{i}{N} \mathbb{K}_{KV}^L \mathbb{V}_{VK}}{1 + \frac{1}{N^2} \mathbb{K}_{KV}^L \mathbb{V}_{VK}^L} \tag{6.46}$$

$$\mathbb{M}_{VK} = \frac{\mathbb{V}_{VK} + \frac{i}{N} \mathbb{V}_{VK}^L \mathbb{K}_{KK}}{1 + \frac{1}{N^2} \mathbb{K}_{KV}^L \mathbb{V}_{VK}^L}. \tag{6.47}$$

The remaining \mathbb{M} -matrix elements are evaluated in an analogous manner. First are the relations

$$\begin{aligned}
\mathbb{M}_{VV} &= \frac{1}{5} \langle\langle \mathbf{J}_V \mathcal{L} : | \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_V \rangle\rangle \\
&= \mathbb{V}_{VV} + \mathbb{V}_{VK} \frac{i}{N} \mathbb{M}_{KV}^R + \mathbb{V}_{VK}^L \frac{i}{N} \mathbb{M}_{KV}
\end{aligned}$$

$$\begin{aligned}
\mathbb{M}_{KV} &= \frac{1}{5} \langle\langle \mathbf{J}_K \mathcal{L} : | \frac{i}{z - \mathcal{L}_P} \mathcal{L} \mathbf{J}_V \rangle\rangle \\
&= \mathbb{K}_{KV} + \mathbb{K}_{KV} \frac{i}{N} \mathbb{M}_{VV}^R + \mathbb{K}_{KV}^L \frac{i}{N} \mathbb{M}_{VV},
\end{aligned} \tag{6.48}$$

which together with the evaluations $\mathbb{M}_{KV}^R = \mathbb{M}_{VV}^R = 0$, give

$$\mathbb{M}_{VV} = \frac{\mathbb{V}_{VV} + \frac{i}{N} \mathbb{K}_{KV} \mathbb{V}_{VK}^L}{1 + \frac{1}{N^2} \mathbb{K}_{KV}^L \mathbb{V}_{VK}^L} \tag{6.49}$$

$$\mathbb{M}_{KV} = \frac{\mathbb{K}_{KV} + \frac{i}{N} \mathbb{V}_{VV} \mathbb{K}_{KV}^L}{1 + \frac{1}{N^2} \mathbb{K}_{KV}^L \mathbb{V}_{VK}^L}. \tag{6.50}$$

The use of two subspace projection operators leads to a formal symmetry in the treatment of the kinetic and potential contributions.

The viscosity coefficient of Eq. (6.35), can be written in terms of the matrix elements of the subspace projected resolvents as

$$\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{N^2 B}{V} \frac{\left\{ \begin{aligned} &2(kT)^2 \left(\mathbb{V}_{VV} + \frac{i}{N} \mathbb{K}_{KV} \mathbb{V}_{VK}^L \right) + A_V^2 \left(\mathbb{K}_{KK} + \frac{i}{N} \mathbb{K}_{KV}^L \mathbb{V}_{VK} \right) \\ &-\sqrt{2} kT A_V \left(\mathbb{V}_{VK} + \mathbb{K}_{KV} + \frac{i}{N} \mathbb{V}_{VK}^L \mathbb{K}_{KK} + \frac{i}{N} \mathbb{V}_{VV} \mathbb{K}_{KV}^L \right) \end{aligned} \right\}}{\mathbb{K}_{KK} \mathbb{V}_{VV} - \mathbb{V}_{VK} \mathbb{K}_{KV}}. \tag{6.51}$$

It is noticed in particular that the common denominator in each of Eqs. (6.46, 6.47, 6.49) and (6.50) cancels out.

6.5 Binary Collision Expansions for the Matrix Elements

In this section, the matrix elements appearing in Eq. (6.51) are evaluated. Binary collision expansions of the resolvents are made and the order of density of the terms retained is indicated. Of the terms, those that contribute up to a first order density correction to the viscosity are explicitly evaluated. The terms \mathbb{K} with resolvents projected onto the $(1 - \mathcal{P}_K)$ subspace lead to divergences which are treated in a manner similar to that of Chapter 4. Evaluation of the \mathbb{K} terms gives rise to a series of higher moment corrections. The formal expression for these corrections is given, but no explicit evaluations of these corrections are attempted. The \mathbb{V} terms do not lead to the same divergences and are calculated directly.

6.5.1 Expansion of \mathbb{K}_{KV}^L

The kinetic term \mathbb{K}_{KV}^L has a structure that can be solved by iteration. The binary collision expansion of the resolvent in this term gives,

$$\begin{aligned}
5\mathbb{K}_{KV}^L &= \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle = N(N-1) \langle\langle \mathbf{J}_{K1} : | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle \\
&= N(N-1) \langle\langle \mathbf{J}_{K1} : | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \\
&\quad \times \left\{ 1 + [(1 + P_{12})(N-2)\mathcal{V}_{13} - \mathcal{P}_K \mathcal{L} - \mathcal{L} \mathcal{P}_K] \frac{1}{z - \mathcal{L}_K} \right\} \mathbf{J}_V \rangle\rangle \\
&= \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{B}_{KV}^L.
\end{aligned} \tag{6.52}$$

The tensorial operator \mathbf{B}_{KV}^L can be simplified by recognizing that $\langle\langle \mathbf{J}_K \frac{1}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle$ vanishes and separating the pair distribution function,

$$\rho_{12}^{(2)} = n^2 \varphi_1 \varphi_2 + \rho_{c12} \tag{6.53}$$

into uncorrelated and correlated parts, the uncorrelated part giving rise to the 1-particle kinetic projector $\mathcal{P}_0 \equiv \mathbf{J}_{K1}(\varphi_1/V) : \text{Tr}_1 \mathbf{J}_{K1}$. Thus

$$\begin{aligned}
\mathbf{B}_{KV}^L &\equiv N(N-1) \text{Tr}_{2..N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rho^{(N)} \\
&\approx \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L \\
&\quad - \frac{1}{N} \text{Tr}_2 \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{c12} \mathbb{K}_{KV}^L \\
&\equiv \mathbf{X}_V^L - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L - \mathbf{C} \mathbb{K}_{KV}^L,
\end{aligned} \tag{6.54}$$

where the approximation involves the “promotion” of φ_2/V through the $1/(z - \mathcal{L}_K)$ superoperator. This is done on the basis that, for a dilute system the opportunity for two particles to recollide is very small. Thus if particle 2 is to be involved in a collision with particle 1, it will not have been involved in any previous collision with particle 1. This procedure eliminates all possible contributions from either three or more particle dynamics or recollision events and also assumes the absence of bound states between the particle pair 1 and 2. Thus the calculations performed are for systems with potentials that do not support bound states.

After “promotion”, the dependence on particle 2 has been expressed in terms of the linearized Boltzmann collision superoperator

$$\mathcal{R}_1 \equiv \frac{in}{\varphi_1} \text{Tr}_2 \mathcal{T}_{12}(z) \varphi_1 \varphi_2 (1 + P_{12}), \tag{6.55}$$

involving the z parameterized transition superoperator

$$\mathcal{T}_{12}(z) \equiv \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (z - \mathcal{K}_{12}) = \mathcal{V}_{12} + \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12}. \quad (6.56)$$

In the limit $z = i\epsilon \rightarrow 0$, the z -parameterized transition superoperator $\mathcal{T}_{12}(z)$ converges to the abstract transition superoperator \mathcal{T}_{12} provided it acts on a function of momentum only. This is appropriate as it is used here since the trace over the remaining particles (3... N) gives a position independent quantity. For large N , the difference between N and $N - 1$ particles should be unimportant, with the consequence that this trace quantity can be approximated as \mathbf{B}_{KV}^L . A more explicit discussion of these points is presented in Chapters 4 and 5.

The tensorial operators \mathbf{X}_V^L and \mathbf{C} are defined by

$$\mathbf{X}_V^L \equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)}, \quad (6.57)$$

$$\mathbf{C} \equiv \frac{1}{N} \text{Tr}_2 \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{c12}. \quad (6.58)$$

Just as for \mathbf{B}_1 of Eq. (4.60), the equation for \mathbf{B}_{KV}^L has the structure

$$\mathbf{B}_{KV}^L = \mathbf{Y}_{KV}^L - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L \quad (6.59)$$

with $\mathbf{Y}_{KV}^L = \mathbf{X}_V^L - \mathbf{C} \mathbb{K}_{KV}^L$. By iteration or by similarity to the solution of Eq. (4.60), in the $z \rightarrow 0$ limit, \mathbf{B}_{KV}^L has the solution,

$$\mathbf{B}_{KV}^L = \mathbf{Y}_{KV}^L - \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{Y}_{KV}^L \quad (6.60)$$

where the projected linearized collision superoperator is

$$\mathcal{R}_K \equiv (1 - \mathcal{P}_0) \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0). \quad (6.61)$$

This implies that \mathbb{K}_{KV}^L in Eq. (6.52) satisfies

$$\begin{aligned} 5\mathbb{K}_{KV}^L &= \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{Y}_{KV}^L - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{Y}_{KV}^L \\ &= \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_V^L - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_V^L \\ &\quad - \left[\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C} \right] \mathbb{K}_{KV}^L \\ \mathbb{K}_{KV}^L &= \frac{\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_V^L - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_V^L}{5 + \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C}}. \end{aligned} \quad (6.62)$$

The final terms in the numerator and denominator are higher moment corrections due to successive binary collisions (Sonine corrections) to the terms preceding them. The order of density of the terms in Eq. (6.62) can be determined. Making use of the normalization of $\rho_{12}^{(2)}$ given in Eq. (6.7) and the density dependence of the subspace flux tensors of Eq. (6.15),

$$\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_V^L = \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} = O(N\sqrt{n}), \quad (6.63)$$

and

$$\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{C} = \frac{1}{N} \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{c12} = O(n). \quad (6.64)$$

The explicit form of this term is evaluated in Appendix E.

To the lowest order in density, in the one-moment approximation, \mathbb{K}_{KV}^L is given by,

$$\mathbb{K}_{KV}^L = \frac{1}{5} \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} = \frac{n^2 \Lambda^6}{5 A_V} \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} \frac{i}{z - \mathcal{L}_{\text{rel}}} [\mathbf{rF}]^{(2)} e^{-\gamma^2 - \mathcal{G}^2 - \beta u} \quad (6.65)$$

Evaluation of the result is aided by expressing the resolvent in terms of the associated time evolution superoperator,

$$\mathbb{K}_{KV}^L = \frac{n^2 \Lambda^6}{5 A_V} \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} : \int_0^\infty dt e^{i(z - \mathcal{L}_{\text{rel}})t} [\mathbf{rF}]^{(2)} e^{-\gamma^2 - \mathcal{G}^2 - \beta u}. \quad (6.66)$$

Ignoring for the moment the condition of taking the symmetric traceless part, the calculation of the time integral is carried out by following a binary collision trajectory according to

$$\lim_{z \rightarrow 0} \int_0^\infty dt e^{i(z - \mathcal{L}_{\text{rel}})t} \mathbf{rF} \rightarrow \int_0^\infty dt \mathbf{r}(-t) \mathbf{F}(-t) = - \lim_{s_0 \rightarrow \infty} \left[\mathbf{r}(-t) \mathbf{p}(-t) \Big|_0^{s_0} + \int_0^{s_0} dt \frac{\mathbf{p}(-t)}{m/2} \mathbf{p}(-t) \right] \quad (6.67)$$

by using Newton's second law and integrating by parts with respect to the time. This is reorganized as,

$$\begin{aligned} & \lim_{s_0 \rightarrow \infty} \left[\mathbf{r} \mathbf{p} - \mathbf{r}(-s_0) \mathbf{p}(-s_0) - \int_0^{s_0} dt \frac{\mathbf{p}(-t)}{m/2} \mathbf{p}(-t) \right] \\ &= \lim_{s_0 \rightarrow \infty} \left\{ \mathbf{r} \mathbf{p} - \left[\mathbf{r}(-s_0) + s_0 \frac{\mathbf{p}(-s_0)}{m/2} \right] \mathbf{p}(-s_0) \right. \\ & \quad \left. + \int_0^{s_0} dt \left[\frac{\mathbf{p}(-s_0)}{m/2} \mathbf{p}(-s_0) - \frac{\mathbf{p}(-t)}{m/2} \mathbf{p}(-t) \right] \right\}. \end{aligned} \quad (6.68)$$

Therefore the time integral contribution to Eq. (6.66) is,

$$\begin{aligned} \mathbb{K}_{KV}^L(\text{time}) &= \frac{n^2 \Lambda^6}{5 A_V} \text{Tr}_{12} \mathbf{J}_{K1} : \mathbf{V}_{12} : \int_0^{s_0} dt \left\{ \frac{[\mathbf{p}(-s_0)]^{(2)}}{m/2} - \frac{[\mathbf{p}(-t)]^{(2)}}{m/2} \right\} e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\ &= \frac{\sqrt{2} N n k T}{5 \pi^{3/2} A_V} \int d\mathbf{r} d\boldsymbol{\gamma} [\boldsymbol{\gamma}]^{(2)} : \mathbf{V}_{12} : \int_0^{s_0} dt \{ [\boldsymbol{\gamma}(-s_0)]^{(2)} - [\boldsymbol{\gamma}(-t)]^{(2)} \} e^{-\gamma^2 - \beta u} \end{aligned} \quad (6.69)$$

In evaluating the contributions to \mathbb{K}_{KV}^L from the remaining (non-time integral) terms in Eq. (6.68), it is first useful to symmetrize the kinetic flux with respect to particles 1 and 2,

$$\mathbf{J}_{K1} + \mathbf{J}_{K2} = \sqrt{2}\{[\mathcal{G}]^{(2)} + [\gamma]^{(2)}\}. \quad (6.70)$$

Integration over the center of mass position and momentum which are unchanged by the binary collision then becomes possible. The relative momentum is next integrated by parts and the non-integral terms in Eq. (6.68) contribute the corrections

$$\mathbb{K}_{KV}^L(\text{non-time}) = \frac{i\sqrt{2}Nn\Lambda_r^3}{5A_V} \text{Tr}_{\text{rel}}[\gamma\mathbf{F}]^{(2)} : \{[\mathbf{r}\gamma]^{(2)} - [\mathbf{r}'\gamma_0]^{(2)}\} e^{-\gamma^2 - \beta u}, \quad (6.71)$$

the first part of which simplifies to

$$\begin{aligned} \frac{i\sqrt{2}Nn\Lambda_r^3}{5A_V} \text{Tr}_{\text{rel}}[\gamma\mathbf{F}]^{(2)} : [\mathbf{r}\gamma]^{(2)} e^{-\gamma^2 - \beta u} &= \frac{i\sqrt{2}Nn\Lambda_r^3}{9A_V} \text{Tr}_{\text{rel}}\gamma^2 F r e^{-\gamma^2 - \beta u} \\ &= \frac{i\sqrt{2}}{A_V} N n k T B(T) \end{aligned} \quad (6.72)$$

while the second part is

$$-\frac{i\sqrt{2}Nn\Lambda_r^3}{5mA_V} \text{Tr}_{\text{rel}}[\gamma\mathbf{F}]^{(2)} : [\mathbf{r}'\gamma_0]^{(2)} e^{-\gamma^2 - \beta u} = \frac{i\sqrt{2}Nn}{5\pi^{3/2}A_V} \left(\frac{-4\pi k T \sigma^3}{3} \right) F_\eta \quad (6.73)$$

whose association with F_η follows from Appendix A.

In summary, to the lowest order in density,

$$\mathbb{K}_{KV}^L = \frac{i\sqrt{2}Nn k T}{A_V} \left[B(T) - \frac{4\sigma^3}{15\pi^{1/2}} F_\eta \right] + \mathbb{K}_{KV}^L(\text{time}) \quad (6.74)$$

6.5.2 Expansion of \mathbb{K}_{KV}

The binary collision expansion of \mathbb{K}_{KV} is carried out in a similar manner,

$$\begin{aligned} 5\mathbb{K}_{KV} &= \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_V \rangle\rangle \\ &= N(N-1) \langle\langle \mathbf{J}_{K1} : | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \\ &\quad \times \left\{ 1 + [(1 + P_{12})(N-2)\mathcal{V}_{13} - \mathcal{P}_K \mathcal{L} - \mathcal{L} \mathcal{P}_K] \frac{1}{z - \mathcal{L}_K} \right\} \mathcal{L} \mathbf{J}_V \rangle\rangle \\ &= \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{B}_{KV}. \end{aligned} \quad (6.75)$$

The definition and solution of \mathbf{B}_{KV} is similar to that for \mathbf{B}_{KV}^L in Eq. (6.54), with the resulting expansion of \mathbb{K}_{KV} in the binary collision approximation as in Eq. (6.62), namely

$$\mathbb{K}_{KV} = \frac{\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_V - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_V}{5 + \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C}}. \quad (6.76)$$

This involves the same C operator as in Eq. (6.58) but has X_V^L replaced by

$$X_V \equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} J_{V12} \rho_{12}^{(2)}. \quad (6.77)$$

Again the only approximation used to arrive at this result is the “promotion” of φ_2/V . The last two terms in the denominator and numerator of Eq. (6.76) give successive binary collision corrections as stated in Section 6.5.1. In this case the $\text{Tr}_1 J_{K1} : X_V$ term vanishes,

$$\begin{aligned} \text{Tr}_1 J_{K1} : X_V &= \text{Tr}_{12} J_{K1} : \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} J_{V12} \rho_{12}^{(2)} \\ &= n^2 \Lambda^6 \text{Tr}_{12} J_{K1} : \mathcal{V}_{12} e^{-\beta H_{12}^{(2)}} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} J_{V12} Y_{[0]}(\mathbf{r}_{12}) \\ &= i n^2 \Lambda^6 \text{Tr}_{12} J_{K1} : \mathcal{V}_{12} e^{-\beta H_{12}^{(2)}} \left(-1 + \frac{z}{z - \mathcal{L}_{12}} \right) J_{V12} Y_{[0]}(\mathbf{r}_{12}) \\ &\rightarrow 0. \end{aligned} \quad (6.78)$$

The first integral (with -1) is odd in both position and momentum directions, so it vanishes on integration over phase space. The second integral gives a term proportional to z , which vanishes in the $z \rightarrow 0$ limit since both sides of the resolvent have functions which constrain the relative position. Thus \mathbb{K}_{KV} has no first order in density contribution.

6.5.3 Expansion of \mathbb{K}_{KK}

The \mathbb{K}_{KK} term is calculated at two levels of approximation. In Section 6.5.3.1, only binary collisions are retained to obtain the approximation shown by \mathbb{K}_{KK}^2 . This limitation is lifted in Section 6.5.3.2, to include collisions of up to three particles and an expression for \mathbb{K}_{KK}^3 is derived.

6.5.3.1. Retaining only two-particle collisions

The expansion of \mathbb{K}_{KK} follows similar lines to that of Section 6.5.1.

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{1}{5} \langle\langle J_K : \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} J_K \rangle\rangle \\ &= \frac{\text{Tr}_1 J_{K1} : X_K - \text{Tr}_1 J_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) X_K}{5 + \text{Tr}_1 J_{K1} : C - \text{Tr}_1 J_{K1} : \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) C}. \end{aligned} \quad (6.79)$$

This involves the same C operator as before, and X_K defined as,

$$X_K \equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (J_{K1} + J_{K2}) \rho_{12}^{(2)}. \quad (6.80)$$

The structure of Eq. (6.79) includes the same successive collision corrections as the previous two matrix elements. The order in particle number N and density n of the $\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_K$ term is determined by using Eqs. (6.7) and (6.15),

$$\text{Tr}_1 \mathbf{J}_{K1} : \mathbf{X}_K = \text{Tr}_{12} \mathbf{J}_{K1} : \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)} = O(Nn) \quad (6.81)$$

With the inclusion of the equilibrium pair correlations, \mathbb{K}_{KK}^2 is identified as the modified Boltzmann collision integral that Hoffman and Curtiss [22] used for estimating the effect of a third particle on the bimolecular Boltzmann collision operator in their generalization of the Enskog equation [92] to soft potentials. Their method for the approximate evaluation of this collision integral is followed here. The evaluation is based on assuming that the factor $Y_{[0]}$ defined in Eq. (6.9) changes little during the collision dynamics so it can be moved to the left of the resolvent, and since it is also only a function of the position, to the left of \mathcal{V}_{12} . With these approximations \mathbb{K}_{KK}^2 in the one-moment approximation is rewritten as

$$\mathbb{K}_{KK}^2 \approx \frac{n^2 \Lambda^6}{10} \text{Tr}_{12} \mathbf{J}_{K1} : Y_{[0]}(\mathbf{r}_{12}) \mathcal{V}_{12} e^{-\beta H_{12}^{(2)}} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} \sqrt{2} [\boldsymbol{\gamma}]^{(2)}, \quad (6.82)$$

which recognizes that the \mathbf{J}_K 's are momentum functions on which only \mathcal{V}_{12} acts. Moreover, after using Eq. (6.70), only the (reduced) relative momentum $\boldsymbol{\gamma}$ is affected by \mathcal{V}_{12} . A subsequent symmetrization of \mathbf{J}_{K1} on the left over particles 1 and 2, conversion to center of mass and relative coordinates and integration over the center of mass position and momentum is then performed. Only the relative motion integral (trace) remains, so the particle labels can be dropped while Λ_r is the thermal de Broglie wavelength for *relative* motion. Furthermore, the combination of operators

$$\lim_{\epsilon \rightarrow 0} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} = \Omega'_{12} - 1 \quad (6.83)$$

is identified in the limit as a restricted form of the Møller superoperator, with the prime denoting the restricted applicability, namely that this operator identity is only valid when acting on a function of the momentum, see Eq. (2.69). This implies that

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{i N n \Lambda_r^3}{5} \text{Tr}_{\text{rel}} [\boldsymbol{\gamma}]^{(2)} : Y_{[0]}(\mathbf{r}) \mathcal{V} e^{-\beta H_{\text{rel}}} (\Omega' - 1) [\boldsymbol{\gamma}]^{(2)} \\ &= - \frac{i N n \Lambda_r^3}{5} \text{Tr}_{\text{rel}} [\boldsymbol{\gamma}]^{(2)} : Y_{[0]}(\mathbf{r}) \mathcal{K} \Omega' e^{-\beta K_{\text{rel}}} [\boldsymbol{\gamma}]^{(2)}. \end{aligned} \quad (6.84)$$

In the final form, the “-1” term vanishes since it is odd in position and momentum directions. The Møller superoperator satisfies the intertwining relation

$$H_{\text{rel}} \Omega' = \Omega' K_{\text{rel}} \quad (6.85)$$

This intertwining relation has allowed the full Boltzmann factor after (to the left of) the Møller superoperator to be replaced by the kinetic Boltzmann factor before (to the right of) the Møller superoperator, i. e.

$$e^{-\beta H_{\text{rel}}} \Omega' = \Omega' e^{-\beta K_{\text{rel}}}. \quad (6.86)$$

The second intertwining relation used is

$$\mathcal{L}\Omega' = \Omega'\mathcal{K}, \quad (6.87)$$

which implies that in the present case

$$\mathcal{V}\Omega' e^{-\beta K_{\text{rel}}}[\gamma]^{(2)} = -\mathcal{K}\Omega' e^{-\beta K_{\text{rel}}}[\gamma]^{(2)}, \quad (6.88)$$

on the basis that the operator on which Ω' acts has zero \mathcal{K} eigenvalue.

With the identification that $\mathcal{K} = -i \frac{\mathbf{p}}{m/2} \cdot \frac{\partial}{\partial \mathbf{r}}$ and expressing the effect of Ω' in terms of the precollisional relative momentum $\Omega'\gamma \equiv \gamma' = \gamma_0$, an integration by parts of the position variable is carried out to give

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{-2Nn}{5m\pi^{3/2}} \iint d\Sigma \cdot \mathbf{p} d\gamma[\gamma]^{(2)} : e^{-\gamma'^2} [\gamma']^{(2)} \\ &+ \frac{2Nn}{5m\pi^{3/2}} \iint d\mathbf{r} d\gamma[\gamma]^{(2)} \mathbf{p} \cdot \frac{\partial Y_{[0]}}{\partial \mathbf{r}} : e^{-\gamma'^2} [\gamma']^{(2)}. \end{aligned} \quad (6.89)$$

The surface integral is proportional to the Chapman - Cowling omega integral [7, 62] $\Omega^{(2,2)}$, and/or the kinetic cross section for viscosity $\mathfrak{S}(20)$ [79],

$$\begin{aligned} \mathbb{K}_{KK}(\text{surf}) &= \frac{16Nn(\pi kT)^{1/2}}{5m^{1/2}} \int_0^\infty \int_0^\infty b db d\gamma \gamma^7 (1 - \cos^2 \chi) e^{-\gamma^2} \\ &= \frac{8Nn}{5} \Omega^{(2,2)} = Nn\langle v \rangle \mathfrak{S}(20). \end{aligned} \quad (6.90)$$

Finally the $Y_{[0]}$ dependent term is related to the Hoffman-Curtiss [22] $R(T)$ function

$$\mathbb{K}_{KK}(\text{Ydep}) = \frac{2Nn(kT)^{1/2}}{5m^{1/2}\pi^{3/2}} \iint d\mathbf{r} d\gamma \gamma \cdot \frac{\partial Y_{[0]}}{\partial \mathbf{r}} (\gamma \cdot \gamma')^2 e^{-\gamma^2 - \beta u} = \frac{2Nn^2(kT)^{1/2}\sigma^2}{5m^{1/2}\pi^{3/2}} R(T). \quad (6.91)$$

Thus, up to terms including linear in density corrections, \mathbb{K}_{KK}^2 is approximated by,

$$\mathbb{K}_{KK}^2 = \frac{8Nn}{5} \Omega^{(2,2)} + \frac{2Nn^2\sigma^2}{5m^{1/2}\pi^{3/2}} (kT)^{1/2} R(T) = \frac{8Nn}{5} \Omega^{(2,2)} \left\{ 1 + \sqrt{\frac{kT}{\pi m}} \frac{n\sigma^2 R(T)}{4\pi \Omega^{(2,2)}} \right\}. \quad (6.92)$$

The \mathbb{K}_{KK}^2 term produces the cross section appropriate to the viscosity along with a correction for the static presence of a third particle on this cross section. The result depends on two approximations, the first being that only binary collisions are considered, and the second that the $Y_{[0]}$ term is assumed constant during a collision.

6.5.3.2. Retaining three-particle collisions

In the case of a collision expansion of general order,

$$\mathbb{K}_{KK} = \frac{1}{5} \langle\langle \mathbf{J}_K : | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rangle\rangle = \frac{1}{5} \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{B}_{KK}, \quad (6.93)$$

the projected resolvent is first expanded in terms of the unprojected N -particle resolvent,

$$\begin{aligned} \mathbf{B}_{KK} &= N(N-1) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rho^{(N)} \\ &= N(N-1) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}} \left[1 - (\mathcal{P}_K \mathcal{L} + \mathcal{L} \mathcal{P}_K) \frac{1}{z - \mathcal{L}_K} \right] \mathcal{L} \mathbf{J}_K \rho^{(N)}. \end{aligned} \quad (6.94)$$

An expansion in this manner provides flexibility in choosing the number of particles taking part in a collision. This expansion was used in Chapter 5 in treating collisions among free molecules and bound pairs which involve different numbers of particles.

Two and three-particle collisions are next extracted from the general N -particle resolvent. The first step is the separation of the dynamics of the collision of the 12 pair from the N -particle resolvent,

$$\mathcal{V}_{12} \frac{i}{z - \mathcal{L}} = \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[1 + \sum_{j=3}^N \mathcal{V}_{1j} \frac{1}{z - \mathcal{L}} \right]. \quad (6.95)$$

Separating the two-particle collision contributions from the other contributions in \mathbf{B}_{KK} gives,

$$\begin{aligned} \mathbf{B}_{KK} &= N(N-1) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[1 - \mathcal{P}_K \mathcal{L} \frac{1}{z - \mathcal{L}_K} \right] \mathcal{L} \mathbf{J}_K \rho^{(N)} \\ &\quad + N(N-1)(N-2) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \\ &\quad \times \mathcal{V}_{13} \frac{1}{z - \mathcal{L}} \left[1 - \mathcal{P}_K \mathcal{L} \frac{1}{z - \mathcal{L}_K} \right] \mathcal{L} \mathbf{J}_K \rho^{(N)}. \end{aligned} \quad (6.96)$$

A further complete expansion of the N -particle resolvent in this expression has been carried out [93]. A simplified version is presented here which emphasizes three-particle interactions without considering further higher order interactions. The linearized Boltzmann collision superoperator \mathcal{R}_1 of Eq. (4.54) is recognized in the projected two particle term and a factor of $1/(z - \mathcal{L}_{13})$ is added and subtracted to the N -particle resolvent,

$$\begin{aligned} \mathbf{B}_{KK} &= \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)} + \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \mathcal{P}_0 \mathbf{B}_{KK} \\ &\quad + N(N-1)(N-2) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \\ &\quad \times \mathcal{V}_{13} \left(\frac{1}{z - \mathcal{L}} - \frac{1}{z - \mathcal{L}_{13}} + \frac{1}{z - \mathcal{L}_{13}} \right) \mathcal{L} \mathbf{J}_K \rho^{(N)} \\ &\quad - N(N-1)(N-2) \text{Tr}_{2\dots N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}} \mathcal{P}_K \mathcal{L} \frac{1}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rho^{(N)} \end{aligned} \quad (6.97)$$

In the part of the third term with $+(z - \mathcal{L}_{13})^{-1}$, the factor φ_2/V is promoted through the \mathcal{V}_{13} and $+(z - \mathcal{L}_{13})^{(-1)}$ superoperators and the structure of an \mathcal{R}_1 superoperator recognized in the remaining result. Furthermore, to limit the contributions of the remaining terms to first order in density, only triple collisions among three particles 1, 2 and 3 are retained. Within these approximations,

$$\begin{aligned} \mathbf{B}_{KK} = & \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)} - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KK} \\ & + \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \mathcal{V}_{13} \left(\frac{1}{z - \mathcal{L}_{123}} - \frac{1}{z - \mathcal{L}_{13}} \right) \mathcal{L}_{123} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \\ & - \text{Tr}_{23} \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \frac{1}{5N} \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{B}_{KK} \quad (6.98) \end{aligned}$$

This expression is simplified with the notation,

$$\begin{aligned} \mathbf{B}_{KK} = & \mathbf{Y}_{KK} - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KK} \\ & - \frac{1}{5N} \text{Tr}_{23} \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{B}_{KK}. \quad (6.99) \end{aligned}$$

The \mathbf{Y}_{KK} term contains the two-particle collision term and a three-particle collision term,

$$\begin{aligned} \mathbf{Y}_{KK} = & \mathbf{Y}_{KK}^2 + \mathbf{Y}_{KK}^3 \\ = & \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)} \\ & + \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \mathcal{V}_{13} \\ & \times \left(\frac{1}{z - \mathcal{L}_{123}} - \frac{1}{z - \mathcal{L}_{13}} \right) \mathcal{L}_{123} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)}. \quad (6.100) \end{aligned}$$

Equation (6.99) is solved by iteration. Retaining only the first iteration, and neglecting higher moment corrections represented by the second term on the right of Eq. (6.99), the solution is approximated as,

$$\begin{aligned} \mathbf{B}_{KK} = & \mathbf{Y}_{KK} \\ & - \frac{1}{5N} \text{Tr}_{23} \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{Y}_{KK}. \quad (6.101) \end{aligned}$$

The collision operator in the three-particle \mathbf{Y}_{KK}^3 term is further analysed in order to reduce it to one of the familiar three-body collision operators given in the literature. With the low density approximation $\rho_{123}^{(3)} = n^3 \varphi_1 \varphi_2 \varphi_3$ for the reduced three-particle distribution function,

$$\mathbf{Y}_{KK}^3 = \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (1 + P_{12}) \mathcal{V}_{13} \left[\frac{1}{z - \mathcal{L}_{123}} (\mathcal{V}_{12} + \mathcal{V}_{13} + \mathcal{V}_{23}) - \frac{1}{z - \mathcal{L}_{13}} \mathcal{V}_{13} \right]$$

$$\begin{aligned}
& \times (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \\
= & \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[(\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} - \mathcal{V}_{13} \frac{1}{z - \mathcal{L}_{13}} - \mathcal{V}_{23} \frac{1}{z - \mathcal{L}_{23}} \right] \\
& \times (z - \mathcal{L}_0) (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)}. \tag{6.102}
\end{aligned}$$

The identities,

$$\begin{aligned}
\frac{1}{z - \mathcal{L}_{123}} (\mathcal{V}_{12} + \mathcal{V}_{13} + \mathcal{V}_{23}) &= \frac{1}{z - \mathcal{L}_{123}} (z - \mathcal{L}_0) - 1 \\
\frac{1}{z - \mathcal{L}_{13}} \mathcal{V}_{13} &= \frac{1}{z - \mathcal{L}_{13}} (z - \mathcal{L}_0) - 1 \tag{6.103}
\end{aligned}$$

have been used. Recognizing the last two operator combinations of the bracket in Eq. (6.102) as transition operators \mathcal{T}_{13} and \mathcal{T}_{23} , the total operator in square brackets can be identified as I^G ; the triple collision operator in the form written by Green [94],

$$\begin{aligned}
\mathbf{Y}_{KK}^3(G) &= \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[(\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} (z - \mathcal{L}_0) - \mathcal{T}_{13} - \mathcal{T}_{23} \right] (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \\
&\equiv \text{Tr}_{23} I^G (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)}. \tag{6.104}
\end{aligned}$$

The \mathbf{Y}_{KK}^3 function of Eq. (6.104) is denoted as $\mathbf{Y}_{KK}^3(G)$ to emphasize the Green form of the operator which appears in its structure. According to calculations of Kawasaki and Oppenheim [95], the Green form of the triple collision operator can be written in terms of the Bogoliubov triple collision operator [10] and a correction term,

$$I^G = I^B - \Delta I, \tag{6.105}$$

which substituted in Eq. (6.104) leads to

$$\mathbf{Y}_{KK}^3(G) = \mathbf{Y}_{KK}^3(B) + \Delta \mathbf{Y}_{KK}^3. \tag{6.106}$$

The $\mathbf{Y}_{KK}^3(B)$ operator is defined as, see Ref. [95],

$$\begin{aligned}
\mathbf{Y}_{KK}^3(B) &= \text{Tr}_{23} \mathcal{V}_{12} \frac{i}{z' - \mathcal{L}_{12}} \left[(\mathcal{V}_{13} + \mathcal{V}_{23}) z \frac{1}{z - \mathcal{L}_{123}} - z \frac{1}{z - \mathcal{L}_{12}} (\mathcal{T}_{13} + \mathcal{T}_{23}) \right] \\
&\quad \times (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \\
&\equiv \text{Tr}_{23} I^B (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)}. \tag{6.107}
\end{aligned}$$

The explicit form of $\Delta \mathbf{Y}_{KK}^3$, with the limit of $s_0 \rightarrow -\infty$ implied is,

$$\Delta \mathbf{Y}_{KK}^3 = -\text{Tr}_2 \mathcal{V}_{12} \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] \text{Tr}_3 (\mathcal{T}_{13} + \mathcal{T}_{23}) (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \varphi_1 \varphi_2 \varphi_3. \tag{6.108}$$

Within a 1-moment approximation, the result of $\text{Tr}_3(\mathcal{T}_{13} + \mathcal{T}_{23})(\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3})\varphi_1\varphi_2\varphi_3$ is a scalar multiple of $(\mathbf{J}_{K1} + \mathbf{J}_{K2})\varphi_1\varphi_2$. Thus it is possible to insert the projection superoperator

$$\mathcal{P}_{12} \equiv (\mathbf{J}_{K1} + \mathbf{J}_{K2})\varphi_1\varphi_2 : \frac{1}{2V^2} \text{Tr}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \quad (6.109)$$

just before the transition superoperators to give,

$$\begin{aligned} \Delta Y_{KK}^3 &= \frac{-1}{2V^2} \text{Tr}_2 \mathcal{V}_{12} \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] (\mathbf{J}_{K1} + \mathbf{J}_{K2})\varphi_1\varphi_2 : \\ &\quad \text{Tr}_{123}(\mathbf{J}_{K1} + \mathbf{J}_{K2})(\mathcal{T}_{13} + \mathcal{T}_{23})(\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3})\varphi_1\varphi_2\varphi_3. \end{aligned} \quad (6.110)$$

The transition superoperator matrix element can be expressed in terms of the kinetic cross-section according to

$$\text{Tr}_{123}(\mathbf{J}_{K1} + \mathbf{J}_{K2})(\mathcal{T}_{13} + \mathcal{T}_{23})(\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3})\varphi_1\varphi_2\varphi_3 = -2in^3V^2\langle v \rangle \mathfrak{S}(20) \mathbf{E}^{(2)}. \quad (6.111)$$

So finally,

$$\Delta Y_{KK}^3 = in^3\langle v \rangle \mathfrak{S}(20) \text{Tr}_2 \mathcal{V}_{12} \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] (\mathbf{J}_{K1} + \mathbf{J}_{K2})\varphi_1\varphi_2. \quad (6.112)$$

Substituting the results of Eqs. (6.106) and (6.112) into Eq. (6.101), the following result is obtained for the three-particle kinetic matrix element \mathbb{K}_{KK}^3 ,

$$\mathbb{K}_{KK}^3 = \mathbb{K}_{KK}^2 + \mathbb{K}_{KK}^3(B) + \Delta \mathbb{K}_{KK}^3 \quad (6.113)$$

with \mathbb{K}_{KK}^2 defined in Eq. (6.92). $\mathbb{K}_{KK}^3(B)$ is the combination of the two terms of Eq. (6.101),

$$\begin{aligned} \mathbb{K}_{KK}^3(B) &= \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{Y}_{KK}^3(B) \\ &\quad - \frac{1}{5N} \text{Tr}_{123} \mathbf{J}_{K1} : \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} - \mathcal{V}_{23}) \frac{1}{z - \mathcal{L}_{123}} \\ &\quad \times (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \text{Tr}_1 \mathbf{J}_{K1} : \mathbf{Y}_{KK}. \end{aligned} \quad (6.114)$$

As suggested by the superscript, these terms give the contribution of three particle dynamics in the Bogoliubov form to the kinetic matrix element. To our knowledge, terms of this sort have not been numerically evaluated. Further study of these terms is of interest, but beyond the scope of the present work.

For $\Delta \mathbb{K}_{KK}^3$, it is seen that,

$$\begin{aligned} \Delta \mathbb{K}_{KK}^3 &= \frac{in^3\langle v \rangle \mathfrak{S}(20)}{5} \text{Tr}_{12} \mathbf{J}_{K1} : \mathcal{V}_{12} \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] (\mathbf{J}_{K1} + \mathbf{J}_{K2})\varphi_1\varphi_2 \\ &= \frac{iNn^2\Lambda_r^3}{5} \langle v \rangle \mathfrak{S}(20) \text{Tr}_{\text{rel}}[\boldsymbol{\gamma}]^{(2)} : \mathcal{V}_{12} \int_0^\infty dt \{ [\boldsymbol{\gamma}(-t)]^{(2)} - [\boldsymbol{\gamma}(-\infty)]^{(2)} \} e^{-\gamma^2 - \beta u} \\ &= \frac{iNn^2}{5\pi^{3/2}} \langle v \rangle \mathfrak{S}(20) \iint d\mathbf{r} d\boldsymbol{\gamma} [\boldsymbol{\gamma}]^{(2)} : \mathcal{V}_{12} \int_0^\infty dt \{ [\boldsymbol{\gamma}(-t)]^{(2)} - [\boldsymbol{\gamma}(-\infty)]^{(2)} \} e^{-\gamma^2 - \beta u}. \end{aligned} \quad (6.115)$$

It is to be noted that the structure of this term has a similarity to that of $\mathbb{K}_{KV}^L(\text{time})$, see Eq. (6.69).

6.5.4 Evaluation of \mathbb{V}_{VV}

From the relations of Section 6.4,

$$\mathbb{V}_{VV} = \frac{1}{5} \langle\langle \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_V \rangle\rangle. \quad (6.116)$$

Using the analogy with Eq. (4.35), it is seen that,

$$\mathbb{V}_{VV} = N^2 / \mathbb{Z}_{VV}. \quad (6.117)$$

The corresponding purely potential term is appropriately approximated by

$$\begin{aligned} \mathbb{Z}_{VV} &= \langle\langle \mathbf{J}_V : \frac{i}{z - \mathcal{L}} \mathbf{J}_V \rangle\rangle \\ &\approx \frac{1}{2} \text{Tr}_{12} \mathbf{J}_{V12} : \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} = O(N). \end{aligned} \quad (6.118)$$

The lowest density approximation to this quantity describes the two particle evolution of the potential flux associated with the pair of particles. It follows that in lowest order in density \mathbb{V}_{VV} is proportional to N and independent of n , which is sufficient for assessing the low density expansion of the viscosity.

6.5.5 Expansion of \mathbb{V}_{VK}

The matrix element \mathbb{V}_{VK} is simplified by using a binary collision expansion

$$\begin{aligned} 5\mathbb{V}_{VK} &= \langle\langle \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_V} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\ &= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \left\{ 1 + \frac{1}{z - \mathcal{L}_V} [(1 + P_{12})(N-2)\mathcal{V}_{13} - \mathcal{P}_V \mathcal{L} - \mathcal{L} \mathcal{P}_V] \right\} \\ &\quad \times \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}). \end{aligned} \quad (6.119)$$

Whenever a particle labeling on the ket is introduced, it is convenient to first move $\rho^{(N)}$ to the left of the Liouville superoperator before introducing the summation over the particle labeling. This is seen in the second equality. The expansion of $i/(z - \mathcal{L}_V)$ is made on the right side of the projected resolvent, and the $i/(z - \mathcal{L}_{12})$ is adjacent to the \mathbf{J}_K side of the matrix element. It is further noted that the $\mathcal{P}_V \mathcal{L}$ term vanishes. Continuing the simplification,

$$5\mathbb{V}_{VK} = \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2})$$

$$\begin{aligned}
& + \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \frac{1}{z - \mathcal{L}_V} (1 + P_{12}) (N-2) \mathcal{V}_{13} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& + \langle \langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_V \rangle \rangle \frac{i(N-1)}{10} \text{Tr}_{1\dots N} \mathbf{J}_V : \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& = (i) + (ii) + (iii)
\end{aligned} \tag{6.120}$$

The first term on the right of Eq. (6.120), has the following contribution at the lowest order in density,

$$(i) = \frac{Nn\Lambda_r^3}{2} \text{Tr}_{\text{rel}} \mathbf{J}_{V12} : e^{-\beta H_{\text{rel}}} \mathcal{L}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} \sqrt{2} [\gamma]^{(2)} + O(Nn\sqrt{n}) = O(Nn\sqrt{n}) \tag{6.121}$$

In the first term of (i), the operator combination $\frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12}$ is the Møller superoperator since it is operating on a function of the momenta. Using the intertwining relation, $\mathcal{L}\Omega = \Omega\mathcal{K}$, it is seen that this term is zero. The second term (ii) involves three particles and is also $O(Nn\sqrt{n})$.

The lowest order contribution to the third term of Eq. (6.120) is,

$$(iii) = 5\mathbb{V}_{VV} \frac{i}{10N} \text{Tr}_{12} \mathbf{J}_{V12} : \frac{i}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) = O(N\sqrt{n}). \tag{6.122}$$

Thus to the lowest order \mathbb{V}_{VK} is approximated by (iii), and both (i) and (ii) are dropped from further consideration.

$$\begin{aligned}
\mathbb{V}_{VK} &= \frac{-\mathbb{V}_{VV}}{10N} \text{Tr}_{12} \mathbf{J}_{V12} : \frac{1}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
&= -\mathbb{V}_{VV} \frac{\sqrt{2}n\Lambda_r^3}{10A_V} \text{Tr}_{\text{rel}} [\mathbf{r}\mathbf{F}]^{(2)} : e^{-\gamma^2 - \beta u} (\Omega - 1) [\gamma]^{(2)} \\
&= -\mathbb{V}_{VV} \frac{\sqrt{2}n\Lambda_r^3}{10A_V} \text{Tr}_{\text{rel}} \frac{1}{r} F e^{-\gamma_0^2} \left[(\mathbf{r} \cdot \boldsymbol{\gamma}_0)^2 - \frac{1}{3} r^2 \gamma_0^2 \right] \\
&= \mathbb{V}_{VV} \frac{\sqrt{2}kT}{A_V} \frac{4n\sqrt{\pi}\sigma^3}{15} N_\eta.
\end{aligned} \tag{6.123}$$

The identification of N_η is made in Appendix B.

6.5.6 Expansion of \mathbb{V}_{VK}^L

The resolvent in \mathbb{V}_{VK}^L can be expanded in a manner similar to that of the resolvent in \mathbb{V}_{VK} of the previous section.

$$\begin{aligned}
5\mathbb{V}_{VK}^L &= \frac{N(N-1)}{2} \langle \langle \mathbf{J}_V : | \mathcal{L} \frac{i}{z - \mathcal{L}_V} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rangle \rangle = O(N\sqrt{n}) \\
&= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \left\{ 1 + \frac{1}{z - \mathcal{L}_V} [(1 + P_{12})(N-2)\mathcal{V}_{13} - \mathcal{P}_V \mathcal{L} - \mathcal{L} \mathcal{P}_V] \right\}
\end{aligned}$$

$$\begin{aligned}
& \times \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& = \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& \quad + \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V : \mathcal{L} \frac{1}{z - \mathcal{L}_V} (1 + P_{12})(N-2) \mathcal{V}_{13} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& \quad + \langle \langle \mathbf{J}_V : \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_V \rangle \rangle \frac{i(N-1)}{10} \text{Tr}_{1\dots N} \mathbf{J}_V : \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
& = (i) + (ii) + (iii)
\end{aligned} \tag{6.124}$$

The lowest order density contribution is from (i),

$$(i) = \frac{1}{2} \text{Tr}_{12} \mathbf{J}_{V12} : \mathcal{L}_{12} \frac{i}{z - \mathcal{L}_{12}} \rho_{12}^{(2)}(\mathbf{J}_{K1} + \mathbf{J}_{K2}). \tag{6.125}$$

Using the commutation property of \mathcal{L}_{12} with the two-particle resolvent, this is simplified to,

$$\frac{\sqrt{2} N n i \Lambda_r^3}{2 A_V} \text{Tr}_{\text{rel}}[\mathbf{rF}]^{(2)} : e^{-\gamma^2 - \beta u} \frac{1}{z - \mathcal{L}_{\text{rel}}} \mathcal{V}[\gamma]^{(2)} = -\frac{\sqrt{2} N n i}{A_V} \frac{4}{3} \sqrt{\pi} \sigma^3 k T N_\eta \tag{6.126}$$

where calculations similar to those appearing in Eq. (6.123) were used for the identification of N_η .

The contribution of the three-particle term (ii) is neglected. The term (iii) of Eq. (6.124) is evaluated in Appendix F. The result is,

$$(iii) = -\sqrt{\frac{\pi m k T}{2}} \frac{4 i \mathbb{V}_{VV} n \sigma^4}{3 A_V} (H_\eta + R_\eta) \tag{6.127}$$

6.6 First Order Density Corrections Within the Two Moment Approximation

The general expression for the viscosity coefficient, considering the zero value of \mathbb{K}_{KV} , is obtained from Eq. (6.35)

$$\begin{aligned}
\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{N n B}{\mathbb{K}_{KK}} & \left[2(kT)^2 + \frac{A_V^2}{\mathbb{V}_{VV}} \left(\mathbb{K}_{KK} + \frac{i}{N} \mathbb{K}_{KV}^L \mathbb{V}_{VK} \right) \right. \\
& \left. - \sqrt{2} k T A_V \left(\frac{\mathbb{V}_{VK}}{\mathbb{V}_{VV}} + \frac{i}{N \mathbb{V}_{VV}} \mathbb{V}_{VK}^L \mathbb{K}_{KK} + \frac{i}{N} \mathbb{K}_{KV}^L \right) \right]. \tag{6.128}
\end{aligned}$$

Within the lowest order in density approximations of Section 6.5, the formula for the viscosity coefficient reduces to,

$$\eta \approx \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{N n k T}{\mathbb{K}_{KK}} \left[1 - \frac{A_V}{\sqrt{2} k T} \left(\frac{\mathbb{V}_{VK}}{\mathbb{V}_{VV}} + \frac{i}{N} \mathbb{K}_{KV}^L \right) \right] + O(n^2) \tag{6.129}$$

Within the three-particle approximation, the \mathbb{K}_{KK} term was found in Section 6.5.3 to be,

$$\begin{aligned}\mathbb{K}_{KK} &= \mathbb{K}_{KK}^2 + \Delta\mathbb{K}_{KK}^3 + \mathbb{K}_{KK}^3(B) \\ &= \frac{8Nn}{5}\Omega^{(2,2)} \left[1 + \frac{nR(T)}{8\pi^2\Omega^{(2,2)*}} + \frac{in}{5\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} [\boldsymbol{\gamma}]^{(2)} : \mathcal{V}_{12} \right. \\ &\quad \left. \times \int_0^\infty dt \left([\boldsymbol{\gamma}(-t)]^{(2)} - [\boldsymbol{\gamma}(-\infty)]^{(2)} \right) e^{-\gamma^2 - \beta u} \right] + \mathbb{K}_{KK}^3(B). \quad (6.130)\end{aligned}$$

The second contribution from Eq. (6.129) is found from Section 6.5.5 to be

$$\frac{-A_V}{\sqrt{2}kT} \frac{\mathbb{V}_{VK}}{\mathbb{V}_{VV}} = \frac{-A_V}{\sqrt{2}kT\mathbb{V}_{VV}} \mathbb{V}_{VV} \frac{\sqrt{2}kT}{A_V} \frac{4n\sqrt{\pi}\sigma^3}{15} N_\eta = -\frac{4n\sqrt{\pi}\sigma^3}{15} N_\eta. \quad (6.131)$$

Finally, the \mathbb{K}_{KV}^L contribution to Eq. (6.129) was determined in Section 6.5.1,

$$\begin{aligned}\frac{-A_V}{\sqrt{2}kT} \frac{i}{N} \mathbb{K}_{KV}^L &= \frac{-iA_V}{\sqrt{2}kTN} \left\{ \frac{i\sqrt{2}NnkT}{A_V} \left[B(T) - \frac{4\sigma^3}{15\pi^{1/2}} F_\eta \right] + \mathbb{K}_{KV}^L(time) \right\} \\ &= nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta \\ &\quad - \frac{in}{5\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} [\boldsymbol{\gamma}]^{(2)} : \mathcal{V} : \int_0^{s_0} dt \{ [\boldsymbol{\gamma}(-s_0)]^{(2)} - [\boldsymbol{\gamma}(-t)]^{(2)} \} e^{-\gamma^2 - \beta u} \quad (6.132)\end{aligned}$$

Substituting the results of Eqs. (6.130) - (6.132) back into Eq. (6.129), it is found that the two time integrals cancel each other and to the first order in density the viscosity becomes,

$$\eta = \frac{5kT}{8\Omega^{(2,2)}} \left[1 + nB(T) - \frac{4n\sigma^3}{15\pi^{1/2}} F_\eta - \frac{nR(T)}{8\pi^2\Omega^{(2,2)*}} - \frac{4n\pi^{1/2}\sigma^3}{15} N_\eta - n\mathbb{K}_{KK}^3(B) \right]. \quad (6.133)$$

6.7 Discussion

The density corrections of Eq. (6.133) are identical to those obtained by Snider and Curtiss from the generalization of the Boltzmann equation, Eq. (6.12). The assumptions and methods of the present approach are quite distinct from those used by Snider and Curtiss and the equivalence of the final results gives greater confidence as to their validity. Assessment of the approximations is also made easier by comparison of the two theories.

The formal expression (6.51) for the transport coefficient, together with the various contributions for the memory kernel matrix elements determined in Section 6.5 is fairly complicated. Inherent in the calculation of the latter has been the approximation of retaining only binary collisions, essentially that the gas density is low so that the final expressions should be interpreted as valid only over a limited range of density. It is a standard approach, and well known, that the retention of only a single moment for an unknown function gives a

good approximation when calculating dilute gas transport coefficients. Here there are two types of unknown functions, one term for each of the kinetic and potential flux functions constituting a two moment approximation. Since J_{K1} and J_{V12} arise naturally, these suggest themselves as the appropriate expansion functions.

The mathematical techniques of the present theory are entirely different from the Chapman - Enskog method and do not involve the solution of integral equations. In the Chapman - Enskog method, one begins with the Boltzmann equation and then utilizes the equations of change to derive equations that are associated with, momentum and temperature gradients. Perturbative solutions to the non-equilibrium distribution function are devised which are required to satisfy a number of orthogonality conditions. The perturbations are expanded in terms of Sonine polynomials of different order and the expansion coefficients can be determined to different levels of approximation. By substituting the explicit form of the non-equilibrium distribution function into the expressions for the pressure tensor and the heat flux vector, formulas for the transport coefficients are obtained. The assumption of limiting the dynamics to binary collisions has been made in deriving the form of the generalized Boltzmann equation, and the detailed dynamics of the binary collision enter in various steps of the calculation. In contrast, aspects of the equations of change have been dealt with when deriving the general time correlation function formulas, Eq. (2.29). Such relations are general and no assumption as to the nature of the dynamics have been made. The steps required for the evaluation of the transport coefficient from the time correlation formula are mostly dynamical in nature, and as such, the connection between the dynamical assumptions and the final form of the transport coefficient may seem more direct. There are complexities with regard to defining proper projection operators, but having done that, the link between dynamics and the final result is straightforward, if tedious, to implement.

The density corrections of the Snider and Curtiss treatment are based on formal generalizations of the Boltzmann equation derived by N. N. Bogoliubov and H. S. Green. The density corrections obtained here are derived directly from the general time correlation function arising naturally from the formulation.

Of the terms inside the bracket in Eq. (6.133), the first to fourth appear in the perturbation amplitude b_0 of the solution of the Boltzmann equation, and arise from the kinetic part of the pressure tensor. The b_0 factor is associated with the perturbation of the distribution function from the local Maxwellian form. In the present theory, these four terms all originate from matrix elements with a kinetic projected resolvent, $\mathbb{K}_{\Theta\Phi}$. These four terms also have analogs in the Enskog theory. Even for hard spheres, the fluid has a second virial coefficient and a third molecule affects the probability that two particles collide.

The collisional transfer contribution N_η , arises in the solution of the Boltzmann equation from the potential part of the pressure tensor. This contribution is independent of b_0 and so is not dependent on the perturbation of the local Maxwellian. In the present formalism, this correction originates from a matrix element with a potential projected resolvent, \mathbb{V}_{VK} . N_η is also present in the Enskog theory, but in a different functional form. For hard spheres, the finite volume of the molecules and thus the possibility of momentum transfer across a boundary without mass transfer leads to this contribution. For soft potentials, it is a momentum transfer of one layer of fluid to another via potential interactions (either attractive, or repulsive), again without the transfer of mass. In dense fluids, this is the major contribution to viscosity since the molecules are not free to move easily between layers. Physically, it is expected that the effect of this contribution will decrease with increasing temperature (except for hard spheres where the contribution is constant), while the kinetic contributions increase with temperature.

The correction for the presence of a third particle on the binary collision cross section is given in Eq. (6.91). The derivation of this term is straightforward and involves incorporating first order density corrections to the spatial distribution function of the system. The derivation of this correction by Hoffman and Curtiss [22] invokes a "factorization principle" to truncate the BBGKY equations. A similar assumption is not required in this case.

Numerical calculation of terms in Eq. (6.133), other than the $\mathbb{K}_{KK}^3(B)$ has been carried out by Rainwater and Friend [8] for the Lennard-Jones (12-6) potential. It was found to be more efficient to combine a number of the integrals involved in the corrections of Eq. (6.133) into a new set of quantities called the I 's in their work. It would be helpful at some stage to separate the combinations into the original terms in Eq. (6.133) and study their individual behaviors. This may provide physical insight into these terms and their relative contributions to the transport coefficients at different temperatures.

The explicit calculation of the transport coefficients via the time correlation function formulation, in terms of functionals of the intermolecular potential has been carried to the level of including all binary collision contributions. The components of this calculation involve the derivation of the lowest order transport coefficient along with its Sonine corrections in Chapter 4, the derivation of the transport coefficient for a binary mixture of free and bound molecules using both the molecular, Chapter 4 and the atomic pictures, Chapter 5, and the present calculation of first order density corrections including the potential flux contribution. Putting the calculation of the present chapter for repulsive forces together with the additive contribution of bound pairs from the binary mixture treatment takes the calculation of the viscosity to the state where the improvement of the Rainwater theory should be introduced.

As discussed in Chapter 2, this involves dividing the phase space of a colliding pair into bound pair and free molecule regions. The terms in Eq. (6.133) arise even for purely repulsive potentials, and the phase space integrations which they involve must be limited to regions where the colliding pair are not bound.

The next step in the procedure would be to incorporate bound pairs and potential flux effects in the same derivation. Although the details need to be worked out and most likely will require modifications in the structure of the theory, the method of approach introduced here should aid in carrying out such a procedure. This would require the explicit calculation of the three-body collision contributions of $\mathbb{K}_{KK}^3(B)$. The formation of bound pairs occurs as a result of "recombination" reactions which involve the collisions of three molecules. The cross section for the formation of bound pairs would need to be determined as would the cross section of decomposition, and rearrangement reactions. The inclusion of these reactive collisions will make a rigorous calculation of the transport coefficients much more complicated and will require much more detailed knowledge of three-particle collisions. The occurrence of bond forming and breaking reactions affects the momentum transfer in a non-equilibrium system and thus the viscosity, and also involves energy changes which affect the thermal conductivity of the gas. The magnitude of the energies involved in these reactions are such that at moderate temperatures, not many bound pair decompositions or rearrangements occur and so the assumption of a constant ratio of bound pairs to free molecules (equal to that of the system at equilibrium) is likely to be a realistic approximation. This is perhaps the reason why the Stogryn - Hirschfelder treatment of bound states is adequate for most purposes.

Chapter 7

Moderately Dense Gas Thermal Conductivity Coefficient via the Time Correlation Formulation

7.1 Introduction

This chapter follows rather closely the pattern of Chapter 6 for the calculation of the first order density corrections to the thermal conductivity. The results of the Snider and Curtiss theory for thermal conductivity [19] are given in Section 7.2. The kinetic and potential projection operators are constructed from the heat flux vector in Section 7.3. This requires extra care in the case of thermal conductivity as the enthalpy term in the heat flux vector has to be divided in such a manner as to make the kinetic and potential contributions to the heat flux orthogonal. The two projection operators allow the calculation of the thermal conductivity to be formulated as a matrix inversion problem. The necessary matrix elements are formally determined in Section 7.4 and simplified in Section 7.5. The results are put together to obtain an expression for the thermal conductivity coefficient in Section 7.6. Appendices provide details of a number of identifications made in this chapter.

7.2 Thermal Conductivity

The Snider - McCourt expression for thermal conductivity is composed of a number of components. The perturbation amplitude a_1 is given by Eqs. (12) and (15) of Snider and McCourt

$$a_1 = \frac{-15}{16n\Omega^{(2,2)}} \left(\frac{2kT}{m} \right)^{1/2} \left[1 + nB(T) - \frac{4n\sigma^3}{3\pi^{1/2}} F_\lambda \right]. \quad (7.1)$$

The expression for the thermal conductivity of a system of monatomic particles interacting with a repulsive intermolecular potential, but neglecting three-body collisions is given by their Eq. (26)

$$\lambda = \frac{-1}{4}nk \left(\frac{2kT}{m} \right)^{1/2} a_1 \left[5 - nT^2 \frac{d^2 B}{dT^2} - \frac{4}{3} \pi^{1/2} n \sigma^3 (N_\lambda - T_\lambda) \right] + \frac{1}{3} n^2 k \sigma^4 \left(\frac{\pi kT}{m} \right)^{1/2} (H_\lambda + R_\lambda - I_\lambda). \quad (7.2)$$

To the first order in density this is,

$$\lambda = \frac{15k(kT)}{32m\Omega(2,2)} \left[5 + 5nB(T) - \frac{20n\sigma^3}{3\pi^{1/2}} F_\lambda - \frac{4}{3} \pi^{1/2} n \sigma^3 N_\lambda - n \frac{7}{3} T \frac{dB}{dT} - n \frac{5}{3} T^2 \frac{d^2 B}{dT^2} \right] + \dots \quad (7.3)$$

This expression, along with the Hoffmann - Curtiss correction which approximates the effect of three-body collisions, applies only to gases with repulsive intermolecular potentials. Bound states can be taken into account by considering the system to be a mixture of free and bound pairs. If bound pairs are included, Rainwater [8] showed that the second virial coefficient and its derivatives which appear in Eq. (7.3) must be limited to the contributions from the free part of phase space to the total second virial coefficient. This thesis does not carry out such elaborations.

The goal of this chapter is to obtain an expression for the first order density correction to the thermal conductivity from the time correlation function formula utilizing the projection operator approach of the previous chapters for systems with a repulsive potential and to compare the results with Eq. (7.3).

7.3 Projection Operators for Thermal Conductivity

For a dense gas both the kinetic and potential components contribute significantly to the heat flux vector \mathbf{J} . The phase space function “ket” and “bra” vectors for the heat flux are specifically

$$|\mathbf{J}\rangle = \left\{ \sum_j \left(\frac{p_j^2}{2m} - h \right) \frac{\mathbf{p}_j}{m} + \frac{1}{2} \sum_{i \neq j} [\mathbf{r}_{ij} \mathbf{F}_{ij} + u(r_{ij}) \mathbf{U}] \cdot \frac{\mathbf{p}_i}{m} \right\} \rho^{(N)}(\mathbf{r}^N \mathbf{p}^N) \quad (7.4)$$

$$\langle\langle \mathbf{J} | = \iint d\mathbf{r}^N d\mathbf{p}^N \left\{ \sum_j \left(\frac{p_j^2}{2m} - h \right) \frac{\mathbf{p}_j}{m} + \frac{1}{2} \sum_{j \neq \ell} [\mathbf{r}_{j\ell} \mathbf{F}_{j\ell} + u(r_{j\ell}) \mathbf{U}] \cdot \frac{\mathbf{p}_j}{m} \right\}, \quad (7.5)$$

where \mathbf{U} is the unit tensor of rank two. For a monatomic gas, the enthalpy per molecule is to first order in density,

$$h = \frac{5}{2}kT + nkT \left[B(T) - T \frac{dB}{dT} \right]. \quad (7.6)$$

The enthalpy per molecule has been broken up into kinetic h_K , and potential h_V , contributions defined as,

$$h_K = \frac{5}{2}kT \quad h_V = nkT \left[B(T) - T \frac{dB}{dT} \right]. \quad (7.7)$$

To simplify future formulae, it is convenient to use the dimensionless momentum $\mathbf{W}_j = \mathbf{p}_j / \sqrt{2mkT}$ of particle j and also to define the dimensionless center of mass momentum, \mathcal{G} and relative momentum γ of the pair 12,

$$\begin{aligned} \mathbf{W}_1 + \mathbf{W}_2 &= \sqrt{2}\mathcal{G} & \mathbf{W}_1 - \mathbf{W}_2 &= \sqrt{2}\gamma \\ \mathbf{W}_1 &= \frac{1}{\sqrt{2}}(\mathcal{G} + \gamma) & \mathbf{W}_2 &= \frac{1}{\sqrt{2}}(\mathcal{G} - \gamma). \end{aligned} \quad (7.8)$$

The formalism requires that the kinetic and potential contributions to the heat flux, denoted by the subscript K and V respectively, be treated separately. It is convenient to define the normalized flux components,

$$\mathbf{J}_K \equiv \frac{2}{\sqrt{5}} \sum_j \left(W_j^2 - \frac{h_K}{kT} \right) \mathbf{W}_j \quad (7.9)$$

and

$$\mathbf{J}_V \equiv \frac{1}{2A_V} \sum_{j \neq \ell} \left[\mathbf{r}_{j\ell} \mathbf{F}_{j\ell} + \left(u_{j\ell} - \frac{2h_V}{N} \right) \mathbf{U} \right] \cdot \sqrt{2} \mathbf{W}_j \quad (7.10)$$

so that

$$\langle \langle \mathbf{J}_K | \mathbf{J}_K \rangle \rangle = \langle \langle \mathbf{J}_V | \mathbf{J}_V \rangle \rangle = NU. \quad (7.11)$$

The heat flux vector belongs to the three-dimensional irreducible representation of the rotation group and \mathbf{U} is the rotationally invariant second rank tensor which acts as the identity in that irreducible representation. In order to make the relations more compact u'_{jk} is defined as

$$u'_{j\ell} = u_{j\ell} - \frac{2h_V}{N}. \quad (7.12)$$

Equation (7.11) for the kinetic flux is confirmed by double contracting both sides of the equation into \mathbf{U} ,

$$3N = \frac{4}{5}N \int d\mathbf{W}_1 \left[W_1^6 - 5W_1^4 + \frac{25}{4}W_1^2 \right] \frac{e^{-W_1^2}}{\pi^{3/2}} = \frac{4}{5}N \left[\frac{105}{8} - \frac{75}{4} + \frac{75}{8} \right] = 3N. \quad (7.13)$$

The potential flux normalization constant A_V can be determined from Eq. (7.11) in a similar manner,

$$3NA_V^2 = \frac{1}{2} \iint d\mathbf{r}^N d\mathbf{p}^N \left[\sum_{j \neq \ell} \left(\mathbf{r}_{j\ell} \mathbf{F}_{j\ell} + u'_{j\ell} \mathbf{U} \right) \cdot \mathbf{W}_j \right].$$

$$\begin{aligned}
& \times \left[\sum_{j' \neq \ell'} \left(\mathbf{r}_{j'\ell'} \mathbf{F}_{j'\ell'} + u'_{j'\ell'} \mathbf{U} \right) \cdot \mathbf{W}_{j'} \right] \rho^{(N)} \\
& = \frac{Nn}{\pi^{3/2}} \iint d\mathbf{r}_{12} d\mathbf{g} [(\mathbf{r}_{12} \mathbf{F}_{12} + u'_{12} \mathbf{U}) \cdot \mathbf{g}] \cdot [(\mathbf{r}_{12} \mathbf{F}_{12} + u'_{12} \mathbf{U}) \cdot \mathbf{g}] e^{-\beta u - \mathbf{g}^2} + O(Nn^2) \\
& \approx \frac{Nn}{2} \int d\mathbf{r} \left[3u^2 - 2ru \frac{du}{dr} + \left(r \frac{du}{dr} \right)^2 \right] e^{-u/kT} + O(Nn^2) = 3Nn\Gamma_\lambda. \quad (7.14)
\end{aligned}$$

Thus

$$A_V = \sqrt{n\Gamma_\lambda}, \quad (7.15)$$

where Γ_λ is given by

$$\Gamma_\lambda = \frac{1}{2} \int d\mathbf{r} \left[3u - 2ru \frac{du}{dr} + \left(r \frac{du}{dr} \right)^2 \right] e^{-u/kT}. \quad (7.16)$$

The integrals with $2h_V/N$ are all of $O(1/N)$ and so are neglected in Eq. (7.14).

The components of the heat flux vector are furthermore orthogonal,

$$\langle\langle \mathbf{J}_K | \mathbf{J}_V \rangle\rangle = \langle\langle \mathbf{J}_V | \mathbf{J}_K \rangle\rangle = 0, \quad (7.17)$$

as can be verified by observing that

$$\begin{aligned}
\langle\langle \mathbf{J}_K \cdot \mathbf{J}_V \rangle\rangle &= \langle\langle \mathbf{J}_V \cdot \mathbf{J}_K \rangle\rangle \\
&= \frac{1}{A_V} \sqrt{\frac{2}{5}} \langle\langle \sum_\ell \left(W_\ell^2 - \frac{5}{2} \right) \mathbf{W}_\ell \cdot \left[\sum_{j \neq k} \left(\mathbf{r}_{jk} \mathbf{F}_{jk} + u'_{jk} \mathbf{U} \right) \cdot \mathbf{W}_j \right] \rangle\rangle \\
&= \frac{N(N-1)}{A_V} \sqrt{\frac{2}{5}} \langle\langle \left(W_1^2 - \frac{5}{2} \right) \mathbf{W}_1 \cdot [(\mathbf{r}_{12} \mathbf{F}_{12} + u'_{12} \mathbf{U}) \cdot \mathbf{W}_1] \rangle\rangle \\
&= \frac{Nn}{3\pi^{3/2} A_V} \sqrt{\frac{2}{5}} \int d\mathbf{r} \left(3u' - r \frac{du}{dr} \right) e^{-\beta u} \int d\mathbf{W}_1 \left(W_1^2 - \frac{5}{2} \right) W_1^2 e^{-W_1^2} = 0 \quad (7.18)
\end{aligned}$$

Both the momentum and position integrals vanish.

In terms of these orthonormal components, the total heat flux operator is,

$$\mathbf{J} = \sqrt{\frac{5kT}{2m}} kT \mathbf{J}_K + \sqrt{\frac{kT}{m}} A_V \mathbf{J}_V. \quad (7.19)$$

As in Chapter 6, separate projectors onto the kinetic and potential fluxes are defined,

$$\begin{aligned}
\mathcal{P}_K &= \frac{1}{N} |\mathbf{J}_K\rangle\rangle \cdot \langle\langle \mathbf{J}_K| \\
\mathcal{P}_V &= \frac{1}{N} |\mathbf{J}_V\rangle\rangle \cdot \langle\langle \mathbf{J}_V| \quad (7.20)
\end{aligned}$$

with multiplication properties

$$\mathcal{P}_K \mathcal{P}_K = \mathcal{P}_K; \quad \mathcal{P}_V \mathcal{P}_V = \mathcal{P}_V; \quad \mathcal{P}_K \mathcal{P}_V = \mathcal{P}_V \mathcal{P}_K = 0. \quad (7.21)$$

The combined projector $\mathcal{P} \equiv \mathcal{P}_K + \mathcal{P}_V$ is also idempotent,

$$\mathcal{P} \mathcal{P} = \mathcal{P} \quad (7.22)$$

and has the property that

$$\begin{aligned} \mathcal{P}|\mathbf{J}\rangle\rangle &= \mathcal{P}_K|\mathbf{J}\rangle\rangle + \mathcal{P}_V|\mathbf{J}\rangle\rangle \\ &= \sqrt{\frac{5kT}{2m}} kT \mathcal{P}_K|\mathbf{J}_K\rangle\rangle + \sqrt{\frac{kT}{m}} A_V \mathcal{P}_V|\mathbf{J}_V\rangle\rangle \\ &= \sqrt{\frac{5kT}{2m}} kT |\mathbf{J}_K\rangle\rangle + \sqrt{\frac{kT}{m}} A_V |\mathbf{J}_V\rangle\rangle \\ &= |\mathbf{J}\rangle\rangle \end{aligned} \quad (7.23)$$

essentially because $|\mathbf{J}\rangle\rangle$ is an element of the 2-dimensional operator space associated with \mathcal{P} .

The thermal conductivity coefficient is given in standard form as a time correlation function,

$$\lambda = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{B}{3V} \langle\langle \mathbf{J} \cdot \frac{i}{z - \mathcal{L}} \mathbf{J} \rangle\rangle, \quad (7.24)$$

where $z \equiv i\epsilon$ and $B = 1/(kT^2)$. From the properties of the projector \mathcal{P} , it is possible to insert \mathcal{P} both before and after the resolvent in this expression and it is recognized that only the part of the resolvent in the \mathcal{P} -space is needed in order to determine the transport coefficient. This has the advantage that by operator manipulations the projected resolvent can be calculated in terms of a related memory kernel, namely

$$\mathcal{P} \frac{i}{z - \mathcal{L}} \mathcal{P} = \frac{\mathcal{P}}{-iz + i\mathcal{P}\mathcal{L}\mathcal{P} + \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} (1 - \mathcal{P})\mathcal{L}\mathcal{P}}. \quad (7.25)$$

Moreover, it is easy to prove that $\mathcal{P}\mathcal{L}\mathcal{P} = 0$, so that in the limit $z \rightarrow 0$, the projected resolvent is just the inverse of the memory kernel. Since the memory kernel is a direct product of a 2×2 matrix and the tensorial identity $E^{(1)}$ of the 3-dimensional irreducible representation of the rotation group, the inverse must be carried out as a matrix. For this purpose it is convenient to introduce the 2-dimensional vector notation

$$|\mathbf{J}_K\rangle\rangle \Longleftrightarrow \begin{pmatrix} \sqrt{N} \\ 0 \end{pmatrix}; \quad |\mathbf{J}_V\rangle\rangle \Longleftrightarrow \begin{pmatrix} 0 \\ \sqrt{N} \end{pmatrix} \quad (7.26)$$

and the analogous row vectors

$$\langle\langle \mathbf{J}_K | \Longleftrightarrow (\sqrt{N} \quad 0); \quad \langle\langle \mathbf{J}_V | \Longleftrightarrow (0 \quad \sqrt{N}). \quad (7.27)$$

In this representation the total flux operator is represented according to

$$\begin{aligned} |\mathbf{J}\rangle\rangle &\Longleftrightarrow \sqrt{\frac{NkT}{m}} \begin{pmatrix} \sqrt{\frac{5}{2}}kT \\ A_V \end{pmatrix}, \\ \langle\langle \mathbf{J}| &\Longleftrightarrow \sqrt{\frac{NkT}{m}} \begin{pmatrix} \sqrt{\frac{5}{2}}kT & A_V \end{pmatrix}. \end{aligned} \quad (7.28)$$

By using the two dimensional vector form of the projection operators, the memory kernel in Eq. (7.25) is represented by the 2×2 matrix

$$\mathcal{P} \mathcal{L} \frac{i}{z - (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P})} \mathcal{L} \mathcal{P} \Longleftrightarrow \frac{1}{N} \begin{pmatrix} \mathbb{M}_{KK} & \mathbb{M}_{KV} \\ \mathbb{M}_{VK} & \mathbb{M}_{VV} \end{pmatrix} \quad (7.29)$$

in which

$$\mathbb{M}_{\Theta\Phi} \equiv \frac{1}{3} \langle\langle \mathbf{J}_{\Theta} \cdot \mathcal{L} \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J}_{\Phi} \rangle\rangle. \quad (7.30)$$

where Θ and Φ represent kinetic (K) or potential (V) components. It is straightforward to determine the inverse of this matrix,

$$\mathcal{P} \frac{i}{z - \mathcal{L}} \mathcal{P} \Longleftrightarrow \frac{N^2}{\mathbb{M}_{KK} \mathbb{M}_{VV} - \mathbb{M}_{KV} \mathbb{M}_{VK}} \begin{pmatrix} \mathbb{M}_{VV} & -\mathbb{M}_{KV} \\ -\mathbb{M}_{VK} & \mathbb{M}_{KK} \end{pmatrix}. \quad (7.31)$$

The phase space integrals $\langle\langle \mathbf{J} \mathcal{L} \frac{i}{z - \mathcal{L}_{\mathcal{P}}} \mathcal{L} \mathbf{J} \rangle\rangle$ are rotational invariants (for an isotropic system), and thus proportional to the identity \mathbf{U} . This allows the matrix elements (7.30) to be expressed as scalars.

The thermal conductivity coefficient λ is thus given in terms of the components of the memory kernel by

$$\lambda = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} N n B \frac{kT}{m} \frac{\begin{pmatrix} \sqrt{\frac{5}{2}}kT & A_V \end{pmatrix} \begin{pmatrix} \mathbb{M}_{VV} & -\mathbb{M}_{KV} \\ -\mathbb{M}_{VK} & \mathbb{M}_{KK} \end{pmatrix} \begin{pmatrix} \sqrt{\frac{5}{2}}kT \\ A_V \end{pmatrix}}{\mathbb{M}_{KK} \mathbb{M}_{VV} - \mathbb{M}_{KV} \mathbb{M}_{VK}}. \quad (7.32)$$

It remains to calculate these four matrix elements of the memory kernel.

7.4 Reduction To Projected Liouville Superoperators

The $\mathbb{M}_{\Theta\Phi}$ involve the projected Liouville superoperator $\mathcal{L}_{\mathcal{P}} \equiv (1 - \mathcal{P}) \mathcal{L} (1 - \mathcal{P})$. But the projected Liouville superoperators

$$\mathcal{L}_K \equiv (1 - \mathcal{P}_K) \mathcal{L} (1 - \mathcal{P}_K), \quad (7.33)$$

$$\mathcal{L}_V \equiv (1 - \mathcal{P}_V) \mathcal{L} (1 - \mathcal{P}_V) \quad (7.34)$$

are the appropriate memory evolution superoperators for the purely kinetic or potential fluxes. The expansion of the resolvent $(z - \mathcal{L})^{-1}$ in terms of the resolvents of these projected Liouville superoperators are the same to those used in Chapter 6. Intermediate steps and further discussion is given there. Only the meanings of \mathbf{J}_K and \mathbf{J}_V and the presence of a single dot product instead of a double dot product differ from the treatment of Chapter 6.

The combination of \mathbb{M} -matrix elements that give the transport coefficient, Eq. (7.32), is written in terms of the projected resolvent matrix elements as,

$$\lambda = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{Nn}{mT} \frac{\left\{ \begin{array}{l} \frac{5}{2}(kT)^2 \left(\mathbb{V}_{VV} + \frac{i}{N} \mathbb{K}_{KV} \mathbb{V}_{VK}^L \right) + A_V^2 \left(\mathbb{K}_{KK} + \frac{i}{N} \mathbb{K}_{KV}^L \mathbb{V}_{VK} \right) \\ - \sqrt{\frac{5}{2}} kT A_V \left(\mathbb{V}_{VK} + \mathbb{K}_{KV} + \frac{i}{N} \mathbb{V}_{VK}^L \mathbb{K}_{KK} + \frac{i}{N} \mathbb{V}_{VV} \mathbb{K}_{KV}^L \right) \end{array} \right\}}{\mathbb{K}_{KK} \mathbb{V}_{VV} - \mathbb{V}_{VK} \mathbb{K}_{KV}}. \quad (7.35)$$

Before explicitly expanding these matrix elements, it is useful to determine the order of density of each of the terms and combinations in Eq. (7.35). This work is limited to the study of first order density corrections to the thermal conductivity, and therefore a number of the terms may be eliminated from further consideration. To determine the order in density and particle number of each of the terms, the normalization conventions of Eq. (6.2) and (6.7) are used. The normalization factor of the potential contribution to the momentum flux, A_V , defined in Eq. (7.15) is density dependent and also affects the outcome. With these relations, it is straightforward to see that,

$$\begin{aligned} \mathbb{K}_{KK} &= O(Nn) & \mathbb{K}_{KV} &= O(N\sqrt{n}) & \mathbb{K}_{KK}^L &= O(N\sqrt{n}), \\ \mathbb{V}_{VV} &= O(N) & \mathbb{V}_{VK} &= O(N\sqrt{n}) & \mathbb{V}_{VK}^L &= O(N\sqrt{n}). \end{aligned} \quad (7.36)$$

Substituting these orders of magnitude into Eq. (7.37), it is seen that to obtain the thermal conductivity up to the first order in density, it is sufficient to calculate

$$\lambda = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{Nn}{mT} \frac{\left\{ \begin{array}{l} \frac{5}{2}(kT)^2 \left(\mathbb{V}_{VV} + \frac{i}{N} \mathbb{K}_{KV} \mathbb{V}_{VK}^L \right) \\ - \sqrt{\frac{5}{2}} kT A_V \left(\mathbb{V}_{VK} + \mathbb{K}_{KV} + \frac{i}{N} \mathbb{V}_{VV} \mathbb{K}_{KV}^L \right) \end{array} \right\}}{\mathbb{K}_{KK} \mathbb{V}_{VV} - \mathbb{V}_{VK} \mathbb{K}_{KV}}. \quad (7.37)$$

7.5 Binary Collision Expansions for the Matrix Elements

In this section, the matrix elements in Eq. (7.37) are expressed, at low density, in terms of the dynamics of binary collisions. The \mathbb{K} matrix elements have resolvents projected onto the $(1 - \mathcal{P}_K)$ subspace, and lead to divergent terms which need to be treated in a manner similar to that of Chapter 4. The \mathbb{V} matrix element can be expanded directly.

7.5.1 Expansion of \mathbb{K}_{KV}^L

The kinetic term \mathbb{K}_{KV}^L has a structure that can be solved by iteration. The binary collision expansion of the resolvent in this term gives,

$$\begin{aligned}
 3\mathbb{K}_{KV}^L &= \langle\langle \mathbf{J}_K \cdot | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle = N(N-1) \langle\langle \mathbf{J}_{K1} \cdot | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle \\
 &= N(N-1) \langle\langle \mathbf{J}_{K1} \cdot | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \\
 &\quad \times \left[1 + \{ (N-2)(\mathcal{V}_{13} + \mathcal{V}_{23}) - \mathcal{P}_K \mathcal{L} - \mathcal{L} \mathcal{P}_K \} \frac{1}{z - \mathcal{L}_K} \right] \mathbf{J}_V \rangle\rangle \\
 &= \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{B}_{KV}^L.
 \end{aligned} \tag{7.38}$$

It is recognized that $\langle\langle \mathbf{J}_K \frac{1}{z - \mathcal{L}_K} \mathbf{J}_V \rangle\rangle$ vanishes and that it is useful to separate the pair density operator into uncorrelated and correlated parts,

$$\rho_{12}^{(2)} = n^2 \varphi_1 \varphi_2 + \rho_{c12}, \tag{7.39}$$

where φ_j are normalized Maxwellian momentum distributions. With the definition of the 1-particle kinetic projector $\mathcal{P}_0 \equiv \mathbf{J}_{K1}(\varphi_1/V) \cdot \text{Tr}_1 \mathbf{J}_{K1}$ and repeating the manipulations used in deriving Eq. (6.54), an expansion for \mathbf{B}_{KV}^L is obtained. Thus

$$\begin{aligned}
 \mathbf{B}_{KV}^L &\equiv N(N-1) \text{Tr}_{2..N} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_K} \mathbf{J}_V \rho^{(N)} \\
 &\approx \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L \\
 &\quad - \frac{1}{N} \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{c12} \mathbb{K}_{KV}^L \\
 &\equiv \mathbf{X}_V^L - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L - \mathbf{C} \mathbb{K}_{KV}^L,
 \end{aligned} \tag{7.40}$$

where the approximation involves the “promotion” of φ_2/V through various Liouville and resolvent superoperators. After “promotion”, the dependence on particle 2 has been expressed in terms of the linearized Boltzmann collision superoperator of Eq. (4.54). This promotion is appropriate as it is used here since the trace over the remaining particles (3...N) gives a position independent quantity. For large N , the difference between N and $N-1$ particles should be unimportant, with the consequence that this trace quantity can be approximated as \mathbf{B}_{KV}^L . A more explicit discussion of these points is presented in Chapter 4.

The vectorial operators \mathbf{X}_V^L and \mathbf{C} are defined by

$$\begin{aligned}
 \mathbf{X}_V^L &\equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} \\
 \mathbf{C} &\equiv \frac{1}{N} \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{c12}.
 \end{aligned} \tag{7.41}$$

The equation for \mathbf{B}_{KV}^L has the structure

$$\mathbf{B}_{KV}^L = \mathbf{Y}_{KV}^L - \frac{i}{z} \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_{KV}^L, \quad (7.42)$$

with $\mathbf{Y}_{KV}^L = \mathbf{X}_V^L - \mathbf{C} \mathbb{K}_{KV}^L$. By iteration or by similarity to the method of solution of Eq. (4.60), \mathbf{B}_{KV}^L has the solution, with $z \rightarrow 0$,

$$\mathbf{B}_{KV}^L = \mathbf{Y}_{KV}^L - \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{Y}_{KV}^L, \quad (7.43)$$

where the projected linearized collision superoperator is

$$\mathcal{R}_K \equiv (1 - \mathcal{P}_0) \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0). \quad (7.44)$$

This implies that \mathbb{K}_{KV}^L satisfies,

$$\mathbb{K}_{KV}^L = \frac{\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_V^L - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_V^L}{3 + \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C}}, \quad (7.45)$$

the proof of which is similar to Eq. (6.62). The final terms in the numerator and denominator are successive binary collision polynomial corrections to the terms preceding them. With a calculation similar to Appendix E it can be demonstrated that $\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{C} = O(n)$.

Making use of the normalization of $\rho_{12}^{(2)}$ given in Eq. (7.39) and the density dependence of the flux vectors given in Eqs. (7.9) and (7.10), it is seen that in the one-moment approximation, to the lowest order in density,

$$\mathbb{K}_{KV}^L = \frac{1}{3} \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_V^L = \frac{1}{3} \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} = O(N\sqrt{n}). \quad (7.46)$$

To simplify the explicit evaluation of this matrix element, it is first noted that the potential flux contribution of a pair of particles can be symmetrized with respect to the momenta of the two particles,

$$\mathbf{J}_{V12} = \frac{1}{A_V} \left[\mathbf{rF} + \left(u - \frac{2h_V}{N} \right) \mathbf{U} \right] \cdot \mathcal{G}. \quad (7.47)$$

It is also convenient to symmetrize the kinetic flux with respect to \mathbf{J}_{K1} and \mathbf{J}_{K2} , the sum of which is,

$$\mathbf{J}_{K1} + \mathbf{J}_{K2} = \sqrt{\frac{2}{5}} (\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2\sqrt{\frac{2}{5}} (\gamma \cdot \mathcal{G}) \gamma. \quad (7.48)$$

Therefore,

$$\begin{aligned} \mathbb{K}_{KV}^L &\approx \frac{1}{6} \text{Tr}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \cdot \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} \\ &= \frac{n^2 \Lambda^6}{6A_V} \text{Tr}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V} \cdot \frac{i}{z - \mathcal{L}_{\text{rel}}} (\mathbf{rF} + u\mathbf{U}) \cdot \mathcal{G} e^{-\mathcal{G}^2 - \gamma^2 - \beta u}. \end{aligned} \quad (7.49)$$

The contribution of the $2h_V/N$ term has no contribution in the limit of $N \rightarrow \infty$ and so u' has been substituted with u . Evaluation of the result is aided by expressing the resolvent in terms of the associated time evolution superoperator,

$$\mathbb{K}_{KV}^L = \frac{n^2 \Lambda^6}{6A_V} \text{Tr}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V} \cdot \int_0^\infty dt e^{i(z - \mathcal{L}_{\text{rel}})t} [\mathbf{r}(\mathbf{F} \cdot \mathcal{G}) + u \mathcal{G}] e^{-\mathcal{G}^2 - \gamma^2 - \beta u}. \quad (7.50)$$

The term containing the potential function u is considered in Eq. (7.53). The remaining time integral is calculated as,

$$\begin{aligned} \lim_{z \rightarrow 0} \int_0^\infty dt e^{i(z - \mathcal{L}_{\text{rel}})t} \mathbf{r}(\mathbf{F} \cdot \mathcal{G}) &\rightarrow \int_0^\infty dt \mathbf{r}(-t) [\mathbf{F}(-t) \cdot \mathcal{G}] \\ &= - \lim_{s_0 \rightarrow \infty} \left\{ \mathbf{r}(-t) [\mathbf{p}(-t) \cdot \mathcal{G}] \Big|_0^{s_0} + \int_0^{s_0} dt \frac{\mathbf{p}(-t)}{m/2} [\mathbf{p}(-t) \cdot \mathcal{G}] \right\} \end{aligned} \quad (7.51)$$

which follows from using Newton's second law and integrating by parts with respect to time.

This can be rewritten as,

$$\begin{aligned} &\lim_{s_0 \rightarrow \infty} \left\{ \mathbf{r}(\mathbf{p} \cdot \mathcal{G}) - \mathbf{r}(-s_0) [\mathbf{p}(-s_0) \cdot \mathcal{G}] - \int_0^{s_0} dt \frac{\mathbf{p}(-t)}{m/2} [\mathbf{p}(-t) \cdot \mathcal{G}] \right\} \\ &= \lim_{s_0 \rightarrow \infty} \left\{ \mathbf{r}(\mathbf{p} \cdot \mathcal{G}) - \left[\mathbf{r}(-s_0) + s_0 \frac{\mathbf{p}(-s_0)}{m/2} \right] [\mathbf{p}(-s_0) \cdot \mathcal{G}] \right. \\ &\quad \left. + \int_0^{s_0} dt \left[\frac{\mathbf{p}(-s_0)}{m/2} (\mathbf{p}(-s_0) \cdot \mathcal{G}) - \frac{\mathbf{p}(-t)}{m/2} (\mathbf{p}(-t) \cdot \mathcal{G}) \right] \right\}. \end{aligned} \quad (7.52)$$

The time integral contribution to Eq. (7.50) is,

$$\begin{aligned} \mathbb{K}_{KV}^L(\text{time}) &= \frac{n^2 \Lambda^6}{6A_V} \text{Tr}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G} : \\ &\quad \times \int_0^{s_0} dt \left[\frac{\mathbf{p}(-s_0)}{m/2} \mathbf{p}(-s_0) - \frac{\mathbf{p}(-t)}{m/2} \mathbf{p}(-t) + u(-t) \mathbf{U} \right] e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\ &= \frac{n^2 k T \Lambda^6}{3A_V} \text{Tr}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G} : \\ &\quad \times \int_0^{s_0} dt \left[\gamma(-s_0) \gamma(-s_0) - \gamma(-t) \gamma(-t) + \frac{u(-t)}{2kT} \mathbf{U} \right] e^{-\mathcal{G}^2 - \gamma^2 - \beta u}. \end{aligned} \quad (7.53)$$

The time integral over the potential is included in this term.

The contribution to Eq. (7.50) from terms not involving the time integral in Eq. (7.52) is

$$\begin{aligned} \mathbb{K}_{KV}^L(\text{non-time}) &= \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{6A_V} \text{Tr}_{12} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\gamma \cdot \mathcal{G}) \gamma \right] \mathcal{V} \cdot \\ &\quad \times [\mathbf{r}(\mathbf{p} \cdot \mathcal{G}) - \mathbf{r}'(\mathbf{p}_0 \cdot \mathcal{G})] e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\ &= \sqrt{\frac{2}{5}} \frac{i n^2 \Lambda^6}{3A_V} \text{Tr}_{12} [(\gamma \cdot \mathbf{F}) \mathcal{G} + (\gamma \cdot \mathcal{G}) \mathbf{F} + (\mathbf{F} \cdot \mathcal{G}) \gamma] \cdot \\ &\quad \times [\mathbf{r}(\gamma \cdot \mathcal{G}) - \mathbf{r}'(\gamma_0 \cdot \mathcal{G})] e^{-\mathcal{G}^2 - \gamma^2 - \beta u}, \end{aligned} \quad (7.54)$$

where an integration by parts with respect to relative momentum has been carried out. This non-time contribution has two parts, the first part being,

$$\begin{aligned}
& \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{3 A_V} \text{Tr}_{12} [(\boldsymbol{\gamma} \cdot \mathbf{F}) \boldsymbol{\mathcal{G}} + (\boldsymbol{\gamma} \cdot \boldsymbol{\mathcal{G}}) \mathbf{F} + (\mathbf{F} \cdot \boldsymbol{\mathcal{G}}) \boldsymbol{\gamma}] \cdot \mathbf{r} (\boldsymbol{\gamma} \cdot \boldsymbol{\mathcal{G}}) e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\
&= \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{3 A_V} \text{Tr}_{12} \frac{1}{3} \mathcal{G}^2 [(\boldsymbol{\gamma} \cdot \mathbf{F})(\boldsymbol{\gamma} \cdot \mathbf{r}) + r F \gamma^2 + (\boldsymbol{\gamma} \cdot \mathbf{F})(\boldsymbol{\gamma} \cdot \mathbf{r})] e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\
&= \sqrt{\frac{2}{5}} \frac{i N n}{6 A_V} \left\{ \frac{3}{2} \int d\mathbf{r} F r e^{-\beta u} + \frac{2}{\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{1}{r} F(\boldsymbol{\gamma} \cdot \mathbf{r})^2 e^{-\gamma^2 - \beta u} \right\} \\
&= \sqrt{\frac{2}{5}} \frac{i N n}{A_V} \left[\frac{3}{2} B k T + \frac{1}{4} \int d\mathbf{r} r F e^{-\beta u} \int_0^\pi d\theta \cos^2 \theta \sin \theta \right] = \sqrt{\frac{2}{5}} \frac{i 5 N n}{2 A_V} k T B(T). \quad (7.55)
\end{aligned}$$

The second part of Eq. (7.54) is also evaluated in a similar fashion,

$$\begin{aligned}
& -i \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{3 A_V} \text{Tr}_{12} [(\boldsymbol{\gamma} \cdot \mathbf{F}) \boldsymbol{\mathcal{G}} + (\boldsymbol{\gamma} \cdot \boldsymbol{\mathcal{G}}) \mathbf{F} + (\mathbf{F} \cdot \boldsymbol{\mathcal{G}}) \boldsymbol{\gamma}] \cdot \mathbf{r}' (\boldsymbol{\gamma}_0 \cdot \boldsymbol{\mathcal{G}}) e^{-\mathcal{G}^2 - \gamma^2 - \beta u} \\
&= -i \sqrt{\frac{2}{5}} \frac{N n \Lambda_r^3}{6 A_V} \text{Tr}_{\text{rel}} \frac{1}{r} F [(\boldsymbol{\gamma} \cdot \mathbf{r})(\boldsymbol{\gamma}_0 \cdot \mathbf{r}') + (\boldsymbol{\gamma} \cdot \boldsymbol{\gamma}_0)(\mathbf{r} \cdot \mathbf{r}') + (\boldsymbol{\gamma}_0 \cdot \mathbf{r})(\boldsymbol{\gamma} \cdot \mathbf{r}')] e^{-\gamma^2 - \beta u} \\
&= -i \sqrt{\frac{2}{5}} \frac{N n}{6 \pi^{3/2} A_V} (20 \pi \sigma^3 k T) F_\lambda. \quad (7.56)
\end{aligned}$$

The association with F_λ is shown in Appendix G.

Summarizing the results of this section, it is seen that, to the lowest order in density,

$$\mathbb{K}_{KV}^L = i \sqrt{\frac{2}{5}} \frac{N n k T}{A_V} \left[\frac{5}{2} B(T) - \frac{20 \sigma^3}{6 \pi^{1/2}} F_\lambda \right] + \mathbb{K}_{KV}^L(\text{time}). \quad (7.57)$$

7.5.2 Expansion of \mathbb{K}_{KV}

The calculation of the result of the binary collision expansion of \mathbb{K}_{KV} requires similar manipulations,

$$\begin{aligned}
3 \mathbb{K}_{KV} &= \langle\langle \mathbf{J}_K \cdot | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_V \rangle\rangle \\
&= N(N-1) \langle\langle \mathbf{J}_{K1} \cdot | \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \\
&\quad \times \left[1 + \{ (N-2)(\mathcal{V}_{13} + \mathcal{V}_{23}) - \mathcal{P}_K \mathcal{L} - \mathcal{L} \mathcal{P}_K \} \frac{1}{z - \mathcal{L}_K} \right] \mathcal{L} \mathbf{J}_V \rangle\rangle \\
&= \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{B}_{KV}. \quad (7.58)
\end{aligned}$$

The equation for \mathbf{B}_{KV} is similar to that for \mathbf{B}_{KV}^L in Eq. (7.40). The resulting evaluation of \mathbb{K}_{KV} in the binary collision approximation is as in Eq. (7.45), namely

$$\mathbb{K}_{KV} = \frac{\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_V - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_V}{3 + \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C}}. \quad (7.59)$$

This involves the same \mathbf{C} operator but has \mathbf{X}_V^L replaced by

$$\mathbf{X}_V \equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} \mathbf{J}_{V12} \rho_{12}^{(2)}. \quad (7.60)$$

Again the only approximation used to arrive at this result is a “promotion” of φ_2/V . The final two terms in Eq. (7.59) give successive collision corrections as stated in Section 7.5.1. The $\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_V$ term is shown to vanish,

$$\begin{aligned} \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_V &= \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} \mathbf{J}_{V12} \rho_{12}^{(2)} \\ &= n^2 \Lambda^6 \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} e^{-H_{12}^{(2)}/kT} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} \mathbf{J}_{V12} Y_{[0]}(\mathbf{r}_{12}) \\ &= i n^2 \Lambda^6 \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} e^{-H_{12}^{(2)}/kT} \left(-1 + \frac{z}{z - \mathcal{L}_{12}} \right) \mathbf{J}_{V12} Y_{[0]}(\mathbf{r}_{12}) \\ &\rightarrow 0. \end{aligned} \quad (7.61)$$

In this contribution, the resolvent has been combined with \mathcal{L}_{12} to give a term proportional to z , which vanishes in the $z \rightarrow 0$ limit since both sides of the resolvent have functions which constrain the relative position, and the remaining integral (with -1) is odd in both position and momentum directions, so it also vanishes on integration over phase space.

7.5.3 Expansion of \mathbb{K}_{KK}

7.5.3.1 Retaining two-particle collisions

The evaluation of \mathbb{K}_{KK} at the binary collision expansion level follows similar lines to that of Section 7.5.1,

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{1}{3} \langle\langle \mathbf{J}_K \cdot | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_K - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{X}_K}{3 + \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{C} - \text{Tr}_1 \mathbf{J}_{K1} \cdot \varphi_1 \mathcal{R}_1 \frac{1}{\varphi_1} \frac{1}{\mathcal{R}_K} (1 - \mathcal{P}_0) \mathbf{C}}. \end{aligned} \quad (7.62)$$

This involves the same \mathbf{C} operator encountered previously and has \mathbf{X}_K defined as,

$$\mathbf{X}_K \equiv \text{Tr}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)}. \quad (7.63)$$

The structure of Eq. (7.62) includes Sonine corrections as in the previous two matrix elements. The order in particle number N , and particle density n of $\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_K$ is determined by using Eqs. (7.39), (7.9) and (7.10),

$$\text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{X}_K = \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \rho_{12}^{(2)} = O(Nn). \quad (7.64)$$

With a correction due to the equilibrium pair correlations, \mathbb{K}_{KK}^2 is identified as the modified Boltzmann collision integral used by Hoffman and Curtiss [22] for including an estimate of the effect that the presence of a third particle has on the bimolecular Boltzmann collision operator. Their method for the approximate evaluation of this collision integral is followed here. They approximated the integral by assuming that the factor $Y_{[0]}$ defined in Eq. (6.9), which describes the spatial correlations of the other particles in the system with pair 12, changes little during the collision dynamics. As a result, this factor can be moved to the left of the resolvent, and since it is also only a function of the position, to the left of \mathcal{V}_{12} . With this approximation \mathbb{K}_{KK}^2 is rewritten as

$$\begin{aligned}\mathbb{K}_{KK}^2 &\approx \frac{n^2\Lambda^6}{3}\text{Tr}_{12}\mathbf{J}_{K1}\cdot Y_{[0]}\mathcal{V}_{12}e^{-\beta H_{12}^{(2)}}\frac{i}{z-\mathcal{L}_{12}}\mathcal{L}_{12}(\mathbf{J}_{K1}+\mathbf{J}_{K2}) \\ &= \sqrt{\frac{2}{5}}\frac{n^2\Lambda^6}{3}\text{Tr}_{12}\mathbf{J}_{K1}\cdot Y_{[0]}\mathcal{V}_{12}e^{-\beta H_{12}^{(2)}}\frac{i}{z-\mathcal{L}_{12}}\mathcal{V}_{12}\left[(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2(\gamma\cdot\mathcal{G})\gamma\right].\end{aligned}\quad (7.65)$$

The second form is obtained by recognizing that the \mathbf{J}_K 's are functions of the momentum so only \mathcal{V}_{12} acts on these, and moreover that it is only the (reduced) relative momentum γ that is affected by \mathcal{V}_{12} . The transformation from individual to relative and center of mass momenta is done as in Eq. (7.48). The combination of operators $\frac{1}{z-\mathcal{L}_{12}}\mathcal{V}_{12}$ is identified in the limit as a restricted form of the Møller superoperator $\Omega'_{12}-1$, with the prime denoting the restricted applicability. This implies that

$$\begin{aligned}\mathbb{K}_{KK}^2 &= \frac{iNn\Lambda^6}{15}\text{Tr}\left[(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2(\gamma\cdot\mathcal{G})\gamma\right]\cdot Y_{[0]}(\mathbf{r})\mathcal{V}e^{-H^{(2)}/kT}(\Omega'-1) \\ &\quad \times \left[(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2(\gamma\cdot\mathcal{G})\gamma\right] \\ &= -\frac{iNn\Lambda^6}{15}\text{Tr}\left[(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2(\gamma\cdot\mathcal{G})\gamma\right]\cdot Y_{[0]}(\mathbf{r})\mathcal{K}\Omega'e^{-K^{(2)}/kT} \\ &\quad \times \left[(\mathcal{G}^2+\gamma^2-5)\mathcal{G}+2(\gamma\cdot\mathcal{G})\gamma\right].\end{aligned}\quad (7.66)$$

In the final form, the “-1” term vanishes since it is odd in position and momentum directions, while the Møller superoperator satisfies the intertwining relations

$$H^{(2)}\Omega' = \Omega'K^{(2)} \quad (7.67)$$

and

$$\mathcal{L}\Omega' = \Omega'\mathcal{K}. \quad (7.68)$$

The first intertwining relation allows the full Boltzmann factor after (to the left of) the Møller superoperator to be replaced by the kinetic Boltzmann factor before (to the right of)

the Møller superoperator. The second relation implies that in the present case

$$\begin{aligned} & \mathcal{V}\Omega'e^{-K^{(2)}/kT} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma} \cdot \mathcal{G}) \boldsymbol{\gamma} \right] \\ &= -\mathcal{K}\Omega'e^{-K^{(2)}/kT} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma} \cdot \mathcal{G}) \boldsymbol{\gamma} \right], \end{aligned} \quad (7.69)$$

on the basis that the operator on which Ω' acts has zero \mathcal{K} eigenvalue. With the definition $\mathcal{K} = -i \frac{\mathbf{p}}{m/2} \cdot \frac{\partial}{\partial \mathbf{r}}$ and expressing the effect of Ω' in terms of the precollisional relative momentum $\Omega' \boldsymbol{\gamma} \equiv \boldsymbol{\gamma}' = \boldsymbol{\gamma}_0$, an integration by parts is carried out on the position variable to give

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{-2Nn}{15m\pi^{3/2}} \iiint d\Sigma \cdot \mathbf{p} d\boldsymbol{\gamma} d\mathcal{G} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma} \cdot \mathcal{G}) \boldsymbol{\gamma} \right] \\ &\quad \times e^{-\gamma_0^2 - \mathcal{G}^2} \left[(\mathcal{G}^2 + \gamma_0^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma}_0 \cdot \mathcal{G}) \boldsymbol{\gamma}_0 \right] \\ &+ \frac{2Nn\Lambda_r^3}{15m\pi^{3/2}} \iiint d\mathbf{r} d\mathbf{p} d\mathcal{G} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma} \cdot \mathcal{G}) \boldsymbol{\gamma} \right] \mathbf{p} \cdot \frac{\partial Y_{[0]}}{\partial \mathbf{r}} \\ &\quad \times e^{-\gamma_0^2 - \mathcal{G}^2} \left[(\mathcal{G}^2 + \gamma_0^2 - 5) \mathcal{G} + 2(\boldsymbol{\gamma}_0 \cdot \mathcal{G}) \boldsymbol{\gamma}_0 \right]. \end{aligned} \quad (7.70)$$

After integrating over the center of mass momentum, the surface integral can be identified as being proportional to the Chapman - Cowling Omega integral [7, 62] $\Omega^{(2,2)}$,

$$\begin{aligned} \mathbb{K}_{KK}^2(\text{surf}) &= \frac{32Nn(\pi kT)^{1/2}}{15m^{1/2}} \int_0^\infty \int_0^\infty b db d\gamma \gamma^7 (1 - \cos^2 \chi) e^{-\gamma^2} \\ &= \frac{16Nn}{15} \Omega^{(2,2)} = \frac{2Nn}{3} \langle v \rangle \mathfrak{S}(20), \end{aligned} \quad (7.71)$$

and/or the kinetic cross section [79] $\mathfrak{S}(20)$, with $\langle v \rangle$ the average relative speed. Finally, after the dot product is explicitly evaluated, in the second term of Eq. (7.70), the only non-zero integral that remains is the one in which \mathbf{p} is multiplied by another angle dependent term. The remaining $Y_{[0]}$ dependent term is related to the Hoffman-Curtiss [22] R function

$$\mathbb{K}_{KK}^2(Y\text{dep}) = \frac{4Nn(kT)^{1/2}}{15m^{1/2}\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} \boldsymbol{\gamma} \cdot \frac{\partial Y_{[0]}}{\partial \mathbf{r}} (\boldsymbol{\gamma} \cdot \boldsymbol{\gamma}')^2 e^{-\gamma^2 - \beta u} = \frac{4Nn^2(kT)^{1/2}\sigma^2}{15m^{1/2}\pi^{3/2}} R(T). \quad (7.72)$$

Thus, up to terms quadratic in density, \mathbb{K}_{KK} is approximated by,

$$\begin{aligned} \mathbb{K}_{KK}^2 &= \frac{16Nn}{15} \Omega^{(2,2)} + \frac{4Nn^2\sigma^2}{15m^{1/2}\pi^{3/2}} (kT)^{1/2} R(T) = \frac{16Nn}{15} \Omega^{(2,2)} \left\{ 1 + \sqrt{\frac{kT}{\pi m}} \frac{n\sigma^2 R(T)}{4\pi \Omega^{(2,2)}} \right\} \\ &= \frac{16Nn}{15} \Omega^{(2,2)} \left\{ 1 + \frac{nR(T)}{8\pi^2 \Omega^{(2,2)*}} \right\}. \end{aligned} \quad (7.73)$$

The \mathbb{K}_{KK}^2 term produces the binary cross section appropriate for the thermal conductivity along with a correction from the static presence of a third particle on this cross section.

7.5.3.2 Retaining three-particle collisions

The inclusion of three-body collisions in \mathbb{K}_{KK} involves the same type of calculations as in Section 6.5.3.2. The difference is related to the presence of the kinetic part of the heat flux vector instead of the momentum flux tensor, and corresponding to this fact, dot products instead of double dot contractions. Numerical factors also differ in the general relations.

The expression for \mathbb{K}_{KK} with a general order of collision is given as

$$\mathbb{K}_{KK} = \frac{1}{3} \langle \langle \mathbf{J}_K \cdot | \mathcal{L} \frac{i}{z - \mathcal{L}_K} \mathcal{L} \mathbf{J}_K \rangle \rangle = \frac{1}{3} \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{B}_{KK}. \quad (7.74)$$

Calculations to determine \mathbf{B}_{KK} are of the same form as Eqs. (6.94) to (6.113) of Section 6.5.3. The final result also has the form,

$$\mathbb{K}_{KK} = \mathbb{K}_{KK}^2 + \mathbb{K}_{KK}^3(B) + \Delta \mathbb{K}_{KK}^3, \quad (7.75)$$

with \mathbb{K}_{KK}^2 defined in Eq. (7.73). $\mathbb{K}_{KK}^3(B)$ is the combination of two terms,

$$\begin{aligned} \mathbb{K}_{KK}^3(B) = & \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{Y}_{KK}^3 \\ & - \frac{1}{3N} \text{Tr}_{123} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathcal{V}_{13} - \mathcal{V}_{23}) \\ & \times \frac{1}{z - \mathcal{L}_{123}} (\mathbf{J}_{K1} + \mathbf{J}_{K2} + \mathbf{J}_{K3}) \rho_{123}^{(3)} \text{Tr}_1 \mathbf{J}_{K1} \cdot \mathbf{Y}_{KK}, \end{aligned} \quad (7.76)$$

which give the contribution of true three-particle dynamics to the matrix element. Further discussion of these terms is beyond the scope of this work.

For $\Delta \mathbb{K}_{KK}^3$, with the limit of $s_0 \rightarrow -\infty$ implied, it is seen that,

$$\begin{aligned} \Delta \mathbb{K}_{KK}^3 = & \frac{in^3}{3} \frac{2\langle v \rangle \mathfrak{S}(20)}{3} \text{Tr}_{12} \mathbf{J}_{K1} \cdot \mathcal{V}_{12} \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \varphi_1 \varphi_2 \\ = & \frac{in^3}{3} \frac{2\langle v \rangle \mathfrak{S}(20)}{3} \sqrt{\frac{2}{5}} \text{Tr}_{12} \mathbf{J}_{K1} \mathcal{V}_{12} \cdot \\ & \times \int_0^\infty dt [e^{-i\mathcal{L}_{12}t} - e^{-i\mathcal{L}_{12}s_0}] [(\mathcal{G}^2 + \gamma^2 - 5)\mathcal{G} + 2(\mathcal{G} \cdot \gamma)\gamma] \varphi_1 \varphi_2 \\ = & \frac{in^3 \Lambda^6}{3} \sqrt{\frac{2}{5}} \frac{2\langle v \rangle \mathfrak{S}(20)}{3} \text{Tr}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G} : \\ & \times \int_0^\infty dt \left[\frac{\gamma^2(-t)}{2} \mathbf{U} - \frac{\gamma^2(-\infty)}{2} \mathbf{U} + \gamma(-t)\gamma(-t) - \gamma(-\infty)\gamma(-\infty) \right] e^{-\gamma^2 - \mathcal{G}^2 - \beta u} \\ = & \frac{in^3 \Lambda^6}{3} \sqrt{\frac{2}{5}} \frac{2\langle v \rangle \mathfrak{S}(20)}{3} \text{Tr}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G} : \\ & \times \int_0^\infty dt \left[\frac{-u(-t)}{2kT} \mathbf{U} + \gamma(-t)\gamma(-t) - \gamma(-\infty)\gamma(-\infty) \right] e^{-\gamma^2 - \mathcal{G}^2 - \beta u}. \end{aligned} \quad (7.77)$$

The equality of $\gamma^2(-t) - \gamma^2(-\infty) = -u(-t)$ was used in the relation above.

7.5.4 Evaluation of \mathbb{V}_{VV}

From the relations of Section 7.4,

$$\mathbb{V}_{VV} = \frac{1}{3} \langle\langle \mathbf{J}_V \cdot \mathcal{L} \frac{i}{z - \mathcal{L}} \mathcal{L} \mathbf{J}_V \rangle\rangle. \quad (7.78)$$

Using the analogy with Eq. (7.25), it is seen that,

$$\mathbb{V}_{VV} = N^2 / \mathbb{Z}_{VV}. \quad (7.79)$$

The corresponding purely potential term is approximated by

$$\begin{aligned} \mathbb{Z}_{VV} &= \langle\langle \mathbf{J}_V \cdot \frac{i}{z - \mathcal{L}_V} \mathbf{J}_V \rangle\rangle \\ &\approx \frac{1}{2} \text{Tr}_{12} \mathbf{J}_{V12} \cdot \frac{i}{z - \mathcal{L}_{12}} \mathbf{J}_{V12} \rho_{12}^{(2)} = O(N), \end{aligned} \quad (7.80)$$

from which it follows that $\mathbb{V}_{VV} = O(N)$ and is therefore an extensive quantity. The intensivity and low density behaviour of the final expression for the thermal conductivity is obtained by assessing the combinations which appear in Eq. (7.37).

7.5.5 Expansion of \mathbb{V}_{VK}

The matrix element \mathbb{V}_{VK} is simplified by using a binary collision expansion

$$\begin{aligned} 3\mathbb{V}_{VK} &= \langle\langle \mathbf{J}_V \cdot \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathcal{L} \mathbf{J}_K \rangle\rangle \\ &= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V \cdot \mathcal{L} \left\{ 1 + \frac{1}{z - \mathcal{L}_V} [(N-2)(\mathcal{V}_{13} + \mathcal{V}_{23}) - \mathcal{L}\mathcal{P}_V] \right\} \\ &\quad \times \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}). \end{aligned} \quad (7.81)$$

It is convenient to first move $\rho^{(N)}$ to the left of the Liouville superoperator before introducing the summation over the particle labeling.

$$\begin{aligned} 3\mathbb{V}_{VK} &= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V \cdot \mathcal{L} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\ &\quad + \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V \cdot \mathcal{L} \frac{1}{z - \mathcal{L}_V} (N-2)(\mathcal{V}_{13} + \mathcal{V}_{23}) \\ &\quad \times \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\ &\quad + 3\mathbb{V}_{VV} \frac{i(N-1)}{6} \text{Tr}_{1\dots N} \mathbf{J}_{V12} \cdot \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\ &= (i) + (ii) + (iii). \end{aligned} \quad (7.82)$$

The (i) term on the right of Eq. (7.82) is,

$$\begin{aligned}
(i) &= \frac{n^2 \Lambda^6}{2} \text{Tr}_{12} \mathbf{J}_{V12} \cdot e^{-\beta H_{12}} \mathcal{L}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) Y_{[0]}(\mathbf{r}_{12}) \\
&= \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{2} \text{Tr}_{12} \mathbf{J}_{V12} \cdot e^{-\beta H_{12}} \mathcal{L}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\gamma \cdot \mathcal{G}) \gamma \right] + O(Nn\sqrt{n}) \\
&= O(Nn\sqrt{n}).
\end{aligned} \tag{7.83}$$

The operator combination $\frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12}$ in the lowest order in density term is identified in terms of the Møller superoperator $\Omega - 1$ since it is operating on a function of the momenta. Using the intertwining relation, $\mathcal{L}\Omega = \Omega\mathcal{K}$, it is seen that this term vanishes. The second term (ii) involves three particles and is also $O(Nn\sqrt{n})$.

The lowest order in density contribution to the (iii) term of Eq. (7.82) is obtained by using a binary collision expansion,

$$(iii) = 3\mathbb{V}_{VV} \frac{i}{6N} \text{Tr}_{12} \mathbf{J}_{V12} \cdot \frac{i}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) = \mathbb{V}_{VV} O(\sqrt{n}). \tag{7.84}$$

The lowest order correction term coming from \mathbb{V}_{VK} is thus

$$\begin{aligned}
\mathbb{V}_{VK} &\approx -\mathbb{V}_{VV} \frac{1}{6N} \text{Tr}_{12} \mathbf{J}_{V12} \cdot \frac{1}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} \mathcal{V}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
&= -\mathbb{V}_{VV} \sqrt{\frac{2}{5}} \frac{n \Lambda^6}{6 A_V} \text{Tr}[(\mathbf{rF} + u' \mathbf{U}) \cdot \mathcal{G}] \cdot e^{-\gamma^2 - \beta u} \frac{1}{z - \mathcal{L}_{\text{rel}}} \mathcal{V} \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\gamma \cdot \mathcal{G}) \gamma \right] \\
&= -\mathbb{V}_{VV} \sqrt{\frac{2}{5}} \frac{n \Lambda^6}{6 A_V} \text{Tr}[(\mathbf{rF} + u \mathbf{U}) \cdot \mathcal{G}] \cdot e^{-\gamma^2 - \beta u} (\Omega - 1) \left[(\mathcal{G}^2 + \gamma^2 - 5) \mathcal{G} + 2(\gamma \cdot \mathcal{G}) \gamma \right] \\
&= -\mathbb{V}_{VV} \sqrt{\frac{2}{5}} \frac{n \Lambda^6}{6 A_V} \text{Tr}[(\mathbf{rF} + u \mathbf{U}) \cdot \mathcal{G}] \cdot e^{-\gamma^2 - \beta u} \left[(\mathcal{G}^2 + \gamma_0^2 - 5) \mathcal{G} + 2(\gamma_0 \cdot \mathcal{G}) \gamma_0 \right] \\
&= -\mathbb{V}_{VV} \sqrt{\frac{2}{5}} \frac{nkT}{6 A_V} \left(-4\pi^{1/2} \sigma^3 N_\lambda - 7T \frac{dB}{dT} - 5T^2 \frac{d^2 B}{dT^2} \right).
\end{aligned} \tag{7.85}$$

The identification of the last equality is made in Appendix H.

7.5.6 Expansion of \mathbb{V}_{VK}^L

From the result that $\mathbb{K}_{KV} = 0$ and Eq. (7.37), it is seen that \mathbb{V}_{VK}^L no longer contributes to the first order density corrections of the thermal conductivity. Nonetheless, the expansion of this term is presented, as it leads to a second order density correction that is identical to a term presented by Snider and McCourt.

Expanding in the manner of the previous quantities,

$$3\mathbb{V}_{VK}^L = \langle\langle \mathbf{J}_V \cdot \mathcal{L} \frac{i}{z - \mathcal{L}_V} \mathbf{J}_{K1} \rangle\rangle$$

$$\begin{aligned}
&= \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V \cdot \mathcal{L} \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
&\quad + \frac{N(N-1)}{2} \text{Tr}_{1\dots N} \mathbf{J}_V \cdot \mathcal{L} \frac{1}{z - \mathcal{L}_V} (N-2)(\mathcal{V}_{13} + \mathcal{V}_{23}) \frac{i}{z - \mathcal{L}_{12}} \rho^{(N)} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
&\quad + 3\mathbb{V}_{VV} \frac{i}{6N} \text{Tr}_{1\dots N} \mathbf{J}_{V12} \cdot \frac{i}{z - \mathcal{L}_{12}} \rho_{12}^{(2)} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \\
&= (i) + (ii) + (iii). \tag{7.86}
\end{aligned}$$

The trace in the first term of this expansion is identical to that of Eq. (7.84) and so the result is,

$$(i) = i\sqrt{\frac{2}{5}} \frac{NnkT}{6A_V} \left(-4\pi^{1/2} \sigma^3 N_\lambda - 7T \frac{dB}{dT} - 5T^2 \frac{d^2B}{dT^2} \right). \tag{7.87}$$

The contribution from the three-particle term is not considered. The (iii) term of Eq. (7.86) is evaluated in Appendix J. It contributes a second order density correction to the thermal conductivity that involves the $H_\lambda + R_\lambda + I_\lambda$ correction of Eq. (26) of Snider and McCourt.

7.6 First Order Density Corrections Within the Two Moment Approximation

Within the lowest order in density approximation of Section 7.5, in particular the zero of \mathbb{K}_{KV} and the nature of \mathbb{V}_{VV} , Eq. (7.37) for the thermal conductivity becomes

$$\lambda \approx \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{Nn}{\mathbb{K}_{KK}} \frac{k^2 T}{m} \left[\frac{5}{2} - \sqrt{\frac{2}{5}} \frac{A_V}{kT} \left(\frac{\mathbb{V}_{VK}}{\mathbb{V}_{VV}} + \frac{i}{N} \mathbb{K}_{KV}^L \right) \right]. \tag{7.88}$$

The contributions from \mathbb{K}_{KK} where determining in Section 7.5.3,

$$\begin{aligned}
\mathbb{K}_{KK} &= \frac{16Nn}{15} \Omega^{(2,2)} \left\{ 1 + \frac{nR(T)}{8\pi^2 \Omega^{(2,2)*}} + \frac{in}{3V} \sqrt{\frac{2}{5}} \text{Tr}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G} \right. \\
&\quad \times \int_0^\infty dt \left[\frac{u(-t)}{2kT} \mathbf{U} + \gamma(-t) \gamma(-t) - \gamma(-\infty) \gamma(-\infty) \right] e^{-\gamma^2 - \mathcal{G}^2 - \beta u} \Big\} + \mathbb{K}_{KK}^3(B). \tag{7.89}
\end{aligned}$$

The matrix element \mathbb{V}_{VK} contributes to Eq. (7.88) with the terms determined in Section 7.5.5,

$$\mathbb{V}_{VK} = -\mathbb{V}_{VV} \sqrt{\frac{2}{5}} \frac{nkT}{6A_V} \left(-4\pi^{1/2} \sigma^3 N_\lambda - 7T \frac{dB}{dT} - 5T^2 \frac{d^2B}{dT^2} \right). \tag{7.90}$$

Finally, the \mathbb{K}_{KV}^L contributions were determined in Section 7.5.1 to be,

$$\mathbb{K}_{KV}^L = i\sqrt{\frac{2}{5}} \frac{NnkT}{A_V} \left[\frac{5}{2} B(T) - \frac{20\sigma^3}{6\pi^{1/2}} F_\lambda \right] + \mathbb{K}_{KV}^L(\text{time}), \tag{7.91}$$

where

$$\begin{aligned} \mathbb{K}_{KV}^L(time) &= \frac{n^2 k T \Lambda^6}{3A_V} \text{Tr}_{12}(\mathbf{J}_{K1} + \mathbf{J}_{K2}) \mathcal{V}_{12} \mathcal{G}: \\ &\quad \times \int_0^{s_0} dt \left[\gamma(-s_0) \gamma(-s_0) - \gamma(-t) \gamma(-t) + \frac{u(-t)}{2kT} \mathbf{U} \right] e^{-g^2 - \gamma^2 - \beta u}. \end{aligned} \quad (7.92)$$

Substituting the values of these matrix elements into Eq. (7.88), the thermal conductivity is found to be

$$\begin{aligned} \lambda &= \frac{15k^2 T}{32m\Omega^{(2,2)}} \left[5 + 5nB(T) - \frac{20n\sigma^3}{3\pi^{1/2}} F_\lambda - \frac{nR(T)}{8\pi^2\Omega^{(2,2)*}} - \frac{4n\pi^{1/2}\sigma^3}{3} N_\lambda \right. \\ &\quad \left. - \frac{7}{3} nT \frac{dB}{dT} - \frac{5}{3} nT^2 \frac{d^2 B}{dT^2} + 5n\mathbb{K}_{KK}^L(B) \right]. \end{aligned} \quad (7.93)$$

The $\Delta\mathbb{K}_{KK}^3$ and $\mathbb{K}_{KV}^L(time)$ contributions to the thermal conductivity cancel.

Chapter 8

Discussion and Conclusions

The calculations of the previous chapters have verified that within a similar set of approximations, the detailed forms of the first order density corrections to the viscosity and the thermal conductivity from the generalized Boltzmann equation are equivalent to those of the time correlation function formalism. The different pathways used in obtaining these results increases our confidence in their correctness. The comparison of the forms of the different approximations made in each of these theories helps to clarify the physical content of the final formulae.

The method of projection operators introduced in this thesis allows the dynamics of the system to be expressed in analytic form in terms of projected resolvents.

For each transport coefficient, the projection operator reflects both the functional form and the tensorial properties of the relevant flux function. In cases where the flux function includes more than one type of contribution, for example, both kinetic and potential contributions, it becomes necessary to define more than a single projection operator for the system. In these cases the calculation of the transport coefficient is expressed in terms of an equivalent matrix inversion problem. Both the calculations of the transport coefficients for a binary mixture and for the density corrections were solved as matrix problems.

There are a number of directions that can be followed for future work. The method can obviously be extended to other transport coefficients like the diffusion coefficient and bulk viscosity, or more interestingly perhaps to the coupled-flux transport coefficients such as the thermal diffusion factor. In the latter case, the nature of the projection operators will have to reflect the different flux functions that appear on the two sides of the resolvent in the time correlation function formula. There also appears to be no reason why the method can not be extended to non-thermal transport coefficients and to other dynamical problems as well.

Another possible extension for future work would be the study of second-order density corrections to the transport coefficient. The explicit study of the three-particle and higher

collision terms may reveal logarithmic singularities [96, 97] in the second order corrections. Other than a great amount of calculational detail, no extra difficulty is anticipated to occur if this is carried out.

The development of greatest interest for future work would be to calculate first order density corrections, including the effects of bound pairs and the various density corrections discussed in this thesis with a unified formulation. Such a project would rigorously account for the effect of bound pairs on transport coefficients and answer questions with regard to the additivity of the contributions as used in the Rainwater - Friend theory.

Bibliography

- [1] M. W. Zemansky and R. H. Dittman, *Heat and Thermodynamics* 6th Ed., (McGraw-Hill, New York, 1984).
- [2] R. P. Feynman, R. B. Leighton, M. Sands, *The Feynman Lectures on Physics, Vol. II*, (Addison - Wesley, Reading Mass. 1964)
- [3] H. J. Kreuzer, *Nonequilibrium Thermodynamics and its Statistical Foundations*, (Oxford University Press, Oxford 1981).
- [4] W. A. Wakeham, A. Nagashima, and J. V. Sengers, Eds. *Experimental Thermodynamics, Vol. III: Measurement of the Transport Properties of Fluids*, (Blackwell Scientific Publications, Oxford, 1991).
- [5] J. Millat, J. H. Dymond, C. A. Nieto de Castro, *Transport Properties of Fluids*, (IUPAC and Cambridge University Press, Cambridge, 1996).
- [6] C. Hoheisel, *Theoretical Treatment of Liquids and Liquid Mixtures*, (Elsevier, Amsterdam, 1993).
- [7] J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, (Wiley, New York, 1954).
- [8] D. G. Friend and J. C. Rainwater, Chem. Phys. Lett. **107**, 590 (1984); J. C. Rainwater and D. G. Friend, Phys. Rev. A, **36**, 40 (1987).
- [9] B. Najafi, Y. Ghayeb, J. C. Rainwater, S. Alavi, and R. F. Snider, Physica A, **260**, 31 (1998).
- [10] N. N. Bogoliubov, In *Studies in Statistical Physics*, G. E. Uhlenbeck and J. de Boer, Eds. (North-Holland, Amsterdam, 1962).
- [11] H. S. Green, *The Molecular Theory of Fluids*, (North-Holland, Amsterdam, 1952).

- [12] S. T. Choh and G. E. Uhlenbeck, *The Kinetic Theory of Phenomena in Dense Gases*, University of Michigan, 1958 (unpublished).
- [13] M. S. Green, J. Chem. Phys. **25**, 836 (1956); Physica **24**, 393 (1958).
- [14] E. G. D. Cohen, Physica **28**, 1025; 1045 (1962).
- [15] E. G. D. Cohen, In *Transport Phenomena in Fluids*, H. J. M. Hanley, Ed. (Marcel Dekker, New York, 1969).
- [16] J. H. Ferziger and H. G. Kaper, *Mathematical Theory of Transport Processes in Gases*, (North-Holland, Amsterdam, 1972).
- [17] R. M. Mazo, *Statistical Mechanical Theories of Transport Properties*, (Pergamon Press, Oxford, 1967).
- [18] B. C. Eu, *Kinetic Theory and Irreversible Thermodynamics*, (Wiley, New York 1992).
- [19] R. F. Snider and C. F. Curtiss, Phys. Fluids **1** 122 (1958); Phys. Fluids **3**, 903 (1960).
- [20] R. F. Snider and F. R. McCourt, Phys. Fluids **6**, 1020 (1963).
- [21] T. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1960).
- [22] D. K. Hoffman and C. F. Curtiss, Phys. Fluids **7** 1887 (1964); **8**, 667,890 (1965).
- [23] D. E. Bennett and C. F. Curtiss, J. Chem. Phys. **51**, 2811 (1969).
- [24] V. M. Kuznetsov, High Temp. Res. **16**, 1005 (1979).
- [25] G. W. Wei, University of British Columbia, dissertation, 1996.
- [26] H. J. M. Hanley, In *Transport Phenomena in Fluids*, H. J. M. Hanley, Ed. (Marcel Dekker, New York, 1969), p.313.
- [27] A. Einstein, Ann. Phys. **7**, 549 (1905).
- [28] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).
- [29] H. B. Callen and T. A. Welton, Phys. Rev. **83**, 34 (1951).
- [30] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II. Nonequilibrium Statistical Mechanics*, (Springer-Verlag, Berlin 1985)

- [31] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 898 (1954).
- [32] R. Kubo, *Some Aspects of Statistical-Mechanical Theory of Irreversible Processes, Lectures in Theoretical Physics* Vol. I (Interscience, New York, 1959).
- [33] D. A. McQuarrie, *Statistical Mechanics*, (Harper - Row, New York, 1976).
- [34] J. A. McLennan, *Introduction to Non-Equilibrium Statistical Mechanics*, (Prentice Hall, Englewood Cliffs, NJ, 1989).
- [35] P. Résibois and M. De Leener, *Classical Kinetic Theory of Fluids*, (Wiley, New York, 1977).
- [36] W. A. Steele, In *Transport Phenomena in Fluids*, H. J. M. Hanley, Ed. (Marcel Dekker, New York, 1969).
- [37] D. Chandler, *Introduction to Modern Statistical Mechanics*, (Oxford University Press, Oxford, 1987).
- [38] R. Balescu, *Statistical Dynamics: Matter Out of Equilibrium*, (Imperial College Press, London, 1997).
- [39] R. Zwanzig, Ann. Rev. Phys. Chem. **16**, 67 (1965).
- [40] M. H. Ernst, L. K. Haines, and J. R. Dorfman, Rev. Mod. Phys. **41**, 296 (1969).
- [41] E. Helfand, Phys. Fluids, **4**, 681 (1961).
- [42] L. I. Schiff, *Quantum Mechanics*, 3rd Ed. (McGraw-Hill, New York, 1968).
- [43] R. L. Liboff, *Introductory Quantum Mechanics*, 2nd Ed. (Addison-Wesley, Reading, Mass. 1992).
- [44] A. Rahman, Phys. Rev. **136A**, 405 (1964).
- [45] P. Résibois, J. Chem. Phys. **41**, 2979 (1964).
- [46] J. W. Dufty and M. J. Lindenfeld, J. Stat. Phys. **30**, 259 (1979).
- [47] M. H. Ernst, J. R. Dorfman and E. G. D. Cohen, Physica **31**, 493 (1965).
- [48] M. H. Ernst, Physica **32**, 209 (1966).
- [49] S. Ono and T. Shizume, J. Phys. Soc. Japan **19**, 815 (1964).

- [50] R. Kapral and R. C. Desai, J. Chem. Phys. **53**, 3640 (1970).
- [51] K. Kawasaki and I. Oppenheim, Phys. Rev. A **136**, 1519 (1964); **139**, 649 (1965).
- [52] R. Zwanzig, Phys. Rev. **129**, 486 (1963).
- [53] K. Kawasaki and I. Oppenheim, Phys. Rev., **139**, A649 (1965).
- [54] J. C. Rainwater, J. Chem. Phys. **81**, 495 (1981).
- [55] R. F. Snider and B. C. Sanctuary, J. Chem. Phys. **55**, 1555 (1971).
- [56] W. Glöckle, *The Quantum Mechanical Few-Body Problem* (Springer-Verlag, Berlin, 1983).
- [57] R. F. Snider, J. Chem. Phys. **88**, 6438 (1988).
- [58] N. Hamer and I. Oppenheim, Phys. Rev. B **2**, 2153 (1970).
- [59] N. Hamer and I. Oppenheim, Physica **66**, 217 (1973).
- [60] The binary collision expansion used here is a generalization of the method introduced by Watson. K. M. Watson, Phys. Rev. **103**, 489 (1956).
- [61] A. J. F. Siegert and E. Teramoto, Phys. Rev. **110**, 1232 (1958).
- [62] S. Chapman and T. G. Cowling, *The Mathematical Theory of Nonuniform Gases*, (Cambridge Univ. Press, Cambridge, 1953).
- [63] H. Mori, Phys. Rev. **112**, 1828 (1958).
- [64] H. S. Green, J. Math. Phys. **2**, 344 (1961).
- [65] R. Zwanzig, In *Lectures in Theoretical Physics*, Vol. 3 (Interscience, New York, 1961), p.106.
- [66] S. Alavi and R. F. Snider, J. Chem. Phys. **109**, 3452 (1998). Eq. (3) of that paper has an extra factor of 1/2. Its removal has no effect on anything else in the paper.
- [67] F. R. W. McCourt, J. J. M. Beenakker, W. E. Köhler and I. Kuščer, *Nonequilibrium Phenomena in Polyatomic Gases*, Vol. 2, (Oxford Scientific Publications, Oxford, 1991).
- [68] E. P. Wigner, *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra*, (Academic Press, New York 1959).

- [69] H. Jeffreys, *Cartesian Tensors*, (Cambridge University Press, Cambridge, 1931).
- [70] J. A. R. Coope, R. F. Snider and F. R. McCourt, J. Chem. Phys. **43**, 2269 (1965).
- [71] S. Nakajima, Prog. Theor. Phys. **20**, 948 (1958).
- [72] R. Zwanzig, J. Chem. Phys **33**, 1338 (1960).
- [73] R. Zwanzig, Phys. Rev. **124**, 983, (1961); Physica **30**, 1109 (1964).
- [74] J. T. Hynes and J. M. Deutsch, In *Physical Chemistry, An Advanced Treatise, Vol. XIB*, D. Henderson, Ed. (Academic Press, New York, 1975).
- [75] H. Grabert, *Projection Operator Techniques in Nonequilibrium Statistical Mechanics*, (Springer-Verlag, Berlin, 1982).
- [76] J. A. R. Coope and R. F. Snider, J. Math. Phys. **11**, 1003 (1970).
- [77] F. M. Chen, H. Moraal and R. F. Snider, J. Chem. Phys. **57**, 542 (1972).
- [78] W. E. Köhler and G. W. t'Hooft, Z. Naturforsch. A **34**, 1255 (1979).
- [79] F. R. W. McCourt, J. J. M. Beenakker, W. E. Köhler and I. Kušcer, *Nonequilibrium Phenomena in Polyatomic Gases*, (Oxford Scientific Publications, Oxford, 1990).
- [80] E. Wigner, Phys. Rev. **40**, 479 (1932).
- [81] J. A. R. Coope and R. F. Snider, J. Chem. Phys. **57**, 4266 (1972).
- [82] W. Nernst, *Boltzmann-Festschrift* 904 (1904) according to J. N. Butler and R. S. Brokaw, J. Chem. Phys. **26**, 1636 (1957).
- [83] D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. **31** 1531, 1545 (1959); **33**, 942 (1960).
- [84] A. Eucken, Physik. Z. **14**, 324 (1913).
- [85] D. G. Friend and J. C. Rainwater, Chem. Phys. Lett., **107**, 590 (1984).
- [86] J. T. Lowry and R. F. Snider, J. Chem. Phys. **61** 2320 (1974).
- [87] R. F. Snider and S. Alavi, J. Chem. Phys., in press.
- [88] R. F. Snider, J. Stat. Phys. **61**, 443 (1990).

- [89] see e. g. R. F. Snider, *Int. Rev. in Phys. Chem.* **17**, 185 (1998).
- [90] R. F. Snider and J. G. Muga, *Can. J. Phys.* **72**, 152 (1993).
- [91] R. Zwanzig and R. Mountain, *J. Chem. Phys.* **43**, 4464 (1965).
- [92] D. Enskog, *Svensk. Akad. Handl.* **63**, No.4 (1922).
- [93] R. F. Snider, unpublished notes.
- [94] M. S. Green, *Physica* **24**, 393 (1958).
- [95] K. Kawasaki and I. Oppenheim, *Phys. Lett.* **11**, 124 (1964).
- [96] K. Kawasaki and I. Oppenheim, *Phys. Rev.* **139**, A1763 (1965).
- [97] E. G. D. Cohen, *Am. J. Phys.* **61**, 524 (1993).

Appendix A

Identification of F_η

The integral in Eq. (3.66) is defined as I . The collision parameter \mathbf{r}' has been written in terms of $R\boldsymbol{\kappa}_R + s_0\mathbf{g}_0$,

$$I = \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{1}{r} \frac{du}{dr} \{[\boldsymbol{\gamma}\mathbf{r}]^{(2)} + [\mathbf{r}\boldsymbol{\gamma}]^{(2)}\} : \{R[\boldsymbol{\kappa}_R\boldsymbol{\gamma}_0]^{(2)} + s_0[\mathbf{g}_0\boldsymbol{\gamma}_0]^{(2)}\} e^{-\gamma^2} e^{-\beta u}. \quad (\text{A.1})$$

This is a six-fold integral over the relative position and momentum. In the following, it is reduced to the form of a standard integral from the work of Snider and McCourt. This facilitates the comparison of the results of the present thesis with previous work.

The first set of contractions gives

$$\{[\boldsymbol{\gamma}\mathbf{r}]^{(2)} + [\mathbf{r}\boldsymbol{\gamma}]^{(2)}\} : [\boldsymbol{\kappa}_R\boldsymbol{\gamma}_0]^{(2)} = (\boldsymbol{\gamma} \cdot \boldsymbol{\kappa}_R)(\mathbf{r} \cdot \boldsymbol{\gamma}_0) + (\mathbf{r} \cdot \boldsymbol{\kappa}_R)(\boldsymbol{\gamma} \cdot \boldsymbol{\gamma}_0) - \frac{2}{3}(\boldsymbol{\gamma} \cdot \mathbf{r})(\boldsymbol{\gamma}_0 \cdot \boldsymbol{\kappa}_R). \quad (\text{A.2})$$

The dot products are given in terms of the collision angles in Chap. 2. Using these relations,

$$\begin{aligned} \{[\boldsymbol{\gamma}\mathbf{r}]^{(2)} + [\mathbf{r}\boldsymbol{\gamma}]^{(2)}\} : [\boldsymbol{\kappa}_R\boldsymbol{\gamma}_0]^{(2)} &= -\gamma\gamma_0 r [\cos\beta_R \cos(\eta_R - \theta) + \cos\eta_R \cos(\beta_R - \theta) \\ &\quad - \frac{2}{3} \cos\theta \cos(\eta_R - \beta_R)] \\ &= -\gamma\gamma_0 r \left[\cos(\beta_R + \eta_R - \theta) + \frac{1}{3} \cos(\eta_R - \beta_R) \cos\theta \right]. \end{aligned} \quad (\text{A.3})$$

Using the definition, $\eta_R = \beta_R + \pi - \phi$ with $\phi = \arcsin[L/R(mE)^{1/2}]$, the right hand side of this expression simplifies to,

$$\cos(\eta_R + \beta_R - \theta) + \frac{1}{3} \cos(\eta_R - \beta_R) \cos\theta = -\cos(2\beta_R - \theta - \phi) - \frac{1}{3} \cos\phi \cos\theta. \quad (\text{A.4})$$

The value of β_R is related to its value at the limit of $R \rightarrow \infty$, β , by the relation, $\beta_R = \beta + \phi$. Substituting this relation, and recognizing that,

$$\cos\phi = 1 - O(1/R^2) \quad \sin\phi = \mathcal{L}/R(mE)^{1/2} \quad (\text{A.5})$$

gives:

$$\begin{aligned}
-\cos(2\beta - \theta + \phi) - \frac{1}{3} \cos \theta &= -\cos(2\beta - \theta) + \frac{\mathcal{L}}{R(mE)^{1/2}} \sin(2\beta - \theta) - \frac{1}{3} \cos \theta \\
&\approx -\cos(2\beta - \theta) + \frac{\gamma r \sin \theta}{R\gamma_0} \sin(2\beta - \theta) - \frac{1}{3} \cos \theta. \quad (\text{A.6})
\end{aligned}$$

With $\beta - \theta = \omega \pm \zeta$ the first set of contractions becomes

$$R\gamma\gamma_0 r [\cos(2\omega + \theta \pm 2\zeta) + 1/3 \cos \theta] - \gamma^2 r^2 \sin \theta \sin(2\omega + \theta \pm 2\zeta). \quad (\text{A.7})$$

The second set of tensorial contractions in Eq.(A.1) are

$$[\gamma \mathbf{r}]^{(2)} : [\gamma_0]^{(2)} = [\mathbf{r} \gamma]^{(2)} : [\gamma_0]^{(2)} = (\gamma \cdot \gamma_0)(\mathbf{r} \cdot \gamma_0) - \frac{1}{3}(\gamma \cdot \mathbf{r})\gamma_0^2, \quad (\text{A.8})$$

which can be written in terms of angles defined in Section 2.5.1,

$$\begin{aligned}
\{[\gamma \mathbf{r}]^{(2)} + [\mathbf{r} \gamma]^{(2)}\} : [\gamma_0]^{(2)} &= -2\gamma\gamma_0^2 r [\cos \eta_R \cos(\eta_R - \theta) - 1/3 \cos \theta] \\
&= -\gamma\gamma_0^2 r [\cos(2\eta_R - \theta) + 1/3 \cos \theta] \\
&= -\gamma\gamma_0^2 r \{\cos(2\omega + \theta \pm 2\zeta) + 1/3 \cos \theta\}, \quad (\text{A.9})
\end{aligned}$$

where terms of order $1/R$ or smaller have been neglected.

Adding the two expressions from Eqs. (A.7) and (A.9) gives,

$$\begin{aligned}
[\gamma \mathbf{r}]^{(2)} : [\gamma_0 \mathbf{r}]^{(2)} &= -\gamma\gamma_0 r [s_0 g_0 - R] \left[\cos(2\omega + \theta \pm 2\zeta) + \frac{\cos \theta}{3} \right] \\
&\quad - \gamma^2 r^2 \sin \theta \sin(2\omega + \theta \pm 2\zeta) \\
&= -\gamma^2 r^2 \sin \theta (X \pm Y) \left[\cos(2\omega + \theta \pm 2\zeta) + \frac{\cos \theta}{3} \right] \\
&\quad - \gamma^2 r^2 \sin \theta \sin(2\omega + \theta \pm 2\zeta), \quad (\text{A.10})
\end{aligned}$$

where the definitions of $X \pm Y$ as given in Eq. (9) of Snider and McCourt were used with $+$ for the incoming and $-$ for the outgoing part of the collision trajectory. Substituting this result into Eq. (A.1) gives,

$$\begin{aligned}
I &= -8\pi^2 \iint dr d\gamma \frac{du}{dr} r^3 e^{-\gamma^2} e^{-\beta u} \gamma^4 \times \\
&\quad \left\{ \int_0^{\pi/2} \{ (X + Y) \left[\cos(2\omega + \theta + 2\zeta) + \frac{\cos \theta}{3} \right] + \sin(2\omega + \theta + 2\zeta) \} \sin^2 \theta d\theta \right. \\
&\quad \left. + \int_{\pi/2}^{\pi} \{ (X - Y) \left[\cos(2\omega + \theta - 2\zeta) + \frac{\cos \theta}{3} \right] + \sin(2\omega + \theta - 2\zeta) \} \sin^2 \theta d\theta \right\}. \quad (\text{A.11})
\end{aligned}$$

Changing variables in the last integral to $\theta' = \pi - \theta$, and then renaming the dummy variable θ' as θ once again gives,

$$\begin{aligned}
I = & -8\pi^2 \iint dr d\gamma \frac{du}{dr} r^3 e^{-\beta u} e^{-\gamma^2} \gamma^4 \\
& \times \left\{ \int_0^{\pi/2} \{ (X + Y) \left[\cos(2\omega + \theta + 2\zeta) + \frac{\cos \theta}{3} \right] + \sin(2\omega + \theta + 2\zeta) \} \sin^2 \theta d\theta \right. \\
& \left. + \int_0^{\pi/2} \{ (Y - X) \left[\cos(2\omega - \theta - 2\zeta) + \frac{\cos \theta}{3} \right] + \sin(2\omega - \theta - 2\zeta) \} \sin^2 \theta d\theta \right\}. \quad (\text{A.12})
\end{aligned}$$

Adding the two integrals together gives,

$$\begin{aligned}
I = & \frac{-16\pi^2}{3} \iiint_0^{\pi/2} \frac{du}{dr} r^3 e^{-\beta u} e^{-\gamma^2} \gamma^4 \sin^2 \theta [Y \cos \theta + 3Y \cos 2\omega \cos(\theta + 2\zeta) \\
& - 3X \sin 2\omega \sin(\theta + 2\zeta) + 3 \cos 2\omega \sin(\theta + 2\zeta)] d\theta dr d\gamma. \quad (\text{A.13})
\end{aligned}$$

The triple integral in this expression is the same as that appearing in the definition of F_η as given by Eq. (25) of Snider and McCourt [20]. Thus

$$I = \frac{-16\pi^2}{3} \left(\frac{kT\sigma^3}{2\pi} F_\eta \right) = \frac{-8\pi kT\sigma^3}{3} F_\eta. \quad (\text{A.14})$$

Appendix B

Identification of N_η

The integral in Eq. (3.72) is denoted as I

$$I = \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{du}{dr} \frac{1}{r} \left[(\mathbf{r} \cdot \boldsymbol{\gamma}_0)^2 - \frac{r^2 \gamma_0^2}{3} \right] e^{-\gamma^2} e^{-\beta u}. \quad (\text{B.1})$$

Simplifying, this becomes,

$$I = \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{du}{dr} r \gamma_0^2 \cos^2(\eta_R - \theta) e^{-\gamma^2} e^{-\beta u} - \frac{1}{3} \int d\mathbf{r} \frac{du}{dr} r e^{-\beta u} \int d\boldsymbol{\gamma} \gamma_0^2 e^{-\gamma^2} = (\text{i}) + (\text{ii}). \quad (\text{B.2})$$

Evaluation of (i) involves simplifications of the angles,

$$(\text{i}) = 8\pi^2 \iiint_0^\pi r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2 \cos^2(\beta_R - \phi - \theta) \sin \theta d\theta dr d\boldsymbol{\gamma}. \quad (\text{B.3})$$

If $\beta_R = \beta + \phi$ is used in the limit $R \rightarrow \infty$, then

$$\cos^2(\beta_R - \phi - \theta) = \cos^2(\beta - \theta) = \cos^2(\omega \pm \zeta). \quad (\text{B.4})$$

This expression is substituted in Eq. (B.3). The resulting integral over θ is written as two parts, one for the incoming and the other for the outgoing trajectory,

$$\begin{aligned} \int_0^\pi \cos^2(\omega \pm \zeta) \sin \theta d\theta &= \int_0^{\pi/2} \cos^2(\omega + \zeta) \sin \theta d\theta + \int_{\pi/2}^\pi \cos^2(\omega - \zeta) \sin \theta d\theta \\ &= \int_0^{\pi/2} \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega + 2\zeta) \right] \sin \theta d\theta \\ &\quad + \int_0^{\pi/2} \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega - 2\zeta) \right] \sin(\pi - \theta') d\theta' \\ &= \int_0^{\pi/2} (1 + \cos 2\omega \cos 2\zeta) \sin \theta d\theta. \end{aligned} \quad (\text{B.5})$$

Putting terms of (i) back together and using the definition of N_λ given in Eq. (31) of Snider and McCourt [20] gives,

$$(\text{i}) = 8\pi^2 \iiint_0^{\pi/2} r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2 (1 + \cos 2\omega \cos 2\zeta) \sin \theta d\theta dr d\boldsymbol{\gamma} = 4\pi^2 kT \sigma^3 N_\lambda. \quad (\text{B.6})$$

The term (ii) is simplified by integrating over relative momentum,

$$(ii) = \frac{-1}{3} \int d\mathbf{r} r \frac{d}{dr} e^{-\beta u} \int d\gamma (\gamma^2 + \beta u) e^{-\gamma^2} = \frac{-\pi^{3/2}}{3} \int d\mathbf{r} \frac{du}{dr} r e^{-\beta u} \left(\frac{3}{2} + \beta u \right), \quad (B.7)$$

and writing the second integral as,

$$(ii) = \frac{-\pi^{3/2}}{3} \left(\frac{3}{2} - T \frac{d}{dT} \right) \int d\mathbf{r} \frac{du}{dr} r e^{-\beta u}. \quad (B.8)$$

Recognizing that the second virial coefficient $B(T)$ can be written in the form,

$$B(T) = \frac{-1}{6kT} \int d\mathbf{r} \frac{du}{dr} r e^{-\beta u}, \quad (B.9)$$

the (ii) term becomes,

$$(ii) = \frac{-\pi^{3/2}}{3} \left(\frac{3}{2} + T \frac{d}{dT} \right) [-6kTB(T)] = \pi^{3/2} kT \left[5B(T) + 2T \frac{dB(T)}{dT} \right]. \quad (B.10)$$

Adding the simplified terms gives an expression for the integral in Eq. (3.72)

$$\begin{aligned} I &= 2\pi^{3/2} kT \left[\frac{5}{2} B(T) + T \frac{dB(T)}{dT} + 2\pi^{1/2} \sigma^3 N_\lambda \right] \\ &= 2\pi^{3/2} kT \frac{4\sigma^3 \pi^{1/2}}{3} \left[\frac{3}{4\sigma^3 \pi^{1/2}} \left(\frac{5}{2} B(T) + \frac{T dB(T)}{dT} \right) + \frac{3}{2} N_\lambda \right] = \frac{8\sigma^3 \pi^2 kT}{3} N_\eta. \end{aligned} \quad (B.11)$$

Appendix C

Binary Mixture Viscosity Cross Sections

The following notation is standard in the theory of the viscosity of a binary mixture [7],

$$[\eta_f] = \frac{5kT}{8\Omega_{ff}^{(2,2)}} \quad [\eta_{fb}] = \frac{5kT}{8\Omega_{fb}^{(2,2)}} \quad A_{fb}^* = \frac{2\Omega_{fb}^{(2,2)}}{\Omega_{fb}^{(1,1)}} \quad (C.1)$$

$$\begin{aligned} H_{ff} &= \frac{X_f^2}{[\eta_f]} + \frac{2X_fX_b}{[\eta_{fb}]} \frac{m_fm_b}{(m_f+m_b)^2} \left(\frac{5}{3A_{fb}^*} + \frac{m_b}{m_f} \right) \\ &= \left[\frac{8}{5} X_f^2 \Omega_{ff}^{(2,2)} + \frac{32}{3} \frac{X_fX_bm_fm_b}{(m_f+m_b)^2} \Omega_{fb}^{(1,1)} + \frac{16}{5} \frac{X_fX_bm_b^2}{(m_f+m_b)^2} \Omega_{fb}^{(2,2)} \right] / kT \end{aligned} \quad (C.2)$$

$$\begin{aligned} H_{fb} &= \frac{-2X_fX_b}{[\eta_{fb}]} \frac{m_fm_b}{(m_f+m_b)^2} \left(\frac{5}{3A_{fb}^*} - 1 \right) \\ &= \left[\frac{-32}{3} \frac{X_fX_bm_fm_b}{(m_f+m_b)^2} \Omega_{fb}^{(1,1)} + \frac{16}{5} \frac{X_fX_bm_b^2}{(m_f+m_b)^2} \Omega_{fb}^{(2,2)} \right] / kT. \end{aligned} \quad (C.3)$$

By permuting the f and b indices, the other two H 's can be obtained,

$$H_{bb} = \left[\frac{8}{5} X_b^2 \Omega_{bb}^{(2,2)} + \frac{32}{3} \frac{X_fX_bm_fm_b}{(m_f+m_b)^2} \Omega_{bf}^{(1,1)} + \frac{16}{5} \frac{X_fX_bm_f^2}{(m_f+m_b)^2} \Omega_{bf}^{(2,2)} \right] / kT \quad (C.4)$$

$$H_{bf} = \left[\frac{-32}{3} \frac{X_fX_bm_fm_b}{(m_f+m_b)^2} \Omega_{bf}^{(1,1)} + \frac{16}{5} \frac{X_fX_bm_f^2}{(m_f+m_b)^2} \Omega_{bf}^{(2,2)} \right] / kT. \quad (C.5)$$

Appendix D

Determination of the Fourth-Rank Identity Tensor

The identity tensor of rank four $E^{(4)}$ must be a linear combination of the three fourth rank rotationally invariant tensors defined in Eq. (4.12),

$$E^{(2)} = a \cup \cup + b \mathbb{W} + c \mathbb{U}. \quad (D.1)$$

The coefficients of this expansion can be determined by utilizing the idempotency property of the identity,

$$E^{(2)} : E^{(2)} = E^{(2)}, \quad (D.2)$$

along with the fact that $E^{(2)}$ must be symmetric traceless with respect to the the first pair of indices and the last pair of indices. This symmetry implies that $b = c$. Therefore, the idempotency condition is written as,

$$[a \cup \cup + b (\mathbb{W} + \mathbb{U})] : [a \cup \cup + b (\mathbb{W} + \mathbb{U})] = a \cup \cup + b (\mathbb{W} + \mathbb{U}). \quad (D.3)$$

It is straightforward to show that

$$\begin{aligned} \cup \cup : \cup \cup &= 3 \cup \cup & \cup \cup : \mathbb{W} &= \cup \cup & \cup \cup : \mathbb{U} &= \cup \cup, \\ \mathbb{W} : \cup \cup &= \cup \cup & \mathbb{W} : \mathbb{W} &= \mathbb{U} & \mathbb{W} : \mathbb{U} &= \mathbb{W}, \\ \mathbb{U} : \cup \cup &= \cup \cup & \mathbb{U} : \mathbb{W} &= \mathbb{W} & \mathbb{U} : \mathbb{U} &= \mathbb{U}. \end{aligned} \quad (D.4)$$

Using these equalities in Eq. (D.2) gives the following set of equations for the unknown coefficients a and b ,

$$3a^2 + 4ab = a \quad 2b^2 = b, \quad (D.5)$$

which have $a = -1/3$ and $b = 1/2$ as their solution. Therefore,

$$E^{(2)} = \frac{1}{2} [\mathbb{W} + \mathbb{U}] - \frac{1}{3} \cup \cup. \quad (D.6)$$

It can be verified that $E^{(2)} \overset{4}{\odot} E^{(2)} = 5$ which is the dimension of the irreducible representation of the three dimensional rotation group of J. This makes use of the following contractions,

$$\begin{aligned}
 UU \overset{4}{\odot} UU &= 9 & UU \overset{4}{\odot} \Psi &= UU \overset{4}{\odot} \mathcal{U} = 3, \\
 \Psi \overset{4}{\odot} \Psi &= 9 & \Psi \overset{4}{\odot} UU &= \Psi \overset{4}{\odot} \mathcal{U} = 3, \\
 \mathcal{U} \overset{4}{\odot} \mathcal{U} &= 9 & \mathcal{U} \overset{4}{\odot} UU &= \mathcal{U} \overset{4}{\odot} \Psi = 3.
 \end{aligned} \tag{D.7}$$

Appendix E

Evaluation of C

The quantity C is defined as,

$$C \equiv \frac{\Lambda^6}{N} \text{Tr}_2 \mathcal{L}_{12} \frac{1}{z - \mathcal{L}_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) n^2 \left(e^{-\beta H_{12}^{(2)}} - e^{-\beta K_{12}} \right). \quad (\text{E.1})$$

Since the two-particle Hamiltonian commutes with the $\mathcal{L}_{12} \frac{1}{z - \mathcal{L}_{12}}$ combination, C is written as,

$$C = \frac{n^2 \Lambda^6}{N} \text{Tr}_2 e^{-\beta H_{12}^{(2)}} \frac{1}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) - \frac{1}{N} \text{Tr}_2 \frac{1}{z - \mathcal{L}_{12}} \mathcal{L}_{12} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) e^{-\beta K_{12}}. \quad (\text{E.2})$$

In both terms, the functions to the right of the operator combinations are only functions of the momentum and the operator combination can be identified as the Møller operator,

$$\frac{1}{z - \mathcal{L}_{12}} \mathcal{L}_{12} \Rightarrow \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} \equiv \Omega' - 1. \quad (\text{E.3})$$

The effect of the Møller operator is,

$$\begin{aligned} C &= \frac{n^2 \Lambda^6}{N} \text{Tr}_2 \left[e^{-\beta H_{12}^{(2)}} (\Omega - 1) (\mathbf{J}_{K1} + \mathbf{J}_{K2}) - (\Omega - 1) e^{-\beta K_{12}} (\mathbf{J}_{K1} + \mathbf{J}_{K2}) \right] \\ &= \frac{n^2 \Lambda^6}{N} \text{Tr}_2 \left(e^{-\beta H_{12}^{(2)}} - e^{-\beta K_{12}} \right) (\mathbf{J}_{K1} + \mathbf{J}_{K2}) = \frac{2n\Lambda^3}{\pi^{3/2}} B(T) \mathbf{J}_{K1} \varphi_1. \end{aligned} \quad (\text{E.4})$$

Appendix F

Determination of $H_\eta + R_\eta$

The integral in Eq. (6.124) has the following form,

$$\begin{aligned}
 (iii) &= \frac{i\mathbb{V}_{KK}n^2\Lambda^6}{2N\sqrt{2kT}} \text{Tr}_{12} \mathbf{J}_{V12} : e^{-\beta H_{12}^{(2)}} \frac{i}{z - \mathcal{L}_{12}} i\mathcal{L}_0 \{ [\mathbf{p}_1 \mathbf{r}_1]^{(2)} + [\mathbf{p}_2 \mathbf{r}_2]^{(2)} \} \\
 &= \frac{i\mathbb{V}_{VV}n^2\Lambda^6}{2N\sqrt{2kT}} \text{Tr}_{12} \mathbf{J}_{V12} : e^{-\beta H_{12}^{(2)}} \Omega_+ \frac{1}{2} \{ [(\mathbf{r}_1 + \mathbf{r}_2)(\mathbf{p}_1 + \mathbf{p}_2)]^{(2)} + [(\mathbf{r}_1 - \mathbf{r}_2)(\mathbf{p}_1 - \mathbf{p}_2)]^{(2)} \} \\
 &= (\text{cm}) + (\text{rel}) + \text{time integral corrections} + \dots
 \end{aligned} \tag{F.1}$$

The centre of mass term does not contribute and the Møller operator changes the relative position and momentum

$$\begin{aligned}
 (iii) &= \frac{-i\mathbb{V}_{VV}n\Lambda_r^3}{2\sqrt{2kT}A_V} \text{Tr}_{\text{rel}} e^{-\beta H_{\text{rel}}} \frac{1}{r} \frac{du}{dr} [\mathbf{r}]^{(2)} : [\mathbf{r}' \mathbf{p}_0]^{(2)} \\
 &= -\sqrt{\frac{m}{2kT\pi^3}} \frac{i\mathbb{V}_{VV}n}{2A_V} \int d\mathbf{r} d\boldsymbol{\gamma} e^{-\gamma^2 - \beta u} \frac{1}{r} \frac{du}{dr} \left[(\mathbf{r} \cdot \boldsymbol{\gamma}_0)(\mathbf{r} \cdot \mathbf{r}') - \frac{1}{3} r^2 (\boldsymbol{\gamma}_0 \cdot \mathbf{r}') \right] \\
 &= -i\sqrt{\frac{m}{2kT\pi^3}} \frac{\mathbb{V}_{VV}n}{2A_V} [(a) + (b)].
 \end{aligned} \tag{F.2}$$

For the first integral, utilizing the definitions of Section 2.5.1 gives

$$(a) = 8\pi^2 \int dr d\theta d\gamma r \sin \theta \gamma^2 e^{-\gamma^2} \frac{du}{dr} r \gamma_0 \cos(\eta_R - \theta) r [R \cos(\beta_R - \theta) + s_0 g_0 \cos(\eta_R - \theta)]. \tag{F.3}$$

Substituting $\eta_R = \beta_R + \pi - \phi$ in the trigonometric functions above, and making use of the fact that in the limit of $R \rightarrow \infty$ the angle $\beta_R \rightarrow \beta + \phi$, and finally making use of the limiting forms,

$$\cos \phi = 1 - O(1/R^2) \qquad \sin \phi = \mathcal{L}/R(mE)^{1/2} \tag{F.4}$$

then gives,

$$R \cos(\beta_R - \theta) \cos(\beta_R + \pi - \phi - \theta) + s_0 g_0 \cos^2(\beta_R + \pi - \phi - \theta)$$

$$\begin{aligned}
&= (s_0 g_0 - R)[\cos(\beta - \theta) \cos \phi - \sin(\beta - \theta) \sin \phi]^2 \\
&= (s_0 g_0 - R) \cos^2(\beta - \theta) + \frac{\gamma}{\gamma_0} r \sin \theta \cos(\beta - \theta) \sin(\beta - \theta) + O(1/R) \\
&= \frac{\gamma}{\gamma_0} r \sin \theta [(X \pm Y) \cos^2(\omega \pm \zeta) + \cos(\omega \pm \zeta) \sin(\omega \pm \zeta)]. \tag{F.5}
\end{aligned}$$

This expression is substituted back into (a) to give,

$$(a) = 8\pi^2 \int \int \int_0^\pi d\theta dr d\gamma r^4 \sin^2 \theta \gamma^3 e^{-\gamma_0^2} \frac{du}{dr} [(X \pm Y) \cos^2(\omega \pm \zeta) + \cos(\omega \pm \zeta) \sin(\omega \pm \zeta)]. \tag{F.6}$$

The integration over θ gives,

$$\begin{aligned}
&\int_0^{\pi/2} d\theta \sin^2 \theta [(X + Y) \cos^2(\omega + \zeta) + \cos(\omega + \zeta) \sin(\omega + \zeta)] \\
&+ \int_{\pi/2}^\pi d\theta \sin^2 \theta [(X - Y) \cos^2(\omega - \zeta) + \cos(\omega - \zeta) \sin(\omega - \zeta)]. \tag{F.7}
\end{aligned}$$

Changing the integration variable in the second integral from θ to $\theta' = \pi - \theta$ gives,

$$\begin{aligned}
&\int_0^{\pi/2} d\theta \sin^2 \theta \{ [(X + Y) \cos^2(\omega + \zeta) + \cos(\omega + \zeta) \sin(\omega + \zeta)] \\
&\quad + [(X - Y) \cos^2(\omega - \zeta) + \cos(\omega - \zeta) \sin(\omega - \zeta)] \} \\
&= \int_0^{\pi/2} d\theta \sin^2 \theta \left\{ (X + Y) \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega + 2\zeta) \right] + \frac{1}{2} \sin(2\omega + 2\zeta) \right. \\
&\quad \left. + (X - Y) \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega - 2\zeta) \right] + \frac{1}{2} \sin(2\omega - 2\zeta) \right\} \\
&= \int_0^{\pi/2} d\theta \sin^2 \theta \left\{ X + \frac{1}{2} (X + Y) (\cos 2\omega \cos 2\zeta - \sin 2\omega \sin 2\zeta) \right. \\
&\quad \left. + \frac{1}{2} \sin 2\omega \cos 2\zeta + \frac{1}{2} \cos 2\omega \sin 2\zeta \right. \\
&\quad \left. + \frac{1}{2} (X - Y) (\cos 2\omega \cos 2\zeta + \sin 2\omega \sin 2\zeta) \right. \\
&\quad \left. + \frac{1}{2} \sin 2\omega \cos 2\zeta - \frac{1}{2} \cos 2\omega \sin 2\zeta \right\} \\
&= \int_0^{\pi/2} d\theta \sin^2 \theta (X + X \cos 2\omega \cos 2\zeta - Y \sin 2\omega \sin 2\zeta + \sin 2\omega \cos 2\zeta). \tag{F.8}
\end{aligned}$$

Thus overall we obtain,

$$\begin{aligned}
(a) &= 8\pi^2 \int \int \int_0^{\pi/2} d\theta dr d\gamma r^4 \sin^2 \theta \gamma^3 e^{-\gamma_0^2} \frac{du}{dr} \\
&\quad \times [X(1 + \cos 2\omega \cos 2\zeta) - Y \sin 2\omega \sin 2\zeta + \sin 2\omega \cos 2\zeta]. \tag{F.9}
\end{aligned}$$

Identifying this integral as Eq. (33) of Snider and McCourt gives,

$$(a) = 4\pi^2 kT \sigma^4 (H_\lambda + R_\lambda). \tag{F.10}$$

For the second integral,

$$\begin{aligned}
(b) &= \int d\mathbf{r} d\gamma r \frac{du}{dr} e^{-\gamma^2 - \beta u} (\mathbf{r}' \cdot \boldsymbol{\gamma}_0) \\
&= 8\pi^2 \iiint_0^\pi d\theta \sin^2 \theta dr d\gamma e^{-\gamma_0^2} \gamma^3 \frac{du}{dr} r^4 (X \pm Y).
\end{aligned} \tag{F.11}$$

Integrating over θ for the incoming and outgoing parts of the trajectories gives,

$$\int_0^{\pi/2} d\theta \sin^2 \theta (X + Y) + \int_{\pi/2}^\pi d\theta \sin^2 \theta (X - Y). \tag{F.12}$$

Changing the variable in the second integral from $\theta \rightarrow \theta' = \pi - \theta$ gives,

$$\int_0^{\pi/2} d\theta \sin^2 \theta (X + Y) + \int_0^{\pi/2} d\theta \sin^2 \theta (X - Y) = 2 \int_0^{\pi/2} d\theta \sin^2 \theta X. \tag{F.13}$$

thus the second integral of Eq. (F.2) is,

$$(b) = 16\pi^2 \iiint_0^{\pi/2} d\theta \sin^2 \theta dr d\gamma e^{-\gamma_0^2} \gamma^3 \frac{du}{dr} r^4 X = 4\pi^2 kT \sigma^4 (H_\kappa + R_\kappa). \tag{F.14}$$

Substituting these results into Eq. (F.2) gives,

$$\begin{aligned}
(iii) &= -\sqrt{\frac{m}{2kT\pi^3}} \frac{i\mathbb{V}_{VV}n}{2A_V} \left[4\pi^2 kT \sigma^4 (H_\lambda + R_\lambda) - \frac{1}{3} 4\pi^2 kT \sigma^4 (H_\kappa + R_\kappa) \right] \\
&= -\sqrt{\frac{\pi mkT}{2}} \frac{4i\mathbb{V}_{KK}n\sigma^4}{3A_V} \left[\frac{3}{2} (H_\lambda + R_\lambda) - \frac{1}{2} (H_\kappa + R_\kappa) \right] \\
&= -\sqrt{\frac{\pi mkT}{2}} \frac{4i\mathbb{V}_{VV}n\sigma^4}{3A_V} (H_\eta + R_\eta).
\end{aligned} \tag{F.15}$$

Appendix G

Evaluation of F_λ

After integrating over the center of mass momentum, I , the integral in Eq. (7.56) becomes,

$$I = \Lambda_r^3 \text{Tr}_{\text{rel}} \frac{1}{r} F[(\boldsymbol{\gamma} \cdot \mathbf{r})(\boldsymbol{\gamma}_0 \cdot \mathbf{r}') + (\boldsymbol{\gamma} \cdot \boldsymbol{\gamma}_0)(\mathbf{r} \cdot \mathbf{r}') + (\boldsymbol{\gamma}_0 \cdot \mathbf{r})(\boldsymbol{\gamma} \cdot \mathbf{r}')] e^{-\gamma^2 - \beta u}. \quad (\text{G.1})$$

Carrying out the dot products of the \mathbf{r} terms gives

$$I = \frac{-1}{\pi^{3/2}} \iint d\mathbf{r} d\boldsymbol{\gamma} e^{-\gamma^2 - \beta u} \frac{du}{dr} \left[-\gamma \cos \theta (\mathbf{r}' \cdot \boldsymbol{\gamma}_0) + \gamma_0 \cos(\eta_R - \theta) (\mathbf{r}' \cdot \boldsymbol{\gamma}) - \frac{1}{r} \gamma \gamma_0 \cos \eta_R (\mathbf{r} \cdot \mathbf{r}') \right]. \quad (\text{G.2})$$

With the definition of $\mathbf{r}' = R\boldsymbol{\kappa}_R + s_0\mathbf{g}_0$, the terms inside the brackets become,

$$\begin{aligned} \{ \dots \} &= \gamma \gamma_0 \{ -\cos \theta [R \cos(\eta_R - \beta_R) + s_0 g_0] + \cos(\eta_R - \theta) [-R \cos \beta_R - s_0 g_0 \cos \eta_R] \\ &\quad - \cos \eta_R [R \cos(\beta_R - \theta) + s_0 g_0 \cos(\eta_R - \theta)] \} \\ &= -\gamma \gamma_0 \{ R [\cos \theta \cos(\eta_R - \beta_R) + \cos \beta_R \cos(\eta_R - \theta) + \cos \eta_R \cos(\beta_R - \theta)] \\ &\quad + g_0 s_0 [\cos \theta + 2 \cos \eta_R \cos(\eta_R - \theta)] \} = (i) + (ii). \end{aligned} \quad (\text{G.3})$$

The factor involving R in Eq. (G.3) is simplified by applying various trigonometric identities,

$$\begin{aligned} (i) &= -\gamma \gamma_0 R \{ \cos \theta \cos(\eta_R - \beta_R) \\ &\quad + \frac{1}{2} [2 \cos(\eta_R - \theta + \beta_R) + \cos(\eta_R - \theta - \beta_R) + \cos(\eta_R - \beta_R + \theta)] \} \\ &= -\gamma \gamma_0 R [\cos(\eta_R + \beta_R - \theta) + 2 \cos(\eta_R - \beta_R) \cos \theta]. \end{aligned} \quad (\text{G.4})$$

Using $\eta_R = \beta_R + \pi - \phi$ with $\phi = \arcsin[\mathcal{L}/R(mE)^{1/2}]$ as given by Snider and McCourt, the above expression simplifies to:

$$\begin{aligned} (i) &= \gamma \gamma_0 R [\cos(2\beta_R - \phi - \theta) + 2 \cos(-\phi) \cos \theta] \\ &\approx \gamma \gamma_0 R \left[\cos(2\beta - \theta) - \frac{\gamma r \sin \theta}{R \gamma_0} \sin(2\beta - \theta) + 2 \cos \theta \right]. \end{aligned} \quad (\text{G.5})$$

The $s_0 g_0$ factor is also simplified,

$$\begin{aligned}
 (ii) &= -\gamma\gamma_0 g_0 s_0 [2 \cos \eta_R \cos(\eta_R - \theta) + \cos \theta] = -\gamma\gamma_0 g_0 s_0 [\cos(2\eta_R - \theta) + 2 \cos \theta] \\
 &= -\gamma\gamma_0 g_0 s_0 [\cos(2\beta_R - 2\phi - \theta) + 2 \cos \theta] \approx -\gamma\gamma_0 g_0 s_0 [\cos(2\beta - \theta) + 2 \cos \theta], \quad (G.6)
 \end{aligned}$$

where terms of order $1/R$ have been neglected. Adding the two parts (i) and (ii) gives

$$(i) + (ii) = -\gamma\gamma_0 (g_0 s_0 - R) [\cos(2\beta - \theta) + 2 \cos \theta] - \gamma^2 r \sin \theta \sin(2\beta - \theta). \quad (G.7)$$

Finally substituting this into Eq. (G.2) gives,

$$\begin{aligned}
 I &= \frac{1}{\pi^{3/2}} \int d\mathbf{r} d\boldsymbol{\gamma} \frac{du}{dr} e^{-\gamma^2 - \beta u} \gamma^2 r \sin \theta \{ (X \pm Y) [\cos(2\beta - \theta) + 2 \cos \theta] + \sin(2\beta - \theta) \} \\
 &= -8\pi^{1/2} \iiint dr d\gamma d\theta \sin^2 \theta r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma^4 \\
 &\quad \times \{ (X \pm Y) [\cos(2\beta - \theta) + 2 \cos \theta] + \sin(2\beta - \theta) \} \\
 &= \frac{20\sigma^3 kT}{\pi^{1/2}} F_\lambda. \quad (G.8)
 \end{aligned}$$

Appendix H

Evaluation of N_λ

The dot product between the two brackets in the integral of Eq. (7.85) (which is denoted as I) is first evaluated,

$$\begin{aligned}
 & \pi^{-3/2} \int d\mathbf{g} e^{-\mathcal{G}^2} [(\mathbf{r}\mathbf{F} + u\mathbf{U}) \cdot \mathbf{g}] \cdot [(\mathcal{G}^2 + \gamma_0^2 - 5) \mathbf{g} + 2(\gamma_0 \cdot \mathbf{g}) \gamma_0] \\
 = & \pi^{-3/2} \int d\mathbf{g} e^{-\mathcal{G}^2} \left[-\frac{r}{3} \frac{du}{dr} (\mathcal{G}^2 + \gamma_0^2 - 5) \mathcal{G}^2 - \frac{2}{3r} \frac{du}{dr} \mathcal{G}^2 (\mathbf{r} \cdot \gamma_0)^2 \right. \\
 & \left. + u (\mathcal{G}^2 + \gamma_0^2 - 5) \mathcal{G}^2 + \frac{2}{3} u \mathcal{G}^2 \gamma_0^2 \right] \\
 = & \pi^{-3/2} \int d\mathbf{g} e^{-\mathcal{G}^2} \left\{ \mathcal{G}^4 \left(\frac{-r}{3} \frac{du}{dr} + u \right) \right. \\
 & \left. + \mathcal{G}^2 \left[\frac{-r}{3} \frac{du}{dr} \gamma_0^2 + \frac{5}{3} r \frac{du}{dr} - \frac{2}{3r} \frac{du}{dr} (\mathbf{r} \cdot \gamma_0)^2 + u \gamma_0^2 - 5u + \frac{2}{3} u \gamma_0^2 \right] \right\}. \quad (\text{H.1})
 \end{aligned}$$

Substituting this back into the expression of Eq. (7.85) and completing the integration over \mathbf{g} gives,

$$\begin{aligned}
 I &= \pi^{-3/2} \int d\mathbf{r} d\gamma e^{-\gamma^2 - \beta u} \left\{ \frac{15}{4} \left(-\frac{r}{3} \frac{du}{dr} + u \right) \right. \\
 & \quad \left. + \frac{3}{2} \left[-\frac{r}{3} \frac{du}{dr} \gamma_0^2 + \frac{5}{3} r \frac{du}{dr} - \frac{2}{3r} \frac{du}{dr} (\mathbf{r} \cdot \gamma_0)^2 + \frac{5}{3} u \gamma_0^2 - 5u \right] \right\} \\
 &= \pi^{-3/2} \int d\mathbf{r} d\gamma e^{-\gamma^2 - \beta u} \left[\frac{5}{4} r \frac{du}{dr} - \frac{15}{4} u - \frac{r}{2} \frac{du}{dr} \gamma_0^2 - \frac{1}{r} \frac{du}{dr} (\mathbf{r} \cdot \gamma_0)^2 + \frac{5}{2} u \gamma_0^2 \right]. \quad (\text{H.2})
 \end{aligned}$$

Using the conservation of energy for the relative motion, $\gamma_0^2 = \gamma^2 + \beta u$, and integrating over the relative momentum, this becomes,

$$\begin{aligned}
 I &= \frac{5}{4} \int d\mathbf{r} r \frac{du}{dr} e^{-\beta u} - \frac{3}{4} \int d\mathbf{r} r \frac{du}{dr} e^{-\beta u} - \frac{1}{2} \int d\mathbf{r} r \beta u \frac{du}{dr} e^{-\beta u} \\
 & \quad - \pi^{-3/2} \iint d\mathbf{r} d\gamma e^{-\gamma^2 - \beta u} \frac{1}{r} \frac{du}{dr} (\mathbf{r} \cdot \gamma_0)^2 + \frac{5}{2\beta} \int d\mathbf{r} (\beta u)^2 e^{-\beta u}
 \end{aligned}$$

$$\begin{aligned}
&= \frac{1}{2} \left[\int d\mathbf{r} r \frac{du}{dr} e^{-\beta u} - \int d\mathbf{r} r \beta u \frac{du}{dr} e^{-\beta u} + \frac{5}{\beta} \int d\mathbf{r} r (\beta u)^2 e^{-\beta u} \right] \\
&\quad - \pi^{-3/2} \iint d\mathbf{r} d\boldsymbol{\gamma} e^{-\gamma^2 - \beta u} \frac{1}{r} \frac{du}{dr} (\mathbf{r} \cdot \boldsymbol{\gamma}_0)^2.
\end{aligned} \tag{H.3}$$

The last integral in Eq. (H.3) is related to N_λ . If the limit of $R \rightarrow \infty$ is used,

$$\pi^{-3/2} \iint d\mathbf{r} d\boldsymbol{\gamma} \frac{du}{dr} r \gamma_0^2 \cos^2(\eta_R - \theta) e^{-\gamma^2 - \beta u} = 8\pi^{1/2} \iiint_0^\pi d\theta \sin \theta dr d\boldsymbol{\gamma} r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2 \cos^2(\omega \pm \zeta). \tag{H.4}$$

The integral over θ is written as two parts, one for the incoming and the other for the outgoing trajectory,

$$\begin{aligned}
\int_0^\pi d\theta \sin \theta \cos^2(\omega \pm \zeta) &= \int_0^{\pi/2} d\theta \sin \theta \cos^2(\omega + \zeta) + \int_{\pi/2}^\pi d\theta \sin \theta \cos^2(\omega - \zeta) \\
&= \int_0^{\pi/2} d\theta \sin \theta \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega + 2\zeta) \right] \\
&\quad + \int_0^{\pi/2} d\theta' \sin(\pi - \theta') \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega - 2\zeta) \right] \\
&= \int_0^{\pi/2} d\theta \sin \theta [1 + \cos 2\omega \cos 2\zeta].
\end{aligned} \tag{H.5}$$

Putting terms back together gives,

$$8\pi^{1/2} \iiint_0^{\pi/2} d\theta \sin \theta dr d\boldsymbol{\gamma} r^3 \frac{du}{dr} e^{-\gamma_0^2} \gamma_0^2 \gamma^2 (1 + \cos 2\omega \cos 2\zeta) = 8\pi^{1/2} \frac{kT\sigma^3}{2} N_\lambda, \tag{H.6}$$

where the definition of N_λ given in Eq.(31) of Snider and McCourt is used.

Using Eqs. (I.4), (I.5) and (I.3) of Appendix I, the integrals in Eq. (H.3) are expressed in terms of the second virial coefficient and its temperature derivatives,

$$I = -kT \left(4\pi^{1/2} \sigma^3 N_\lambda + 7T \frac{dB}{dT} + 5T^2 \frac{d^2 B}{dT^2} \right). \tag{H.7}$$

Appendix I

The Second Virial Coefficient and its Temperature Derivatives

Some useful identities with the second virial coefficient:

$$B(T) = -\frac{1}{2} \int d\mathbf{r} (e^{-\beta u} - 1), \quad (\text{I.1})$$

$$T \frac{dB}{dT} = -\frac{1}{2} \int d\mathbf{r} \beta u e^{-\beta u}, \quad (\text{I.2})$$

$$T^2 \frac{d^2 B}{dT^2} = -2T \frac{dB}{dT} - \frac{1}{2} \int d\mathbf{r} (\beta u)^2 e^{-\beta u}. \quad (\text{I.3})$$

In terms of an alternate representation of the second virial coefficient, these relations are:

$$B(T) = -\frac{\beta}{6} \int d\mathbf{r} r \frac{du}{dr} e^{-\beta u}, \quad (\text{I.4})$$

$$T \frac{dB}{dT} = -B(T) + \frac{\beta}{6} \int d\mathbf{r} r \beta u \frac{du}{dr} e^{-\beta u}, \quad (\text{I.5})$$

$$T^2 \frac{d^2 B}{dT^2} = -2B(T) - 4T \frac{dB}{dT} + \frac{\beta}{6} \int d\mathbf{r} r (\beta u)^2 \frac{du}{dr} e^{-\beta u}. \quad (\text{I.6})$$

Appendix J

Determination of $H_\lambda + R_\lambda - I_\lambda$

The integral in the last term on the right hand side of Eq. (7.86) has the following form,

$$\begin{aligned}
 I &= \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{kT(mkT)^{1/2} A_V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 [(\mathbf{r}_{12} \mathbf{F}_{12} + u_{12} \mathbf{U}) \cdot \mathbf{G}] \cdot e^{-\beta H_{12}} \\
 &\quad \times \frac{i}{z - \mathcal{L}_{12}} i\mathcal{L}_0 \left[\left(\frac{p_1^2}{2m} - h \right) \mathbf{r}_1 + \left(\frac{p_2^2}{2m} - h \right) \mathbf{r}_2 \right] \\
 &= \sqrt{\frac{2}{5}} \frac{n^2 \Lambda^6}{kT(mkT)^{1/2} A_V} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{p}_1 d\mathbf{p}_2 e^{-\beta H_{12}} [(\mathbf{r}_{12} \mathbf{F}_{12} + u_{12} \mathbf{U}) \cdot \mathbf{G}] \cdot \\
 &\quad \times \Omega(12) \left[\frac{1}{2} \left(\frac{p_1^2}{2m} + \frac{p_2^2}{2m} - 2h \right) (\mathbf{r}_1 + \mathbf{r}_2) + \frac{1}{2} \left(\frac{p_1^2}{2m} - \frac{p_2^2}{2m} \right) (\mathbf{r}_1 - \mathbf{r}_2) \right]. \quad (\text{J.1})
 \end{aligned}$$

The centre of mass part of the above expression vanishes, so that

$$\begin{aligned}
 I &= \sqrt{\frac{2}{5}} \frac{Nn}{(mkT)^{1/2} \pi^3 A_V} \int d\mathbf{r} d\gamma d\mathbf{G} [(\mathbf{r} \mathbf{F} + u \mathbf{U}) \cdot \mathbf{G}] \cdot e^{-\beta H_{12}} \Omega(12) (\mathbf{G} \cdot \boldsymbol{\gamma}) \mathbf{r} \\
 &= \sqrt{\frac{2}{5}} \frac{Nn}{(mkT)^{1/2} \pi^3 A_V} \int d\mathbf{r} d\gamma d\mathbf{G} [(\mathbf{r} \mathbf{F} + u \mathbf{U}) \cdot \mathbf{G}] \cdot e^{-\beta H_{12}} (\mathbf{G} \cdot \boldsymbol{\gamma}_0) \mathbf{r}'. \quad (\text{J.2})
 \end{aligned}$$

Retaining only contributions with even powers of the center of mass momentum components gives,

$$\begin{aligned}
 I &= \sqrt{\frac{2}{5}} \frac{Nn}{(mkT)^{1/2} \pi^3 A_V} \int d\mathbf{r} d\gamma d\mathbf{G} e^{-\beta H_{12}} \frac{1}{3} \mathcal{G}^2 \left[\frac{-du}{rdr} (\mathbf{r} \cdot \boldsymbol{\gamma}_0) (\mathbf{r} \cdot \mathbf{r}') + u (\mathbf{r}' \cdot \boldsymbol{\gamma}_0) \right] \\
 &= \sqrt{\frac{2}{5}} \frac{Nn}{2(mkT)^{1/2} \pi^{3/2} A_V} \int d\mathbf{r} d\gamma \gamma^2 e^{-\gamma_0^2} \left[\frac{-du}{rdr} (\mathbf{r} \cdot \boldsymbol{\gamma}_0) (\mathbf{r} \cdot \mathbf{r}') + u (\mathbf{r}' \cdot \boldsymbol{\gamma}_0) \right] \\
 &= \sqrt{\frac{2}{5}} \frac{Nn}{2(mkT)^{1/2} \pi^{3/2} A_V} [(\text{rel})' + (\text{rel})'']. \quad (\text{J.3})
 \end{aligned}$$

Similar to the work of simplifying (b) in Appendix F, the (rel)'' term may be simplified as,

$$(\text{rel})'' = 16\pi^2 \int \int \int_0^{\pi/2} d\theta \sin^2 \theta dr d\gamma e^{\gamma_0^2} \gamma^3 u r^3 X = 4\pi^2 kT \sigma^4 I_\lambda. \quad (\text{J.4})$$

The (rel)' can also be simplified as

$$(\text{rel})' = -8\pi^2 \int dr d\theta d\gamma r \sin \theta \gamma^2 e^{-\gamma_0^2 \frac{du}{dr}} r \gamma_0 \cos(\eta_R - \theta) r [R \cos(\beta_R - \theta) - s_0 \gamma_0 \cos(\eta_R - \theta)]. \quad (\text{J.5})$$

Substituting $\eta_r = \beta_R + \pi - \phi$ in the trigonometric functions above, and making use of the fact that in the limit of $R \rightarrow \infty$ the angle $\beta_R \rightarrow \beta + \phi$, and finally using the limiting forms

$$\cos \phi = 1 - O(1/R^2) \quad \sin \phi = \mathcal{L}/R((mE)^{1/2}) \quad (\text{J.6})$$

gives,

$$\begin{aligned} & R \cos(\beta_R - \theta) \cos(\beta_R + \pi - \phi - \theta) + s_0 \gamma_0 \cos^2(\beta_R + \pi - \phi - \theta) \\ &= (s_0 \gamma_0 - R) \cos^2(\beta - \theta + \phi) = (s_0 \gamma_0 - R) [\cos(\beta - \theta) \cos \phi - \sin(\beta - \theta) \sin \phi]^2 \\ &= (s_0 \gamma_0 - R) \cos^2(\beta - \theta) + \frac{\gamma}{\gamma_0} r \sin \theta \cos(\beta - \theta) \sin(\beta - \theta) + O(1/R) \\ &= \frac{\gamma}{\gamma_0} r \sin \theta [(X \pm Y) \cos^2(\omega \pm \zeta) + \cos(\omega \pm \zeta) \sin(\omega \pm \zeta)]. \end{aligned} \quad (\text{J.7})$$

This expression is substituted back into the (rel)' expression to give

$$(\text{rel})' = -8\pi^2 \iiint_0^\pi d\theta \sin^2 \theta d\gamma dr r^4 \gamma^3 e^{-\gamma_0^2 \frac{du}{dr}} [(X \pm Y) \cos^2(\omega \pm \zeta) + \cos(\omega \pm \zeta) \sin(\omega \pm \zeta)] \quad (\text{J.8})$$

Integrating over θ then gives

$$\begin{aligned} & \int_0^{\pi/2} d\theta \sin^2 \theta [(X + Y) \cos^2(\omega + \zeta) + \cos(\omega + \zeta) \sin(\omega + \zeta)] \\ &+ \int_{\pi/2}^\pi d\theta \sin^2 \theta [(X - Y) \cos^2(\omega - \zeta) + \cos(\omega - \zeta) \sin(\omega - \zeta)]. \end{aligned} \quad (\text{J.9})$$

Changing the integration variable in the second integral from θ to $\theta' = \pi - \theta$ gives,

$$\begin{aligned} & \int_0^{\pi/2} d\theta \sin^2 \theta \{ [(X + Y) \cos^2(\omega + \zeta) + \cos(\omega + \zeta) \sin(\omega + \zeta)] \\ &+ [(X - Y) \cos^2(\omega - \zeta) + \cos(\omega - \zeta) \sin(\omega - \zeta)] \} \\ &= \int_0^{\pi/2} d\theta \sin^2 \theta \{ (X + Y) \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega + 2\zeta) \right] + \frac{1}{2} \sin(2\omega + 2\zeta) \\ &+ (X - Y) \left[\frac{1}{2} + \frac{1}{2} \cos(2\omega - 2\zeta) \right] + \frac{1}{2} \sin(2\omega - 2\zeta) \} \\ &= \int_0^{\pi/2} d\theta \sin^2 \theta \left[X + \frac{1}{2} (X + Y) (\cos 2\omega \cos 2\zeta - \sin 2\omega \sin 2\zeta) \right. \\ &\quad \left. + \frac{1}{2} (X - Y) (\cos 2\omega \cos 2\zeta + \sin 2\omega \sin 2\zeta) \sin 2\omega \cos 2\zeta \right] \\ &= \int_0^{\pi/2} d\theta \sin^2 \theta (X + \sin 2\omega \cos 2\zeta + X \cos 2\omega \cos 2\zeta - Y \sin 2\omega \sin 2\zeta). \end{aligned} \quad (\text{J.10})$$

Thus overall,

$$\begin{aligned}
 (\text{rel})' &= -8\pi^2 \iiint_0^{\pi/2} d\theta \sin^2 \theta d\gamma dr r^4 \gamma^3 e^{-\gamma_0^2} \frac{du}{dr} \\
 &\quad \times [X(1 + \cos 2\omega \cos 2\zeta) + \sin 2\omega \cos 2\zeta - Y \sin 2\omega \sin 2\zeta]. \quad (\text{J.11})
 \end{aligned}$$

This integral agrees with the form given in Eq. (33) of Snider and McCourt, that is

$$(\text{rel})' = -4\pi^2 kT \sigma^4 (H_\lambda + R_\lambda), \quad (\text{J.12})$$

So that all together,

$$I = -\sqrt{\frac{2}{5}} \frac{\pi^{1/2} N n}{(mkT)^{1/2} A_V} 2kT \sigma^4 (H_\lambda + R_\lambda - I_\lambda). \quad (\text{J.13})$$

The contribution to the thermal conductivity from this term in Eq. (7.35) is

$$\begin{aligned}
 &\sqrt{\frac{5}{2}} N n k_B A_V \frac{i}{N \mathbb{V}_{VV}} \mathbb{V}_{VV} \frac{i}{6N} \sqrt{\frac{2}{5}} \frac{-2(\pi kT)^{1/2} N n}{(m)^{1/2} A_V} \sigma^4 (H_\lambda + R_\lambda - I_\lambda) \\
 &= \frac{1}{3} n^2 k \sigma^4 \sqrt{\frac{\pi kT}{m}} (H_\lambda + R_\lambda - I_\lambda). \quad (\text{J.14})
 \end{aligned}$$

This agrees exactly with the second order in density correction given in Eq. (26) of Snider and McCourt.

List of Symbols

A_V	normalization factor for the potential flux functions
b	impact parameter
$b_j^{(0)}$	j th coefficient in the Sonine expansion of $B^0(p_1)$
B	scale factor in transport coefficient expression
$B^0(p_1)$	unknown function which arises in the inversion of $\mathcal{G}(\epsilon)$
$B(T)$	second pressure virial coefficient
B_η	second viscosity virial coefficient
B_λ	second thermal conductivity virial coefficient
$\mathbf{B}_1^{(N)}$	reduced flux evolution vector
$\mathbf{B}_{\Theta\Phi}$	reduced $\Theta\Phi$ matrix elements of the kinetic projected resolvent for thermal conductivity
$\mathbf{B}_{\Theta\Phi}$	reduced $\Theta\Phi$ matrix elements of the kinetic projected resolvent for viscosity
E	relative energy of a colliding pair, $E = \mu g_0^2/2$
$\mathbf{E}^{(\alpha)}$	Cartesian tensor identity for the irreducible representation of $SO(3)$ of weight α
$f^{(1)}(\mathbf{v}, \mathbf{r}, t)$	one-particle distribution function
$\mathbf{F}_{j\ell}$	force between particles j and ℓ
F_σ	a first order non-locality density correction to the transport coefficient σ in Snider-Curtiss theory
g_0	relative speed of approach of the 12 pair prior to collision
g_{12}	relative speed of approach of the 12 pair
$G(z)$	resolvent with an N -particle Liouville operator $i/(z - \mathcal{L})$
G_0	resolvent of a system with non-interacting particles $i/(z - \mathcal{K})$
$G_2(12)$	resolvent of a system with only particles 1 and 2 interacting $i/(z - \mathcal{L}_{12})$
\mathcal{G}	dimensionless center of mass momentum for particles 1 and 2
$\mathcal{G}(\epsilon)$	N -particle resolvent expanded in powers of $1/\epsilon$

h	enthalpy per molecule, divided into kinetic h_K and potential h_V parts
H_{12}	total hamiltonian of a pair of particles
$H_{\xi\zeta}$	binary collision cross section for a $\xi\zeta$ mixture
I^B	the Bogoliubov form of the triple collision operator
I^G	the Green form of the triple collision operator
J_1	correction to the Boltzmann equation
J_2	correction to the Boltzmann equation
\mathbf{J}	flux tensor of general rank
\mathbf{J}_K	kinetic contribution to the flux tensor
\mathbf{J}_V	potential contribution to the flux tensor
\mathbf{J}	symmetric traceless momentum flux tensor of rank 2
K_{12}	kinetic energy of the pair of particles
\mathcal{K}	the kinetic contribution to the Liouville operator
$\mathbb{K}_{\Theta\Phi}$	$\Theta\Phi$ matrix elements of the resolvent of \mathcal{L}_K
\mathcal{L}_1	Kawasaki - Oppenheim binary collision operator
\mathcal{L}	N -particle Liouville operator
$\mathcal{L}_{\mathcal{P}}$	$(1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})$
\mathcal{L}_K	$(1 - \mathcal{P}_K)\mathcal{L}(1 - \mathcal{P}_K)$
\mathcal{L}_V	$(1 - \mathcal{P}_V)\mathcal{L}(1 - \mathcal{P}_V)$
$\mathbb{M}_{\Theta\Phi}$	$\Theta\Phi$ matrix elements of the resolvent of \mathcal{L}
n	number density
N	the number of particles in the system, $N \rightarrow \infty$
N_σ	a first order collisional transfer density correction to the transport coefficient σ in Snider - Curtiss theory
\mathbf{p}	relative momentum of particles 1 and 2
\mathbf{p}_0	relative momentum of 1 and 2 prior to collision
\mathbf{p}_ξ	relative momentum for a general point ξ on a 2-particle trajectory
\mathbf{P}	the center of mass momentum of particles 1 and 2
\mathcal{P}	projection operator, $ \mathbf{J}\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J} $
\mathcal{P}_0	projection operator onto the flux of particle 1, $ \mathbf{J}_1\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J}_1 $
\mathcal{P}_K	$1/N \mathbf{J}_K\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J}_K $
\mathcal{P}_V	$1/N \mathbf{J}_V\rangle\rangle \overset{\alpha}{\odot} \langle\langle \mathbf{J}_V $
\wp_s	species projection operator
\mathbf{r}	relative position of particle 1 with respect to particle 2, $\mathbf{r}_1 - \mathbf{r}_2$
\mathbf{r}'	$\Omega_{12}\mathbf{r}$

\mathbf{R}	center of mass position of particles 1 and 2, $(\mathbf{r}_1 + \mathbf{r}_2)/2$
\mathcal{R}	linearized Boltzmann binary collision operator
\mathcal{R}_K	projected linearized collision operator, $(1 - \mathcal{P}_0)\varphi_1\mathcal{R}_1\frac{1}{\varphi_1}(1 - \mathcal{P}_0)$
$\mathcal{R}_{a,b}$	ab binary collision operator matrix element
$R(T)$	Hoffman - Curtiss correction integral
R	cutoff distance for the intermolecular potential
s_0	time from the start of the collision interaction to the reference point of the trajectory
\mathfrak{S}	binary collision kinetic cross section
\mathcal{T}	transition superoperator
$u(r)$	intermolecular potential
u'	$u - h_V$
$U_{12}^{(2)}$	two-particle Ursell function
\mathbf{U}	2nd rank unit tensor
X_R	b^{-1} times the projection of \mathbf{r}'_m on the asymptotic collision direction
X_s	mole fraction of species s
$\langle v \rangle$	average speed of relative approach
$\mathbb{V}_{\Theta\Phi}$	$\Theta\Phi$ matrix elements of the resolvent \mathcal{L}_V
\mathcal{V}	the potential contribution to the Liouville superoperator
\mathbf{W}_j	dimensionless momentum of particle j
Y	collision parameter related the projection of \mathbf{r}' on the asymptotic collision direction
$Y_{[0]}$	density expansion factor for the 2-particle reduced distribution function
$\mathbb{Z}_{\Theta\Phi}$	$\Theta\Phi$ matrix elements over the resolvent of \mathcal{L}
α	weight of the irreducible representation of $SO(3)$
β	$1/k_B T$
β_ξ	angle of the general relative position vector ξ with respect to $-\mathbf{p}$
γ	dimensionless relative momentum of particles 1 and 2
γ_0	dimensionless relative momentum of 1 and 2 prior to collision
Γ_σ	integrals over the potential function found in determination of A_V
Δ	correction term to the Boltzmann equation
Δ_1	correction from displacing the particle positions from \mathbf{r}_1 and \mathbf{r}_2 to \mathbf{R}_{cm} and time t_0 to t in the generalized Boltzmann equation

Δ_2	correction from displacing the center of mass position to \mathbf{r}_1 in the generalized Boltzmann equation
ϵ	a small, real convergence parameter, $\epsilon \rightarrow 0_+$
ζ	angle between \mathbf{r}_m and the reference point \mathbf{r}
η	shear viscosity coefficient
η_0	low density limit to the shear viscosity coefficient
η_ξ	angle of the general momentum vector \mathbf{p}_ξ with $-\mathbf{p}$
$H_{\xi\zeta}$	binary collision cross sections for a $\xi\zeta$ mixture
θ	angle between \mathbf{r} and $-\mathbf{p}$ at the reference point of the trajectory
κ_ξ	unit vector in the direction of the general relative position vector ξ
κ'_ξ	unit vector in the direction of the general relative momentum vector p_ξ
λ	thermal conductivity coefficient
μ	reduced mass
ξ	a general position on the collision trajectory
$\rho_{1\dots s}^{(s)}$	s -particle reduced distribution function
$\rho^{(N)}$	N -particle distribution function
σ	position scale parameter for the intermolecular potential
φ_j	the normalized Maxwellian momentum distribution for particle j
χ	deflection angle in a binary collision
χ_s	identification state matrix for species s
ω_R	angle of \mathbf{r}_m and the asymptotic direction of approach
Ω'_{12}	Møller superoperator
$\Omega^{(2,2)}(T)$	Omega collision integral
$\Omega^{(2,2)*}(T^*)$	reduced Omega collision integral