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Complete binary collision approximation for the gas transport coefficients via the time correlation formulation

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The connection between the low density limit of the time correlation equations for the transport coefficients and the solution of the Boltzmann equation to lowest order approximation appear to have been made in essentially two different ways. Either the time correlation function is evaluated by using the time dependent (linearized) Boltzmann equation, or by utilizing a resummation of an expansion in the reciprocal of a convergence parameter. As well, the connection is often made to only the lowest order solution of the Boltzmann equation, ignoring the possible importance of higher order moments (Sonine polynomials) in the solution of the Boltzmann equation. The present work uses a projection operator method and a subsequent binary collision expansion of the time correlation function to retain all contributions to the transport coefficient from binary collisions. This explicitly avoids an expansion in a divergent parameter and reproduces all Sonine polynomial contributions to the transport coefficient. Gas transport coefficients for a binary mixture are obtained in a similar manner. © 1998 American Institute of Physics. [S0021-9606(98)51333-5]

I. INTRODUCTION

Since the pioneering work of Green¹ and Kubo,² the dynamic evolution of many systems has been expressed in terms of time correlation functions. For an N -particle system, a time correlation function has the general form

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

where \mathbf{I} is a tensor valued phase space function of rank α belonging to an irreducible representation of dimension $2\alpha+1$ of the 3-dimensional rotation group, \odot represents an α -fold dot (tensorial) contraction, \mathcal{L} is the N -particle Liouville operator and the bracket designates a thermal average over the phase space of an N -particle system of volume V . Time correlation functions have found application in many fields including light and inelastic neutron scattering, spectroscopy, the theory of electrical conductance and in the calculation of thermal transport coefficients.³

A transport coefficient σ is the particular limiting form of the Fourier transform of the time correlation function of the flux \mathbf{I} of some property, specifically

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

Here B is a factor appropriate for each transport coefficient and the introduction of the volume factor V recognizes the extensivity of a flux and the intensivity of a transport coefficient. The flux may be a scalar (bulk viscosity), a vector (diffusion and thermal conductivity) or a second rank tensor (shear viscosity). For diffusion and thermal conductivity, α is thus 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 contraction. In most of the literature it is standard to use the tensorial components, thus for the shear viscosity, η , the thermal average is typically seen as

$$\eta = \lim_{\epsilon \rightarrow 0^+} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{i}{2kTV} \left\langle \left\langle \mathbf{I}_{xy} \frac{1}{i\epsilon - \mathcal{L}} \mathbf{I}_{xy} \right\rangle \right\rangle. \quad (3)$$

Since \mathbf{I}_{xy} is one component of a second rank symmetric traceless tensor, it belongs to the 5-dimensional irreducible representation of the rotation group. By the rotational invariance of \mathcal{L} and of the thermal average, the quantity of Eq. (3) is 1/5th the sum over all traceless symmetric components, which appears in Eq. (2). 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.

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.⁴ 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 states play in gas transport. As a closed equation for the transport coefficient, Eq. (2) 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 equation⁵⁻⁹ evaluate the time correlation function using the Boltzmann equation or some generalized kinetic equation. In contrast,

Zwanzig¹⁰ uses a binary collision expansion to deduce that the evaluation of Eq. (2) 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 $\epsilon \rightarrow 0$. Kawasaki and Oppenheim¹¹ have 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,¹³ 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 paper to show how these higher moments arise solely from the time correlation formulation. Thus the applications presented 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 will be used when expressions for the density corrections to the transport coefficients are derived in later work.

In Sec. II, projection operators are defined and used to carry out a direct resolvent expansion of the time correlation function for a transport coefficient, to derive a result similar to that of Zwanzig.¹³ For dilute gases it is clear that a binary collision expansion¹⁴ is needed at some point in this relation. In Sec. III, \mathbf{I} 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 Sec. IV, this solution is interpreted as including the complete set of Sonine polynomials. Section V reinterprets the formalism of Sec. III 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 paper ends with a discussion.

II. PROJECTION OPERATOR—RESOLVENT RELATIONS

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

$$\begin{aligned}\langle\langle\mathbf{X}|\rangle\rangle &\equiv \int d\mathbf{x}^N \mathbf{X} \equiv \text{Tr}_{1\dots N} \mathbf{X}, \quad |\mathbf{Y}\rangle\rangle \equiv \mathbf{Y} f^{(N)} \equiv \frac{1}{2} [\mathbf{Y}, \rho^{(N)}]_+ \\ \langle\langle\mathbf{X}|\mathbf{Y}\rangle\rangle &\equiv \int d\mathbf{x}^N \mathbf{X} \mathbf{Y} f^{(N)} \equiv \frac{1}{2} \text{Tr}_{1\dots N} \mathbf{X} [\mathbf{Y}, \rho^{(N)}]_+, \quad (4)\end{aligned}$$

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 will be 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 paper.

While $\mathbf{I}(t)$ changes as it evolves with time, only its component along the phase space \mathbf{I} 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{I} . The generalization of Zwanzig's¹³ projection operator is the projection operator \mathcal{P} onto the $2\alpha+1$ -dimensional subspace spanned by the components of \mathbf{I}

$$\mathcal{P} = A |\mathbf{I}\rangle\rangle \langle\langle\mathbf{I}|. \quad (5)$$

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

$$\mathcal{P}^2 = A^2 |\mathbf{I}\rangle\rangle \langle\langle\mathbf{I}| \mathbf{I}\rangle\rangle \langle\langle\mathbf{I}| = A |\mathbf{I}\rangle\rangle \langle\langle\mathbf{I}| = \mathcal{P}. \quad (6)$$

On the assumption that the equilibrium density operator (distribution function) is rotationally invariant, and that the flux operator \mathbf{I} has no preference for any particular direction in space, it follows that $\langle\langle\mathbf{I}|\mathbf{I}\rangle\rangle$ is a 2α -dimensional tensor which must be a rotational invariant. $\langle\langle\mathbf{I}|\mathbf{I}\rangle\rangle$ 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.¹⁵ Thus

$$\langle\langle\mathbf{I}|\mathbf{I}\rangle\rangle = a \mathbf{E}^{(\alpha)} \quad (7)$$

with a proportionality constant a determined by taking the contraction of both sides of Eq. (7) with $\mathbf{E}^{(\alpha)}$ to show that

$$a = \frac{\langle\langle\mathbf{I}|\mathbf{I}\rangle\rangle}{2\alpha+1} \quad (8)$$

and by substituting Eq. (7) into Eq. (6),

$$A = \frac{2\alpha+1}{\langle\langle\mathbf{I}|\mathbf{I}\rangle\rangle}. \quad (9)$$

Since \mathcal{P} projects onto the subspace of functions determined by the components of \mathbf{I} , it follows that the transport coefficient can be written

$$\sigma = \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha+1)V} \left\langle \left\langle \mathbf{I} \odot \left| \mathcal{P} \frac{1}{i\epsilon - \mathcal{L}} \mathcal{P} \mathbf{I} \right\rangle \right\rangle, \quad (10)$$

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 $z = i\epsilon$)

$$\begin{aligned} \mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} &= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} [z - \mathcal{L} + (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P}) \\ &\quad + \mathcal{P}\mathcal{L}(1 - \mathcal{P}) + (1 - \mathcal{P})\mathcal{L}\mathcal{P}] \frac{1}{z - \mathcal{L}} \mathcal{P} \\ &= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P} + \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \frac{1}{z - \mathcal{L}} \mathcal{P}, \\ &= \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P} + \mathcal{P} \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P}} \mathcal{P}\mathcal{L}(1 - \mathcal{P}) \\ &\quad \times \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P}. \end{aligned} \quad (11)$$

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

$$\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} = \frac{1}{z - \mathcal{P}\mathcal{L}\mathcal{P} - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} (1 - \mathcal{P})\mathcal{L}\mathcal{P}}. \quad (12)$$

Since the \mathbf{I} '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 proof¹³ states that $\langle \langle \mathbf{I} | \mathcal{L} | \mathbf{I} \rangle \rangle$ can be written as $\langle \langle \mathbf{I} | \dot{\mathbf{I}} \rangle \rangle$, which is proportional to $d\langle \langle \mathbf{I} | \mathbf{I} \rangle \rangle / dt$. Since the equilibrium ensemble is constant with time, so is $\langle \langle \mathbf{I} | \mathbf{I} \rangle \rangle$, its time derivative vanishes, $\mathcal{P}\mathcal{L}\mathcal{P} = 0$ and Eq. (12) is simplified to

$$\mathcal{P} \frac{1}{z - \mathcal{L}} \mathcal{P} = \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}}. \quad (13)$$

With this expression for the projected resolvent, the transport coefficient expression, Eq. (10), becomes

$$\begin{aligned} \sigma &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha+1)V} \\ &\quad \times \left\langle \left\langle \mathbf{I} \odot \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}} \right| \mathbf{I} \right\rangle \right\rangle \\ &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{iB}{(2\alpha+1)V} \langle \langle \mathbf{I} \odot | \mathbf{X} \rangle \rangle, \end{aligned} \quad (14)$$

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

$$|\mathbf{X}\rangle\rangle = \frac{1}{z - \mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P}} |\mathbf{I}\rangle\rangle. \quad (15)$$

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

$$|\mathbf{I}\rangle\rangle = -\mathcal{P}\mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L}\mathcal{P} |\mathbf{X}\rangle\rangle. \quad (16)$$

The phase space inner product of this with \mathbf{I} implies that

$$\mathbf{E}^{(\alpha)} = -A \left\langle \left\langle \mathbf{I} \mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} \right| \mathbf{I} \right\rangle \right\rangle^{\alpha} \odot A \langle \langle \mathbf{I} | \mathbf{X} \rangle \rangle. \quad (17)$$

Since both brackets 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. (7) and (8) give

$$1 = \frac{-A}{2\alpha+1} \left\langle \left\langle \mathbf{I} \odot \mathcal{L} \frac{1}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} \right| \mathbf{I} \right\rangle \right\rangle^{\alpha} \frac{AV\sigma}{iB}, \quad (18)$$

which gives an expression for the transport coefficient in the form

$$\begin{aligned} \frac{1}{\sigma} &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{A^2 V}{(2\alpha+1)B} \\ &\quad \times \left\langle \left\langle \mathbf{I} \odot \mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} \right| \mathbf{I} \right\rangle \right\rangle^{\alpha}. \end{aligned} \quad (19)$$

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 $\epsilon \rightarrow 0$ limit of a transition operator has well understood convergence properties.

Zwanzig¹³ simplified this to the equivalent form

$$\begin{aligned} \frac{1}{\sigma} &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{A^2 V}{(2\alpha+1)B} \\ &\quad \times \left\langle \left\langle \mathbf{I} \odot \mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}} \right| \mathbf{I} \right\rangle \right\rangle^{\alpha}. \end{aligned} \quad (20)$$

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.

III. 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. Collisions disrupt these kinetic motions, giving rise to the transfer of motion from one molecule to another, interrupting the transport and giving 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{I} 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

$$\mathcal{L} = \sum_j \mathcal{K}_j + \sum_{j < \ell} \mathcal{V}_{j\ell}; \quad (21)$$

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{I} is an additive property of the individual molecules in the system,

$$\mathbf{I} \equiv \sum_{j=1}^N \mathbf{J}_j, \quad (22)$$

whose contribution, \mathbf{J}_j , 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}_j is normalized so that

$$\langle \langle \mathbf{J}_j | \mathbf{J}_j \rangle \rangle = \mathbf{E}^{(\alpha)}, \text{ equivalently } \langle \langle \mathbf{J}_j \odot | \mathbf{J}_j \rangle \rangle = 2\alpha + 1. \quad (23)$$

Provided the distribution function for the gas

$$f^{(N)} = \prod_{j=1}^N \frac{\varphi_j}{V}, \quad (24)$$

is a product of one-particle distribution functions which are normalized

$$\int \frac{\varphi_j}{V} d\mathbf{x}_j = 1, \quad (25)$$

then the inner product of Eq. (8) is $N(2\alpha + 1)$ and the normalization factor for the projector of Eq. (5) becomes $A = 1/N$.

Equation (19) for the transport coefficient can then be written

$$\begin{aligned} \frac{1}{\sigma} &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{V}{BN(2\alpha + 1)} \\ &\times \left\langle \left\langle \mathbf{J}_1 \odot \mathcal{L} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} \mathbf{I} \right\rangle \right\rangle \\ &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{(N-1)V}{BN(2\alpha + 1)} \\ &\times \left\langle \left\langle \mathbf{J}_1 \odot \mathcal{V}_{12} \frac{i}{z - (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P})} \mathcal{L} \mathbf{I} \right\rangle \right\rangle \\ &\equiv \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{(N-1)V}{BN(2\alpha + 1)} \int d\mathbf{x}_1 \mathbf{J}_1 \odot \mathbf{B}_1^{(N)}, \quad (26) \end{aligned}$$

on the basis, first that \mathbf{I} is a sum with all particles contributing equally, and second, that only the potential part of \mathcal{L} has any effect on \mathbf{J}_1 , with particle 2 being a typical particle interacting with particle 1. In the following a closed expression for the vector valued function

$$\mathbf{B}_1^{(N)} \equiv \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)}, \quad (27)$$

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

Since, in Eq. (27) 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 $\mathcal{L}_{12} \equiv \mathcal{K}_1 + \mathcal{K}_2 + \mathcal{V}_{12}$, so that, after reorganization, $\mathbf{B}_1^{(N)}$ can be written in the form

$$\begin{aligned} \mathbf{B}_1^{(N)} &= \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \\ &\times [z - \mathcal{L}_p + (1 - \mathcal{P})\mathcal{L}(1 - \mathcal{P}) - \mathcal{L}_{12}] \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)} \\ &= \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L} \mathbf{I} f^{(N)} \\ &+ \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[\sum_{\substack{k < \ell \\ k\ell \neq 12}} \mathcal{V}_{k\ell} - \mathcal{P}\mathcal{L} \right] \\ &\times \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)}. \quad (28) \end{aligned}$$

This is a generalization of Watson's¹⁴ binary collision expansion. Since the two left-most operators in the integrals of this equation involve only particles 1 and 2, and these in a symmetrical manner, the integration over all the other particles can be carried out before getting to these operators. Moreover, the equations can be simplified by emphasizing only the behavior 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

$$\mathcal{T}_{12} \equiv \mathcal{V}_{12} + \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} \mathcal{V}_{12} = \mathcal{V}_{12} \frac{1}{z - \mathcal{L}_{12}} (z - \mathcal{K}_{12}) \quad (29)$$

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

$$\begin{aligned} & \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{L} \mathbf{I} f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \mathcal{V}_{12} (1 + P_{12}) \mathbf{J}_1 f_{12}^{(2)} \\ &= \int d\mathbf{x}_2 i \mathcal{T}_{12} (1 + P_{12}) \mathbf{J}_1 \varphi_1 \varphi_2 / V^2 = \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_1, \end{aligned} \quad (30)$$

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

$$\begin{aligned} & \int d\mathbf{x}^{(N-1)} \mathcal{V}_{12} \frac{i}{z - \mathcal{L}_{12}} \left[\sum_{k \neq 1} \mathcal{V}_{k1} - \mathcal{P} \mathcal{L} \right] \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{T}_{12} \frac{i}{z - \mathcal{K}_{12}} (1 + P_{12}) \left[(N-2) \int d\mathbf{x}^{(N-2)} \mathcal{V}_{13} - \mathbf{J}_1 \frac{f_{12}^{(2)}}{N} \int d\mathbf{x}^N \mathcal{L} \right] \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)} \\ &= \int d\mathbf{x}_2 \mathcal{T}_{12} \frac{i}{z - \mathcal{K}_{12}} (1 + P_{12}) \left[(N-2) \int d\mathbf{x}^{(N-2)} - \mathbf{J}_1 f_{12}^{(2)} (N-1) \int d\mathbf{x}^N \mathbf{J}_1 \right] \mathcal{V}_{13} \frac{1}{z - \mathcal{L}_p} \mathcal{L} \mathbf{I} f^{(N)} \\ &= \int d\mathbf{x}_2 i \mathcal{T}_{12} \frac{1}{z} (1 + P_{12}) \left[(N-2) \mathbf{B}_{12}^{(N)} - f_{12}^{(2)} \mathbf{J}_1 (N-1) \int d\mathbf{x}_1 \mathbf{J}_1 \mathbf{B}_1^{(N)} \right] (-i) \end{aligned} \quad (32)$$

with a reasonably obvious definition for $\mathbf{B}_{12}^{(N)}$, which will be discussed further below. The last term of Eq. (32) can be simplified by the use of the projection operator

$$\mathcal{P}_0 \equiv \varphi_1 \mathbf{J}_1 \odot \int d\mathbf{p}_1 \mathbf{J}_1. \quad (33)$$

This is a projection onto the subspace determined by \mathbf{J}_1 in the momentum space of particle 1. On collecting the various expressions, $\mathbf{B}_1^{(N)}$ satisfies the equation

$$\begin{aligned} \mathbf{B}_1^{(N)} &= \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_1 - \frac{i}{z} \int d\mathbf{x}_2 i \mathcal{T}_{12} (1 + P_{12}) \\ &\quad \times \left[(N-2) \mathbf{B}_{12}^{(N)} - \frac{N-1}{V^2} \varphi_2 \mathcal{P}_0 \int d\mathbf{r}_1 \mathbf{B}_1^{(N)} \right]. \end{aligned} \quad (34)$$

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

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

$$\mathcal{R}_1 \equiv \frac{n}{\varphi_1} \int d\mathbf{x}_2 i \mathcal{T}_{12} (1 + P_{12}) \varphi_1 \varphi_2. \quad (31)$$

Technically, terms involving a third particle, such as $\int d\mathbf{x}_3 \mathcal{V}_{13} (\mathbf{J}_1 + \mathbf{J}_3) \varphi_1 \varphi_2 \varphi_3$ arise in simplifying the integral of Eq. (30). It is argued that the potential between particles 1 and 3 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 doesn't appear in the first line of Eq. (30) but whose integration over the position of particle 2 gives a null value. This same procedure is not valid for the term that has been kept because of the presence of other \mathbf{r}_{12} dependent terms.

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

$$= \frac{\varphi_2}{V} \mathbf{B}_1^{(N-1)} \approx \frac{\varphi_2}{V} \mathbf{B}_1^{(N)}. \quad (35)$$

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 labelling 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 position independent, it follows that $\int d\mathbf{r}_1 \mathbf{B}_1 = V \mathbf{B}_1$ and Eq. (34) becomes a closed equation for \mathbf{B}_1 , specifically

$$\mathbf{B}_1 = \frac{\varphi_1}{VN} \mathcal{R}_1 \mathbf{J}_1 - \frac{i\varphi_1}{z} \mathcal{R}_1 \frac{1}{\varphi_1} (1 - \mathcal{P}_0) \mathbf{B}_1. \quad (36)$$

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.

Since Eq. (36) 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. (36) by $(1 - \mathcal{P}_0)$ gives

$$(1 - \mathcal{P}_0)\mathbf{B} = (1 - \mathcal{P}_0) \frac{\varphi}{VN} \mathcal{R} \mathbf{J} - \frac{i}{z} (1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \mathbf{B}, \quad (37)$$

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

$$(1 - \mathcal{P}_0)\mathbf{B} = \frac{z}{z + i(1 - \mathcal{P}_0)\varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \frac{\varphi}{VN} \mathcal{R} \mathbf{J}. \quad (38)$$

Substituting this back into Eq. (36), taking the tensor contraction with \mathbf{J} , and integrating over the momentum of particle 1 gives

$$\begin{aligned} \int d\mathbf{p} \mathbf{J} \odot \mathbf{B} &= \frac{1}{VN} \left[\int d\mathbf{p} \mathbf{J} \odot \varphi \mathcal{R} \mathbf{J} - \frac{i}{z} \int d\mathbf{p} \mathbf{J} \odot \varphi \mathcal{R} \frac{1}{\varphi} \frac{z}{z + i(1 - \mathcal{P}_0)\varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \varphi \mathcal{R} \mathbf{J} \right] \\ &= \frac{1}{VN} \left[(2\alpha + 1) \mathcal{R}_{0,0} - \int d\mathbf{p} \mathbf{J} \odot \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \frac{1}{(1 - \mathcal{P}_0)\varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0)} (1 - \mathcal{P}_0) \varphi \mathcal{R} \mathbf{J} \right]. \end{aligned} \quad (39)$$

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 orthogonal to the eigenvectors of \mathcal{R} whose eigenvalues are zero. Furthermore, for convenience, the basis should have $\mathbf{J} = \mathbf{O}_0(\mathbf{p})$ 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

$$\int d\mathbf{p} \mathbf{O}_j(\mathbf{p}) \varphi \mathbf{O}_\ell(\mathbf{p}) = \delta_{j,\ell} \mathbf{E}^{(\alpha)}. \quad (40)$$

Matrix elements of \mathcal{R} , after taking their rotational invariance into account, are usually expressed in term of kinetic cross sections \mathfrak{S} ,¹⁶⁻¹⁸ namely

$$\int d\mathbf{p} \mathbf{O}_j \varphi \mathcal{R} \mathbf{O}_\ell \equiv \mathcal{R}_{j,\ell} \mathbf{E}^{(\alpha)} = n \langle v \rangle \mathfrak{S}_{j,\ell} \mathbf{E}^{(\alpha)}, \quad (41)$$

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

$$\begin{aligned} \int d\mathbf{p} \mathbf{J} \odot \mathbf{B} &= \frac{2\alpha + 1}{VN} \left[\mathcal{R}_{0,0} - \sum_{j,\ell \neq 0} \mathcal{R}_{0,j} \left(\frac{1}{\mathcal{R}} \right)_{j,\ell} \mathcal{R}_{\ell,0} \right] \\ &= \frac{(2\alpha + 1) \langle v \rangle}{V^2} \left[\mathfrak{S}_{0,0} - \sum_{j,\ell \neq 0} \mathfrak{S}_{0,j} \left(\frac{1}{\mathfrak{S}} \right)_{j,\ell} \mathfrak{S}_{\ell,0} \right]. \end{aligned} \quad (42)$$

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

$$\begin{aligned} \frac{1}{\sigma} &= \lim_{\epsilon \rightarrow 0} \lim_{\substack{N, V \rightarrow \infty \\ N/V = \text{const.}}} \frac{V^2}{(2\alpha + 1)B} \int d\mathbf{p} \mathbf{J} \odot \mathbf{B} \\ &= \frac{\langle v \rangle}{B} \left[\mathfrak{S}_{0,0} - \sum_{j,\ell \neq 0} \mathfrak{S}_{0,j} \left(\frac{1}{\mathfrak{S}} \right)_{j,\ell} \mathfrak{S}_{\ell,0} \right]. \end{aligned} \quad (43)$$

The result usually presented (see for example Ref. 10) as the evaluation of a dilute gas transport coefficient according to the time correlation function method is the first term in Eq. (43), 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.

IV. THE COMPLETE SONINE EXPANSION

In solving the Boltzmann equation for the purpose of calculating the 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 . 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) equation¹⁸⁻²⁰ can be expressed in the present notation as

$$\mathbf{J} = \mathcal{R} \phi \quad (44)$$

and the transport coefficient is given by

$$\sigma = \frac{nB}{2\alpha + 1} \int d\mathbf{p} \mathbf{J} \odot \phi \varphi, \quad (45)$$

with the factor nB chosen to agree with the normalization of Eq. (2). 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,

$$\int d\mathbf{p} \phi \psi \varphi = 0, \quad (46)$$

to any (collisional) summational invariant ψ , these being the mass, momentum and energy.

The solution of the Chapman Enskog Eq. (44) can be calculated in a number of different ways. A first approximation is to assume $\phi = b\mathbf{J}$ is proportional to \mathbf{J} . In that case, a matrix element of Eq. (44) with \mathbf{J} gives

$$b = 1/n\langle v \rangle \mathfrak{S}_{0,0} \quad (47)$$

and the transport coefficient

$$\sigma = B/\langle v \rangle \mathfrak{S}_{0,0}, \quad (48)$$

compare with the first term in Eq. (43). 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

$$\sigma = \frac{nB}{2\alpha+1} \int d\mathbf{p} \mathbf{J} \odot \varphi \left(\frac{1}{\mathcal{R}} \right) \mathbf{J}. \quad (49)$$

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 $\mathbf{W} \equiv \mathbf{p}/\sqrt{2mk_B T}$ and a Sonine (equivalently associated Laguerre) polynomial in W^2 . The normalized version of this is¹⁶

$$\mathbf{L}^{\alpha s}(\mathbf{W}) \equiv \sqrt{\frac{\sqrt{\pi}(2\alpha+1)\Gamma(s+1)}{2^{\alpha+1}(\alpha!)^2\Gamma(s+\alpha+3/2)}} L_s^{\alpha+1/2}(W^2) [\mathbf{W}]^{(\alpha)}, \quad (50)$$

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 $\mathbf{J} = \mathbf{L}^{\alpha 0}$ corresponds to $s=0$ whereas for the thermal conductivity, $\mathbf{J} = \mathbf{L}^{11}$.

The standard method²⁰ of solving Eq. (44) 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} , 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. (12) is

$$\frac{1}{\mathcal{R}} \mathcal{P}_0 = \frac{1}{\mathcal{P}_0 \mathcal{R} \mathcal{P}_0 - \mathcal{P}_0 \mathcal{R} \frac{1}{(1-\mathcal{P}_0) \mathcal{R} (1-\mathcal{P}_0)} \mathcal{R} \mathcal{P}_0} \mathcal{P}_0. \quad (51)$$

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

$$\frac{1}{\sigma} = \frac{1}{nB} \left[\mathcal{R}_{0,0} - \sum_{j,j' \neq 0} \mathcal{R}_{0,j} \left(\frac{1}{\mathcal{R}} \right)_{j,j'} \mathcal{R}_{j',0} \right] \quad (52)$$

which, when converted to kinetic cross sections, is identical to Eq. (43).

The above formalism has inherently assumed that the molecules have only translational states. In case the molecules have internal states, the flux operators will in general 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 function²¹ 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. (29), 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.²² 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 only spans the diagonal-in-internal-state-energy part of the space of operators on internal states.

V. 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 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 Sec. III by considering the two species, labeled a and b , as being equivalent to two different internal states of a molecule, with of course the mass now dependent on the internal state.

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

$$\int d\mathbf{x} = \sum_s \int \int d\mathbf{p} d\mathbf{r}, \quad (53)$$

as well as the 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

$$\frac{\varphi}{V} = \sum_s \chi_s X_s \frac{\varphi_s}{V}, \quad (54)$$

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 ordered distribution functions can be considered as products of the one-particle distribution functions, compare Eq. (24), ignoring the constraint that only $X_a N$ of the 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

$$\chi_a \Leftrightarrow \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \chi_b \Leftrightarrow \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \varphi \Leftrightarrow \begin{pmatrix} X_a \varphi_a \\ X_b \varphi_b \end{pmatrix}. \quad (55)$$

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

$$\mathbf{J} = \sum_s \wp_s \mathbf{J}_s, \quad (56)$$

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

$$\wp_a \Leftrightarrow \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \wp_b \Leftrightarrow \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}. \quad (57)$$

The analogous trace over molecular states becomes the row vector

$$\frac{1}{V} \text{Tr} \mathbf{J} = \sum_s \int d\mathbf{p} \mathbf{J}_s \chi_s^\dagger \Leftrightarrow \int d\mathbf{p} (\mathbf{J}_a \mathbf{J}_b). \quad (58)$$

Equations (26) and (39) 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

$$(\mathcal{P}_0)_{ss'} = \left(\varphi \mathbf{J} \odot \int d\mathbf{p} \mathbf{J} \right)_{ss'} = \chi_s X_s \varphi_s \mathbf{J}_s \odot \int d\mathbf{p} \mathbf{J}_s' \chi_{s'}^\dagger, \quad (59)$$

or in matrix form

$$\mathcal{P}_0 \Leftrightarrow \begin{pmatrix} X_a \varphi_a \mathbf{J}_a \\ X_b \varphi_b \mathbf{J}_b \end{pmatrix} \odot \int d\mathbf{p} (\mathbf{J}_a \mathbf{J}_b). \quad (60)$$

There are analogous species flux projectors

$$\mathcal{P}_s \Leftrightarrow \varphi_s \mathbf{J}_s \odot \int d\mathbf{p} \mathbf{J}_s \begin{pmatrix} \delta_{a,s} & 0 \\ 0 & \delta_{b,s} \end{pmatrix}. \quad (61)$$

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

$$1 - \mathcal{P}_0 \Leftrightarrow \begin{pmatrix} X_b \mathcal{P}_a & -(\mathcal{P}_0)_{ab} \\ -(\mathcal{P}_0)_{ba} & X_b \mathcal{P}_b \end{pmatrix} = \boldsymbol{\zeta} \odot \boldsymbol{\zeta}^\dagger. \quad (62)$$

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

$$\boldsymbol{\zeta} \Leftrightarrow \begin{pmatrix} \varphi_a \mathbf{J}_a \\ -\varphi_b \mathbf{J}_b \end{pmatrix} \quad \boldsymbol{\xi} \Leftrightarrow \int d\mathbf{p} \begin{pmatrix} X_b \mathbf{J}_a \\ -X_a \mathbf{J}_b \end{pmatrix}. \quad (63)$$

Equation (62) represents, of course, the projection onto the vector $\boldsymbol{\zeta}$ in the space of species flux.

A transport coefficient of a one-particle property is given by Eq. (26) with the integral evaluated by Eq. (39). 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

$$\left[(1 - \mathcal{P}_0) \varphi \mathcal{R} \frac{1}{\varphi} (1 - \mathcal{P}_0) \right]^{-1} = \frac{1}{\text{Den}} \boldsymbol{\zeta} \odot \boldsymbol{\zeta}^\dagger \quad (64)$$

in which the denominator is

$$\begin{aligned} \text{Den} &= \frac{1}{2\alpha + 1} \boldsymbol{\zeta}^\dagger \odot \varphi \mathcal{R} \frac{1}{\varphi} \boldsymbol{\zeta} \\ &= X_b \mathcal{R}_{a,a} + X_a \mathcal{R}_{b,b} - X_a \mathcal{R}_{a,b} - X_b \mathcal{R}_{b,a}. \end{aligned} \quad (65)$$

This involves the collision matrix elements

$$\begin{aligned} \mathcal{R}_{a,a} &= \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_a \odot \varphi_a \mathcal{R} \mathbf{J}_a \\ &= n X_a \langle v \rangle_a \mathfrak{S} \begin{pmatrix} \alpha 0 | a \\ \alpha 0 | a \end{pmatrix}_{aa} + n X_b \langle v \rangle_{ab} \mathfrak{S} \begin{pmatrix} \alpha 0 | a \\ \alpha 0 | a \end{pmatrix}_{ab} \end{aligned} \quad (66)$$

and

$$\mathcal{R}_{a,b} = \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J}_a \odot \varphi_a \mathcal{R} \mathbf{J}_b = n X_b \langle v \rangle_{ab} \mathfrak{S} \begin{pmatrix} \alpha 0 | a \\ \alpha 0 | b \end{pmatrix}_{ab}, \quad (67)$$

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. 17 and 18.

Equation (39) requires the evaluation of the inner product

$$\begin{aligned}
& \int d\mathbf{p} \mathbf{J} \odot \varphi \mathcal{R} \frac{1}{\varphi} \xi^{\odot} \xi^{\dagger} \varphi \mathcal{R} \mathbf{J} \\
&= \int d\mathbf{p} (\mathbf{J}_a \mathbf{J}_b) \odot \varphi \mathcal{R} \left(\frac{\mathbf{J}_a}{X_a} \right) \odot \\
&\quad \times \int d\mathbf{p} (X_b \mathbf{J}_a - X_a \mathbf{J}_b) \varphi \mathcal{R} \left(\frac{\mathbf{J}_a}{\mathbf{J}_b} \right) \\
&= (2\alpha + 1) \left[\mathcal{R}_{a,a} - \frac{X_a}{X_b} \mathcal{R}_{a,b} + \frac{X_b}{X_a} \mathcal{R}_{b,a} - \mathcal{R}_{b,b} \right] \\
&\quad \times X_a X_b [\mathcal{R}_{a,a} + \mathcal{R}_{a,b} - \mathcal{R}_{b,a} - \mathcal{R}_{b,b}] \\
&= (2\alpha + 1) X_a X_b [\mathcal{R}_{a,a} + \mathcal{R}_{a,b} - \mathcal{R}_{b,a} - \mathcal{R}_{b,b}]^2. \quad (68)
\end{aligned}$$

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

$$X_a \mathcal{R}_{a,b} = X_b \mathcal{R}_{b,a}. \quad (69)$$

Also required is the matrix element

$$\begin{aligned}
\mathcal{R}_{0,0} &= \frac{1}{2\alpha + 1} \int d\mathbf{p} \mathbf{J} \odot \varphi \mathcal{R} \mathbf{J} \\
&= X_a \mathcal{R}_{a,a} + X_a \mathcal{R}_{a,b} + X_b \mathcal{R}_{b,a} + X_b \mathcal{R}_{b,b}. \quad (70)
\end{aligned}$$

Putting these results into Eqs. (26) and (39), together with simplifying the result by an extensive use of the symmetry of Eq. (69), the mixture transport coefficient becomes

$$\frac{\sigma}{nB} = \frac{X_b \mathcal{R}_{a,a} + X_a \mathcal{R}_{b,b} - X_a \mathcal{R}_{a,b} - X_b \mathcal{R}_{b,a}}{\mathcal{R}_{a,a} \mathcal{R}_{b,b} - \mathcal{R}_{a,b} \mathcal{R}_{b,a}}. \quad (71)$$

This expression is exactly the same as that obtained from the Boltzmann equation, as found for example in McCourt, *et al.*¹⁸ for binary mixtures where it is expressed in terms of kinetic cross sections.

VI. 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{I} , 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) 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{I} 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. (35). The meaning of the binary collision operator \mathcal{R} will be different for each case, but the formalism is otherwise the same.

For an \mathbf{I} 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 paper must be changed, and it is not clear whether a closed expression for \mathbf{B} can be obtained. 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 will be illustrated for viscosity and thermal conductivity in future work.

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