

A Collisional Approach to the Calculation of Time Correlation Functions. Transport Coefficients of Gases

John E. Reissner¹ and William A. Steele¹

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A method of successive approximations is proposed for the evaluation of the time-correlation functions such as those that give the thermal transport coefficients of gases. The method is based on a calculation of the changes in correlations of appropriate functions of the molecular velocity which are a result of collisions in the gas. The decaying rates of the correlations are expressed as integrals of the differential collision cross section. When the first approximation is introduced in the expressions for thermal transport coefficients, results are obtained for the coefficient of binary diffusion and the viscosity and thermal conductivity of single-component systems which are identical with those of the first Chapman-Enskog solutions of the Boltzmann and Enskog equations. For the coefficients of viscosity and thermal conductivity in multicomponent systems, it is shown that the first approximation leads to expressions of the form of the Sutherland and Wassiljewa relations, respectively.

KEY WORDS: Diffusion; gases; kinetic theory; Sutherland-Wassiljewa relations; thermal conductivity; time correlation functions; viscosity.

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¹ Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania.

1. INTRODUCTION

The use of collision-rate and mean-free-path concepts in calculations of the transport coefficients of gases has a long history.⁽¹⁻⁵⁾ In part, the appeal of this approach relative to the more rigorous Chapman-Enskog analysis of the Boltzmann equation lies in the physical picture that accompanies the collision theory, but which is almost completely obscured by the mathematical formalism required to solve the integrodifferential equation that specifies the velocity distribution function in a dilute nonequilibrium system. From a pedagogical point of view, it is often found convenient to give an introductory discussion of the kinetic theory of gases based on collision theory, in spite of the fact that the expressions derived are not in complete agreement with Chapman-Enskog theory. In one of the most sophisticated versions of collision theory, Monchick and Mason⁽⁶⁾ have succeeded in recovering the Chapman-Enskog results for Maxwellian molecules, and obtained transport coefficients for more general interaction potentials which differ only slightly from the most rigorous expressions.

In this paper, we will present an extension of the collision theory ideas which leads precisely to the explicit Chapman-Enskog first approximation for the transport coefficients of pure gases. The derivation is of interest because it completely avoids attempts to solve the Boltzmann equation, thus avoiding the mathematical complexity that invariably seems to accompany this problem. Our approach is based on the time-correlation function description of nonequilibrium systems.^(7,8) In this theory, which is tantamount to a perturbation solution of the full Liouville equation, expressions for transport coefficients are obtained in terms of the equilibrium averages of the time evolution of appropriate molecular variables. The evaluation of these time-correlation function expressions for one-component gases at low density has been considered by Mori and others, who have shown that the explicit Chapman-Enskog first approximation results for several transport coefficients could be obtained by writing the time correlations as exponentially decaying functions of time, with decay constants given by the approximate eigenvalues of the binary collision operator.⁽⁹⁾ Obtaining approximations to these eigenvalues continues to provide an area of active research.⁽¹⁰⁾

The validity of the time-correlation function approach was confirmed, and the applicability of the general method extended to the study of the density dependence of transport coefficients, by Zwanzig,⁽¹¹⁾ Kawasaki and Oppenheim,⁽¹²⁾ and others.⁽¹³⁻¹⁵⁾ Other approaches to the problem by-passed the need for sophisticated mathematical analysis implicit in these efforts by evaluating the time correlation formulas in terms of samples of molecular trajectories taken from computer simulations of the system,⁽¹⁶⁾ and by using hypothetical functional forms for the "memory function" appearing in the equation of change of the correlation itself.^(17,18)

Work such as this has provided valuable results and tremendous impetus to the field, at the expense of extensive computational effort. More heuristic analyses that have been developed^(19,20) have led to results that were rather limited as to the intermolecular potentials they could accommodate, and gave no indications on how systematic improvements might be accomplished.

The method described here for evaluating time-correlation functions is based on the ideas of mean-free-path theory in the sense that results are obtained by calculating collisional changes in the time-correlation functions in lieu of solving an integral equation with collisional effects appearing in its kernel. While earlier rigorous studies of the time-correlation method have shown that obtaining the solution of the Boltzmann equation is equivalent to evaluating the time-correlation function expressions, they have not shown that direct evaluation of the time-correlation functions could yield transport coefficients of kinetic-equation quality except for hard spheres. The method of this paper provides a means of achieving this goal.

Our approach to the problem is based on a calculation of the probabilities that a molecule in the system will participate in a chain of specified collisions in a given interval of time. These are then used to compute the time dependence of the distribution functions for the variables appearing in each time-correlation function expression. The time-correlation functions themselves are easily obtained from these distributions. If the physical assumptions implicit in the Boltzmann and Enskog equations are made that collisions only occur between pairs of molecules and that the precollision velocities of the molecules participating in a specified collision are uncorrelated with one another, the collision chain probabilities are obtained in terms of the differential collision cross sections for the system. In this way, approximations to the transport coefficients are obtained whose accuracy depends on the number of collisions included in the chain. It is found that the first approximations lead to expressions for the binary diffusion coefficient and the kinetic contributions to the coefficients of viscosity and thermal conductivity in single-component systems that are identical to those of the first approximation of the Chapman-Enskog solutions of the equations of Boltzmann and of Enskog, respectively. For the coefficients of viscosity and thermal conductivity in multicomponent systems, our first approximation leads to expressions having the form of the semiempirical Sutherland and Wassiljewa equations, respectively.

2. PROBABILITIES OF COLLISION CHAINS

We consider here elastic collisions of pairs of molecules that interact through spherically symmetric central forces. The species of molecules are denoted by lower case Greek letters ν, μ, κ, \dots , with $\nu = \mu$ corresponding to the case of a pair of atoms of like species. In the collisions, a precollision

relative velocity $\mathbf{g} = \mathbf{v}_{v1} - \mathbf{v}_{\mu2}$ is rotated without change of length g through an angle χ . Neglecting any quantum "degeneracy effects," the differential collision rate per molecule of species ν and velocity \mathbf{v}_{v1} is proportional to the density of appropriate collision partners and to the solid angle $2\pi \sin \chi d\chi$. The corresponding proportionality constant $\alpha_{\nu\mu}(g, \chi)$ may be calculated by quantum mechanics or classically.⁽²⁾ In the latter case, an impact parameter b may be assigned to each collision and the angle χ is a function of b and g so that

$$\alpha_{\nu\mu}(g, \chi) = g \sum_i b_i |db_i/d\chi| / \sin \chi \quad (1)$$

where the summation is over impact parameters b_i , which, with g , correspond to trajectories leading to the particular value of χ .

The density of molecules of type μ with velocities around $\mathbf{v}_{\mu2}$ that will collide with a specified species ν molecule during an interval dt is thus $n_\mu G_{\nu\mu}(\sigma_{\nu\mu}) f_\mu(v_{\mu2}) d\mathbf{v}_{\mu2}$, where $f_\mu d\mathbf{v}_{\mu2}$ is the Maxwell-Boltzmann function

$$f_\mu(v_{\mu2}) = (m_\mu/2\pi kT)^{3/2} \exp(-m_\mu v_{\mu2}^2/2kT) \quad (2)$$

When the radial distribution function $G_{\nu\mu}$ that appears in this relation is multiplied by the macroscopic density n_μ and is evaluated at the contact distance $\sigma_{\nu\mu}$, it gives the density of μ molecules at distance $\sigma_{\nu\mu}$ from a specified ν molecule. In this expression, the contact distance must be defined as the intermolecular distance which is attained if and only if a collision occurs, and for hard sphere molecules, this distance is the hard sphere diameter $\sigma_{\nu\mu}$. Realistic potentials which are nonvanishing for large interparticle separations require the use of a cutoff at some reasonable intermolecular separation beyond which the potential energy of interaction vanishes. In this case, the collision rates will be well behaved. It will be seen that the results of this work allow the passage to the limit of the cutoff at infinity, in which case $G = 1$, without difficulty. The differential collision rate now can be written in the well-known form⁽³⁾

$$\omega = 2\pi n_\mu G_{\nu\mu} f_\mu d\mathbf{v}_{\mu2} \alpha_{\nu\mu} \sin \chi d\chi \quad (3)$$

(The dependence of ω on all the variables specifying the collision is left implicit.) We shall also require the total collision rate of a molecule of velocity \mathbf{v}_{v1} , which we denote by $\Sigma\omega$,

$$\Sigma\omega = 2\pi \sum_\mu n_\mu G_{\nu\mu} \int f_\mu(v_{\mu2}) d\mathbf{v}_{\mu2} \int \alpha_{\nu\mu} \sin \chi d\chi \quad (4)$$

We now use the differential collision rates ω and $\Sigma\omega$ to construct the probability that a specified chain of n collisions will occur in an interval of time t . The rates enter the analysis because the probability of a ν molecule

of velocity \mathbf{v}_{v1} undergoing a specified collision during the limiting interval dt is ωdt . We shall assume that no more than one collision may occur in this limiting interval of time and ignore the effects of instantaneous ternary or higher order collisions. Further, we shall adopt a "stosszahlansatz" that the only collisions occurring are those for which the precollision velocities of the two molecules are uncorrelated with one another.

If the velocity of a single molecule was not affected by its collisions, or if its total collision rate did not depend on its velocity, the collision chain probabilities would be obtained from the Poisson distribution for the probability of n collisions, each of a different probability ωdt , occurring during $N = t/dt$ intervals of time. This leads to the result that the probability of a chain of n collisions during an interval of time t , $f^{(n)}$, is the product of the n rates of the collisions occurring in the chain and a factor $(t^n/n!) \exp(-t\Sigma\omega)$, where $\Sigma\omega$ is the overall collision rate of the molecule initiating the chain and the factor $1/n!$ restricts the calculation to that for one particular sequence of the collisions in time. This result correctly provides the probability $f^{(0)}$ that a molecule of species ν and velocity \mathbf{v}_{v1} survives an interval t without collision,

$$f^{(0)} = \exp(-t\Sigma\omega) \quad (5)$$

and the probability $f^{(1)}$ that it undergoes only one specified collision in that interval,

$$f^{(1)} = t\omega \exp(-t\Sigma\omega) \quad (6)$$

For chains of two or more collisions, however, the velocities of the molecules change in collisions and the total collision rates depend on velocity between collisions, so that a modification of the Poisson distribution is required. For the collisions we are considering, a specified sequence of n collisions during a time interval t corresponds to the three mutually independent events, (a) no collision during an interval of time $\tau < t$, (b) the first collision in the succeeding interval of time $d\tau$, and (c) the subsequent chain of $n - 1$ collisions over the interval $t - \tau$. The probability of events (a) and (b) together is $[\exp(-\tau\Sigma\omega)]\omega d\tau$. The n -collision chain and $(n - 1)$ -collision chain probabilities are related by the condition that

$$f^{(n)}(t) = \omega \int_0^t d\tau e^{-\tau\Sigma\omega} f^{(n-1)}(t - \tau) \quad (7)$$

We now prove that the expansion in powers of t of $f^{(n)}$ exists, and has no coefficient of order less than n . By inspection of Eqs. (3) and (4) for $f^{(0)}$ and $f^{(1)}$, this is true for these two cases, and we may consider the consequences of the assumption that

$$f^{(n-1)}(t - \tau) = a_{n-1}(t - \tau)^{n-1} + a_n(t - \tau)^n + \dots$$

for successively larger values of n . When this expression is substituted into Eq. (5), there follows a corresponding expansion for $f^{(n)}$ with no power of t lower than t^n , thus proving our result. Explicit expressions for any $f^{(n)}$ with $n \geq 2$ may be obtained by this procedure; since these functions are not required at the level of approximation used in this paper, they will not be discussed further.

3. CORRELATIONS OF DYNAMICAL VARIABLES

The time-correlation function formulas for transport coefficients L are of the form

$$L = CV^{-1} \int_0^{\infty} dt \Psi(t) \quad (8)$$

where $\Psi(t)$ is the scalar product correlation function for a pair of dynamical variables A and B of common tensorial character⁽⁸⁾

$$\Psi(t) = \langle A(0)B(t) \rangle = (1/N!) \int d\{N\} W_N A(0)B(t) \quad (9)$$

In this equation, W_N is the equilibrium N -particle distribution function, $d\{N\}$ is the volume element for integration over the phase space of the N particles, and $1/N!$ is the normalization to unity for integration of W_N over this phase space, where $N!$ is the product of $N_\nu!$ over all species ν in the system.

For dilute gases, A and B are, respectively, sums over molecules of functions A_{v_i} and B_{v_i} of the single molecule velocities. These functions vary in time with the occurrence of collisions. Because A_{v_i} and B_{v_i} are odd functions of velocity, the averages of products $A_{v_i}B_{\mu_j}$ will vanish for $v_i \neq \mu_j$ when the velocities of the indicated molecules are uncorrelated, as they are at $t = 0$. Thus, we may write Eq. (9) as

$$\Psi(t) = \left\langle \sum_{\nu} N_{\nu} [A_{\nu 1}(0)B_{\nu 1}(0) + A_{\nu 1}(0) \Delta B(t)] \right\rangle \quad (10)$$

with

$$\Delta B(t) = \sum_{\mu} \sum_j [B_{\mu_j}(t) - B_{\mu_j}(0)] \quad (11)$$

This form applies when A and B include sums over all species. When, as is the case for the diffusion coefficient expression, A and B are sums over the molecules of species ν and μ , respectively, the summation over μ in Eq. (11) should be dropped.

In addition, $\mu \neq \nu$ in the expressions for mutual diffusion coefficients

and consequently the time-independent term in Eq. (10) is absent for those correlation functions. When $\mu = \nu$, that term is given by

$$\langle A_{\nu 1} B_{\nu 1} \rangle = \int d\mathbf{v}_{\nu 1} f_{\nu}(v_{\nu 1}) A_{\nu 1} B_{\nu 1} \quad (12)$$

where f_{ν} is given by Eq. (2).

The second average appearing in Eq. (10) can be written in terms of the joint probability density $W(A_{\nu 1}(0), \Delta \mathbf{B}(t))$:

$$\langle A_{\nu 1}(0) \Delta \mathbf{B}(t) \rangle = \int dA_{\nu 1}(0) d\Delta \mathbf{B}(t) A_{\nu 1}(0) \Delta \mathbf{B}(t) W(A_{\nu 1}(0), \Delta \mathbf{B}(t)) \quad (13)$$

The probability that values $A_{\nu 1}(0)$ and $\Delta \mathbf{B}(t)$ will occur can be written as the product of the probability that $A_{\nu 1}(0)$ will occur at $t = 0$ and the conditional probability that $\Delta \mathbf{B}(t)$ will occur at time t if it is known that $A_{\nu 1}(0)$ exists at time zero. The distribution of $A_{\nu 1}(0)$ can be written as

$$W(A_{\nu 1}(0)) \int d\mathbf{v}_{\nu 1} f_{\nu}(v_{\nu 1}) \delta(A_{\nu 1} - A_{\nu 1}(0)) \quad (14)$$

Furthermore, the probability of obtaining some value of $\Delta \mathbf{B}(t)$ is equal to the probability of the collision chains leading to that value of the variable at time t . If $\Delta \mathbf{B}^{(n)}$ is the change in \mathbf{B} caused by a chain of n collisions, this conditional probability is

$$W(\Delta \mathbf{B}(t); A_{\nu 1}(0)) = \sum_{n \geq 0} \sum \sum \dots \sum f^{(n)} \delta(\Delta \mathbf{B}^{(n)} - \Delta \mathbf{B}(t)) \quad (15)$$

In this equation, the set of unindexed summations is over all chains of n collisions initiated by a molecule possessing the value of $A_{\nu 1} = A_{\nu 1}(0)$ at $t = 0$.

The product of Eqs. (14) and (15) provides the joint probability density in Eq. (13). When this expression is substituted into Eq. (10), one obtains a formal equation relating $\Psi(t)$ to the differential collision chain probabilities:

$$\Psi(t) = \sum_{\nu} N_{\nu} \left(\langle A_{\nu 1} B_{\nu 1} \rangle + \sum_{n \geq 0} \int d\mathbf{v}_{\nu 1} f_{\nu}(v_{\nu 1}) A_{\nu 1} \sum \sum \sum \dots \sum f^{(n)} \Delta \mathbf{B}^{(n)} \right) \quad (16)$$

We now consider in detail the first two terms in this expansion:

$$\Psi(t) = \sum_{\nu} N_{\nu} \left(\langle A_{\nu 1} B_{\nu 1} \rangle + \int d\mathbf{v}_{\nu 1} f_{\nu}(v_{\nu 1}) A_{\nu 1} \sum f^{(1)} \Delta \mathbf{B}^{(1)} + \dots \right) \quad (17)$$

To evaluate the term including $f^{(1)}$, we again use the fact that the average of $A_{\nu 1} B_{\mu j}$ vanishes unless the velocities of molecules $\nu 1$ and μj are correlated. After only one collision, such correlations will only exist in two instances,

first, when $\mu j = \nu 1$, and second, when two molecules μj and $\nu 1$ have collided. Therefore, $\Delta \mathbf{B}^{(1)}$ will contain two terms contributing to Eq. (17), one with $\Delta B_{\nu 1}^{(1)}$ and the other with $\Delta B_{\mu 2}^{(1)}$, where $\mu 2$ refers to the molecule colliding with $\nu 1$ during time t , with probability $f^{(1)}$. Consequently, the expression for the time correlation function $\Psi(t)$ is

$$\Psi(t) = \sum_{\nu} N_{\nu} \left(\langle A_{\nu 1} B_{\nu 1} \rangle + \int d\mathbf{v}_{\nu 1} f_{\nu}(v_{\nu 1}) A_{\nu 1} \sum f^{(1)} (\Delta B_{\nu 1}^{(1)} + \Delta B_{\mu 2}^{(1)}) + \dots \right) \quad (18)$$

In this equation, $\langle A_{\nu 1} B_{\nu 1} \rangle$ and the term involving $\Delta B_{\nu 1}^{(1)}$ reflect the decay of the autocorrelation of $A_{\nu 1}$ and $B_{\nu 1}$, while the remaining term describes the growth of the collision-mediated correlation of $B_{\mu 2}$ with $A_{\nu 1}$.

The unspecified terms in Eqs. (15)–(17) correspond to the contributions of chains of two or more collisions to $\Psi(t)$. We reserve the consideration of these terms for later work, demonstrating below that realistic expressions for transport coefficients may be obtained by considering “chains” of no more than one collision.

4. TRANSPORT COEFFICIENTS

We now see that the explicit time dependence of the correlation function $\Psi(t)$ is contained entirely in the $f^{(n)}$. Equation (6) gives an explicit expression for $f^{(n)}$; the argument given subsequent to Eq. (6) indicates that one can write

$$\Psi = \sum_{\nu} (\Psi_{\nu 0} + \Psi_{\nu 1} t + \Psi_{\nu 2} t^2 + \dots)$$

(The summation over all species can be omitted for one-component gases.) In order to use these expressions in Eq. (8) for the transport coefficients, it is necessary to re-sum the expansion to obtain convergence of that integral. We sum from the series those terms that lead to a decaying exponential in time, yielding

$$\Psi = \sum_{\nu} \Psi_{\nu 0} e^{-\lambda_{\nu} t} [1 + O(t^2)] \quad (19)$$

where the decay constants λ_{ν} have the expressions

$$\lambda_{\nu} = -\Psi_{\nu 1} / \Psi_{\nu 0} \quad (20)$$

These decay constants turn out to be positive for all relevant cases. A natural hierarchy of approximation then follows by truncation of the power series multiplying the exponential to include successively larger number of terms. It can now be seen from the time dependences of the $f^{(n)}$ that: $\Psi_{\nu 0}$ involves only an average over the equilibrium ensemble; $\Psi_{\nu 1}$ involves the dynamics of single collisions as well as the properties of the equilibrium ensemble (i.e.,

uncollided molecules); the term of order t^n is given by a sum of terms involving the dynamics of collision chains of length n and less.

We can now perform the time integration in Eq. (8) to obtain a general expression for the transport coefficient L :

$$L = \frac{C}{V} \sum \frac{\Psi_{v_0}}{\lambda_v} [1 + \text{corrections from terms } O(t^2)] \quad (21)$$

With the use of Eq. (20), the first approximation (corresponding to exponential decay) can be written as

$$L^{(1)} = - \frac{C}{V} \sum_v \frac{\Psi_{v_0}^2}{\Psi_{v_1}} \quad (22)$$

We now proceed to explicitly evaluate this expression. In fact, the required coefficients Ψ_{v_0} and Ψ_{v_1} are familiar integrals. Equation (18) yields

$$\Psi_{v_0} = N_v \langle A_{v_1} B_{v_1} \rangle \quad (23)$$

since each of the chain probabilities $f^{(n)}$ contributes only to coefficients of no lower power of t than the n th.

For the same reasons, the coefficient Ψ_{v_1} is obtained by expanding the term involving $f^{(1)}$ in Eq. (18) and retaining only terms linear in time. With the use of Eq. (6) for $f^{(1)}$ and Eq. (2) for the collision rate ω , the resulting expression may be written in terms of bracket integrals of the type discussed by Chapman and Cowling.⁽³⁾ Defining such integrals by

$$\begin{aligned} [A_{v_1}, B_{\kappa j}]_{v_1, \mu 2} &= 2\pi \iint dv_{v_1} dv_{\mu 2} f_v(v_{v_1}) f_\mu(v_{\mu 2}) \\ &\times \int \alpha_{v\mu} \sin \chi d\chi A_{v_1}(B_{\kappa j} - B_{\kappa j}^{(1)}) \end{aligned} \quad (24)$$

the procedure we have outlined lead to

$$\Psi_{v_1} = -N_v \sum_\mu n_\mu G_{v\mu} ([A_{v_1}, B_{v_1}]_{v_1, \mu 2} + [A_{v_1}, B_{\mu 2}]_{v_1, \mu 2}) \quad (25)$$

The terms in this sum corresponding to $\nu = \mu$ reduce to a function of the bracket integral defined by Chapman and Cowling:

$$\begin{aligned} [A, B]_{v_1} &= 2\pi \iint dv_{v_1} dv_{v_2} f_v(v_{v_1}) f_v(v_{v_2}) \\ &\times \int \alpha_{vv} \sin \chi d\chi A_{v_1}(B_{v_1} + B_{v_2} - B_{v_1}^{(1)} - B_{v_2}^{(1)}) \end{aligned} \quad (26)$$

With this definition, the equation for these terms is

$$-N_v n_v G_{vv} ([A_{v_1}, B_{v_1}]_{v_1, v_2} + [A_{v_1}, B_{v_2}]_{v_1, v_2}) = -N_v n_v G_{vv} [A, B]_{v_1} \quad (27)$$

and this becomes the bracket integral expression for Ψ_{v_1} in a single-component system.

Examples of these bracket integrals for various choices of the variables $A_{\nu i}$ and $B_{\mu j}$ expressed in terms of dimensionless velocities

$$\mathcal{C}_{\nu i} = (m_{\nu}/2kT)^{1/2} \mathbf{v}_{\nu i} \quad (28)$$

are evaluated by Chapman and Cowling in terms of the collision integrals $\Omega_{\nu\mu}^{(l)}(s)$, which are defined by

$$\Omega_{\nu\mu}^{(l)}(s) = \pi^{1/2} \int_0^{\infty} d\mathcal{C}_{\nu\mu} (\exp -\mathcal{C}_{\nu\mu}^2) \mathcal{C}_{\nu\mu}^{2s+2} \int_0^{\pi} \alpha_{\nu\mu} \sin \chi d\chi (1 - \cos^l \chi) \quad (29)$$

where

$$\mathcal{C}_{\nu\mu} = (m_{\nu\mu}/2kT)^{1/2} \mathbf{g} \quad (30)$$

and $m_{\nu\mu}$ is the reduced mass

$$m_{\nu\mu} = m_{\nu} m_{\mu} / (m_{\nu} + m_{\mu}) \quad (31)$$

The examples they give include all cases required for the thermal transport coefficients.

5. DIFFUSION

In an isothermal binary system of species a and b , where the mass fluxes J_{ν} are linear functions of the gradients of the partial specific Gibbs free energies μ_{ν} , phenomenological coefficients are defined so as to satisfy the linear phenomenological relation⁽²¹⁾

$$-\mathbf{J}_{\nu} = (L_{\nu a}/T) \nabla \mu_a + (L_{\nu b}/T) \nabla \mu_b, \quad \nu = a \text{ or } b \quad (32)$$

The explicit time-correlation function expressions⁽⁶⁾ for these phenomenological coefficients can be written as

$$L_{\nu\kappa}/T = \frac{2}{3} (m_{\nu} m_{\kappa})^{1/2} V^{-1} \int_0^{\infty} \left\langle \sum_{\nu i} \sum_{\kappa j} \mathcal{C}_{\nu i}(0) \cdot \mathcal{C}_{\kappa j}(t) \right\rangle dt \quad (33)$$

This equation corresponds to Eq. (8), with the constant $C_{\nu\kappa}$ given by

$$C_{\nu\kappa} = \frac{2}{3} (m_{\nu} m_{\kappa})^{1/2} \quad (34)$$

At $t = 0$, however, Eq. (33) is identically zero for $\nu \neq \kappa$, which requires that the coefficient $\Psi_{\nu\kappa 0}$ in the series expansion of $\Psi_{\nu\kappa}$ vanishes as well. The apparent vanishing of $L_{\nu\kappa}^{(1)}/T$, as given by (22), proves no real difficulty.

In fact, with Eqs. (21) and (23) applied to the results of Section 3 for this case, we obtain

$$\Psi_{\nu\kappa} = C_{\nu\kappa} \begin{cases} N_{\nu} \left(\langle \mathcal{C}_{\nu 1}^2 \rangle - t \left(n_{\nu} G_{\nu\nu} [\mathcal{C}_{\nu 1}, \mathcal{C}_{\nu 2}]_{\nu 1, \nu 2} \right. \right. \\ \left. \left. + \sum_{\mu=a, b} n_{\mu} G_{\nu\mu} [\mathcal{C}_{\nu 1}, \mathcal{C}_{\nu 1}]_{\nu 1, \mu 2} \right) + O(t^2) \right), & \nu = \kappa \\ -t N_{\nu} n_{\kappa} G_{\nu\kappa} [\mathcal{C}_{\nu 1}, \mathcal{C}_{\kappa 2}]_{\nu 1, \kappa 2} + O(t^2), & \nu \neq \kappa \end{cases} \quad (35)$$

Furthermore, the coefficients $L_{\nu\kappa}/T$ are not independently measurable quantities, since the gradients of chemical potential are related by the Gibbs–Duhem relation:

$$\rho_a \nabla \mu_a + \rho_b \nabla \mu_b = 0 \quad (36)$$

Consequently, Eq. (32) may be written as

$$-\mathbf{J}_\nu = L_\nu \nabla \mu_\nu, \quad \nu = a, b \quad (37)$$

where the numerical values of the observable coefficients are given by

$$L_a = L_{aa}/T - (\rho_a/\rho_b)L_{ab}/T \quad (38)$$

Equation (35) may be used with Eq. (38) to obtain the time-correlation function expression for L_a . (The expression for L_b follows upon interchange of a and b .) The result is

$$\begin{aligned} \Psi_a = N_a \langle \mathcal{C}_a \cdot \mathcal{C}_a \rangle - t \{ n_a G_{aa} ([\mathcal{C}_{a1}, \mathcal{C}_{a1}]_{a1,a2} + [\mathcal{C}_{a1}, \mathcal{C}_{a2}]_{a1,m2}) \\ + n_b G_{ab} ([\mathcal{C}_{a1}, \mathcal{C}_{a1}]_{a1,b2} - (\rho_2/\rho_b)(m_b/m_a)^{1/2} [\mathcal{C}_{a1}, \mathcal{C}_{b2}]_{a1,b2}) \} + O(t^2) \end{aligned} \quad (39)$$

with

$$C_a = \frac{2}{3}m_a, \quad L_a = C_a V^{-1} \int_0^\infty dt \Psi_a \quad (40)$$

Equation (39) is the key equation in this calculation of the diffusion coefficient, since it leads directly to the Chapman–Enskog result (as will be proved below). It is therefore of interest to consider the physical significance of the individual terms shown there. Basically, the correlation function Ψ_a is

$$\Psi_a = \left\langle \mathcal{C}_{a1} \cdot \sum_{j=1}^N \mathcal{C}_j \right\rangle \quad (41)$$

and thus represents the correlation between the velocity of a molecule of species a and the velocities of all the other molecules in the system, regardless of species. The leading term in Eq. (39) gives the correlation before collisions have occurred; the only nonzero terms present when one has a random distribution of velocities are the autocorrelations. (We note that $\langle \mathcal{C}_a \cdot \mathcal{C}_a \rangle = \frac{3}{2}$.) The set of coefficients multiplying t gives the rate of change of Ψ_a which is due to single collisional events; the first of these $[\mathcal{C}_{a1}, \mathcal{C}_{a1}]_{a1,a2}$ represents the loss of the autocorrelation of the velocity of a species a molecule resulting from collision with another species a molecule, and the third $[\mathcal{C}_{a1}, \mathcal{C}_{a1}]_{a1,b2}$ represents the loss of autocorrelation caused by collision with a b molecule. The second term arises from a growth of correlation between the velocities of two a molecules subsequent to a collision between

them, and the fourth term represents growth of correlation between the velocities of an a and a b molecule due to their collision. Finally, the term of $O(t^2)$ will, when written out in detail, contain terms that describe the changes in correlation that arise from the various types of two-collision chains possible in an a - b mixture when one of the initial collision partners is restricted to be an a molecule.

Collision integral expressions for all these bracket integrals are presented by Chapman and Cowling, and specifically with Eqs. (9.6, 1), (9.6, 4), and (9.6, 7) of their work, we find that Eqs. (39) and (40) can be rewritten as

$$L_a = \rho_a \int_0^\infty dt \left(1 - \frac{16}{3} t \frac{G_{ab} \Omega_{ab}^{(1)}(1)}{M_{ab}} \rho + O(t^2) \right), \quad M_{ab} = m_a + m_b \quad (42)$$

Equation (42) includes the familiar approximation that the binary diffusion coefficient depends only on interactions of unlike molecules. To order t , this restriction arises through the exact cancellation of the decay of autocorrelations mediated by like-molecule collisions [term one in curly brackets in Eq. (39)] by the growth of correlations between velocities of molecules of like species (term two). This leaves the evolution of correlations through collisions of unlike molecules as the only single-collision contribution to the diffusion coefficient at nonzero time.

The integral in Eq. (42) can be evaluated by the exponential resummation scheme described in Section 4; the first approximation to L_a is thus

$$L_a^{(1)} = (3/16) \rho_a M_{ab} / \rho G_{ab} \Omega_{ab}^{(1)}(1) \quad (43)$$

This equation and the corresponding example for $L_b^{(1)}/T$ may be used in Eq. (36) for \mathbf{J}_v to obtain a relation for the relative diffusion velocity $\mathbf{v}_a - \mathbf{v}_b$. If, further, the gradients of μ_v are related to the gradient of mole fraction $\nabla x_a = -\nabla x_b$ by

$$\nabla \mu_v = (kT/m_v x_v) \nabla x_v$$

the equation for $\mathbf{v}_a - \mathbf{v}_b$ may be cast into the form that defines the gas-kinetic binary diffusion coefficient, namely

$$\mathbf{v}_a - \mathbf{v}_b = -(n^2/n_a n_b) \mathcal{D}_{ab} \nabla x_a \quad (44)$$

The result of our calculation for \mathcal{D}_{ab} is then

$$\mathcal{D}_{ab} = (3/16) kT / n m_{ab} G_{ab} \Omega_{ab}^{(1)}(1) \quad (45)$$

where m_{ab} is the reduced mass. For hard spheres, this is the result obtained by the first Chapman-Enskog solution of the Enskog equation.⁽²²⁾ For more general interactions, for which we must take $G_{ab} = 1$, it is the result obtained by the corresponding solution of the Boltzmann equation (Ref. 2, p. 527).

6. VISCOSITY AND THERMAL CONDUCTIVITY

To calculate the viscosity in terms of bracket integrals that are evaluated in the literature, we introduce the traceless diad $\mathcal{C}^0\mathcal{C}$, defined in terms of its components $(\mathcal{C}^0\mathcal{C})_{\alpha\beta}$ by the equation

$$(\mathcal{C}^0\mathcal{C})_{\alpha\beta} = \mathcal{C}_\alpha\mathcal{C}_\beta - \frac{1}{3}\mathcal{C}^2\delta_{\alpha\beta} \tag{46}$$

If we denote this tensor by \mathfrak{C} , the time-correlation function expression for the kinetic component of the viscosity in a multicomponent isotropic system is given by⁽⁸⁾

$$\eta = \frac{2}{3}kTV^{-1} \int_0^\infty dt \sum_\nu \sum_i \sum_\mu \sum_j \langle \mathfrak{C}_{\mu i}(0) : \mathfrak{C}_{\mu j}(t) \rangle \tag{47}$$

where i and j denote molecules of species ν and μ , respectively. This relation is of the form of Eq. (8), with

$$C = \frac{2}{3}kT \tag{48}$$

and

$$A_{vi} = B_{vi} = \mathfrak{C}_{vi} = \mathcal{C}_{vi}^0 \mathcal{C}_{vi} \tag{49}$$

With these expressions, we may evaluate Eqs. (23) and (25) for the values of $\Psi_{\nu 0}$ and $\Psi_{\nu 1}$ applicable to η , and use them in Eq. (22) for the transport coefficients themselves. The nonzero contributions to the coefficient $\Psi_{\nu 0}$ are due only to autocorrelations, just as in the diffusion coefficient calculation. One finds

$$\Psi_{\nu 0} = \frac{5}{2}N_\nu \tag{50}$$

For simplicity, consider a single-component system, and write $\Psi_0 = \frac{5}{2}N$; Ψ_1 then represents the change in correlation of \mathfrak{C}_i due to single collisional events, and contains two terms that give the collisional loss in autocorrelation for the \mathfrak{C} tensor of molecule 1; and the gain in mutual correlation between the \mathfrak{C} tensors of molecules 1 and 2. Equation (25) can be simplified to

$$\Psi_1 = -NG([\mathfrak{C}_1, \mathfrak{C}_1]_{12} + [\mathfrak{C}_1, \mathfrak{C}_2]_{12}) \tag{51}$$

Explicit expressions for these bracket integrals are given in Eqs. (9.6, 14) and (9.6, 15) of Chapman and Cowling; when molecules 1 and 2 have identical masses, the sum of the bracket integrals leads to an expression for the exponential decay constant [defined in Eq. (19)] which is

$$\lambda = (8/5)nG\Omega^{(2)} \tag{52}$$

and thus to a first approximation to the viscosity which is

$$\eta^{(1)} = \frac{5}{8}kT/G\Omega^{(2)} \tag{53}$$

The $G = 1$ limit, which applies to all potentials in the limit of zero density, yields the same result obtained from the first Chapman–Enskog solution to the Boltzmann equation, as given by Chapman and Cowling's equation (9.7, 3). For hard spheres at arbitrary densities, Eq. (53) is the result obtained from the corresponding Chapman–Enskog approximation to the solution of the Enskog equation.⁽²²⁾

In multicomponent systems, two significant alterations are necessary. In our first approximation, the correlation function becomes a sum of exponentially decaying terms, one for each component in the gas. Second, the rate of change of the \mathcal{C} -tensor correlation for a molecule of species ν is due not just to collisions with ν molecules, but to collisions with all other molecules. Consequently, the decay constant λ_ν for species ν is

$$\lambda_\nu = -\Psi'_{\nu 1}/\Psi'_{\nu 0} = \frac{2}{5} \sum_{\mu} n_{\mu} G_{\nu\mu} ([\mathcal{C}_{\nu 1}, \mathcal{C}_{\nu 1}]_{\nu 1, \mu 2} + [\mathcal{C}_{\nu 1}, \mathcal{C}_{\mu 2}]_{\nu 1, \mu 2}) \quad (54)$$

where the sum over μ includes species ν as well as $\mu \neq \nu$ components. The first sum of bracket integrals in this equation reflects the decay of the auto-correlation of \mathcal{C}_1 through collisions with each of the species in the system, and the second sum reflects the growth of the mutual correlations. Equations (9.6, 15) and (9.6, 14) of Chapman and Cowling provide the collision integral relations for these bracket integrals:

$$[\mathcal{C}_{\nu 1}, \mathcal{C}_{\nu 1}]_{\nu 1, \mu 2} = (16/3)[5m_{\nu\mu}\Omega_{\nu\mu}^{(1)}(1)/M_{\nu\mu} + \frac{3}{2}m_{\mu}^2\Omega_{\nu\mu}^{(2)}(2)/M_{\nu\mu}^2] \quad (54a)$$

and

$$[\mathcal{C}_{\nu 1}, \mathcal{C}_{\mu 2}]_{\nu 1, \mu 2} = -(16/3)m_{\nu\mu}[5\Omega_{\nu\mu}^{(1)}(1) - \frac{3}{2}m_{\nu\mu}\Omega_{\nu\mu}^{(2)}(2)/M_{\nu\mu}] \quad (54b)$$

respectively. In the sum appearing in Eq. (54), the collision integrals $\Omega_{\nu\mu}^{(1)}(1)$ vanish, and after some rearrangement we are left with

$$\lambda_\nu = (32/5) \sum_{\mu} n_{\mu} G_{\nu\mu} m_{\mu} \Omega_{\nu\mu}^{(2)}(2)/M_{\nu\mu} \quad (55)$$

When this result is substituted into Eq. (22) together with the expressions for C [Eq. (48)] and $\Psi'_{\nu 0}$, one obtains an expression for the viscosity in a multicomponent system. For such a system with mole fractions x_ν , it is convenient to define a "mixture viscosity" $\eta_{\nu\mu}^{(1)}$ by the equation

$$\eta_{\nu\mu}^{(1)} = \frac{5}{8} kT/G_{\nu\mu} \Omega_{\nu\mu}^{(2)}(2) \quad (56)$$

and define as $\eta_\nu^{(1)}$ the viscosity of a single-component system of ν -molecules. In this case the expression for the viscosity may be rearranged into

$$\eta^{(1)} = \sum_{\nu} \left(\frac{1}{\eta_\nu^{(1)}} + 2 \sum_{\mu \neq \nu} \frac{x_\mu}{x_\nu} \frac{m_\mu}{M_{\nu\mu}} \frac{1}{\eta_{\nu\mu}^{(1)}} \right)^{-1} \quad (57)$$

This equation is not identical with the first Chapman–Enskog solutions of the Boltzmann or Enskog equations. It is, in fact, an expression of the “Sutherland type,” a relation that has been used in the past as the basis of empirical correlations of the viscosities of mixtures.

Buddenberg and Wilke²³ fit data from 116 binary mixtures to a relation of this form, and proposed the expression

$$\eta = \frac{\eta_a}{1 + (x_b/x_a)(1.385\eta_a/D_{ab}\rho_a^*)} + \frac{\eta_b}{1 + (x_a/x_b)(1.385\eta_b/D_{ab}\rho_b^*)} \quad (58)$$

where ρ_v^* is the density of pure ν at the pressure and temperature to which η applies. They report this relation fitted the compilation of the data they considered with an average deviation of 3.7%. To compare our results with their correlation, we use our Eqs. (57) and (44) to write

$$\eta_{ab} = \frac{2}{3}m_{ab}n\mathcal{D}^{(1)}/A \quad (59)$$

with

$$A = \frac{1}{2}\Omega_{ab}^{(2)}(2)/\Omega_{ab}^{(1)}(1) \quad (60)$$

With this result, which also appears in the exact kinetic theory (Ref. 3, pp. 163, 265), we may rearrange the binary example of eq. (57) into

$$n^{(1)} = \frac{\eta_a}{1 + 3A(x_b/x_a)[\eta_a^{(1)}/\mathcal{D}^{(1)}](1/\rho_a^*)} + \frac{\eta_b}{1 + 3A(x_a/x_b)[\eta_b^{(1)}/\mathcal{D}^{(1)}](1/\rho_b^*)} \quad (61)$$

The ratio of integrals A in this equation depends only weakly on the temperature or species, $3A$ typically being within 1% of 1.32 when calculated for Lennard-Jones 6–12 potentials appropriate to real systems.

Equation (61) was also obtained by Chapman and Cowling (Ref. 3, p. 243ff) as a result of approximating the Chapman–Enskog result in an ad hoc way so as to obtain an expression of the Sutherland form. It arises here from our having limited the correlations to be species-additive, as displayed in Eq. (54). If longer chains of collisions were considered in detail, each chain of more than one collision would have additive contributions from each possible sequence of species in the chain. The more complicated result of the Chapman–Enskog theory implicitly describes this greater diversity of collisional events.

The most revealing comparison of Sutherland and Chapman–Enskog expressions for mixture viscosities is based on a nonlinear least squares fit of theory to experiment with values of the collision integrals themselves as the fitting parameters. When this is done for Ar–He mixtures,⁽²⁴⁾ it is found that the Chapman–Enskog expression can be fitted to the data to within experimental accuracy of 0.1%,⁽²⁵⁾ but that the Sutherland fit is less successful, deviating from the data as much as 0.5%.

The time-correlation function expression for the thermal conductivity of a monatomic fluid is⁽⁸⁾

$$\kappa = \frac{2}{3} \frac{k^2 T}{(m_v m_\mu)^{1/2}} \int_0^\infty dt \sum_v \sum_i \sum_\mu \sum_j \left(\mathcal{E}_{vi}^2 - \frac{5}{2} \right) \mathcal{E}_{vi}(0) \cdot \left(\mathcal{E}_{\mu j}^2 - \frac{5}{2} \right) \mathcal{E}_{\mu j}^{(t)} \quad (62)$$

This equation may be written in the form of Eqs. (8) and (9) for

$$A_{vi} = B_{vi} = m_v^{-1/2} \left(\mathcal{E}_{vi}^2 - \frac{5}{2} \right) \mathcal{E}_{vi} \quad (63)$$

and

$$C = \frac{3}{2} k^2 T \quad (64)$$

For these variables Ψ_{v0} is evaluated to give

$$\Psi_{v0} = (15/4) N_v / m_v \quad (65)$$

and the coefficient Ψ_{v1} is given in terms of tabulated bracket integrals of the Sonine polynomial expression (Ref. 3, p. 127)

$$S_{5/2}^{(1)}(\mathcal{E}^2) \mathcal{E} = \left(\frac{5}{2} - \mathcal{E}^2 \right) \mathcal{E} \quad (66)$$

We may use Chapman and Cowling's equation (9.6, 8) to evaluate the bracket integral in Eq. (28), and combine this result with Eqs. (64) and (65) in Eq. (22) to obtain the kinetic contribution to the thermal conductivity. For a single-component system, with the specific heat denoted by \bar{c}_v ,

$$\bar{c}_v = \frac{3}{2} k / m_v \quad (67)$$

We may rearrange the result to

$$\kappa^{(1)} = \frac{25}{16} \frac{\bar{c}_v k T}{G \Omega^{(2)}(2)} \quad (68)$$

In the limit of low densities, this is identical with Chapman and Cowling's equation (9.7, 3), and for hard spheres, it corresponds to the kinetic contribution to the thermal conductivity calculated from the Enskog equation.⁽²²⁾

In the case of a multicomponent system, the procedure leading to the expression for the thermal conductivity corresponds closely to that applied to the calculation of the viscosity, though with somewhat more algebra. If we define the quantity $B_{v\mu}$ by

$$\begin{aligned} B_{v\mu} = & \frac{16}{15} \frac{1}{k^2 T} \frac{m_v^{3/2}}{m_\mu^{1/2}} \frac{1}{(m_v + m_\mu)^3} \{ (6m_v^2 - 11m_v^{3/2}m_\mu^{1/2} + 5m_\mu^2) \Omega_{v\mu}^{(1)}(1) \\ & + 4m_\mu^{1/2}(m_v^{3/2} - m_\mu^{3/2})(\Omega_{v\mu}^{(1)}(2) - \frac{1}{5}\Omega_v^{(1)}(3)) \} \quad (69) \end{aligned}$$

it can be shown that the thermal conductivity is

$$\kappa^{(1)} = \sum_v \left(\frac{1}{\kappa_v^{(1)}} + \sum_{\mu \neq v} \frac{x_\mu}{x_v} G_{v\mu} B_{v\mu} \right)^{-1} \quad (70)$$

As in the case of the viscosity, this result differs in form from the results of the Chapman–Enskog solution, being of a simpler form that has in the past been inferred as an empirical correlation (Ref. 3, p. 255; Ref. 26).

7. DISCUSSION

A derivation that gives accurate expressions for transport coefficients while by-passing the mathematical complexities of solutions to the Boltzmann equation should be of considerable pedagogical value, and it is satisfying that many of the physically appealing arguments of mean-free-path theory are explicitly incorporated in the treatment. In most cases the first Chapman–Enskog approximations have been recovered. Additionally, a prescription is obtained for generating higher approximations by including the effects of longer chains of uncorrelated collisions. This hierarchy of approximations reflects an increasingly accurate description of the randomization of molecular velocities, which is necessitated by the fact that averages over one collision do not lead to complete randomization, so that longer collision chains are required before correlation with the initial velocity is completely lost. The effects of cyclic collision chains are neglected in this picture; much effort has been and is being expended in calculating such correlations in more exact work.⁽¹⁾

Our method does lead to results for the multicomponent viscosity and thermal conductivity that differ from the lowest order Chapman–Enskog solutions to the Boltzmann equation. Relations such as those obtained here for these properties were originally obtained from mean-free-path-type arguments in which transfers of momentum and energy were additively affected by collisions of a molecule with others of each species in the system.⁽²⁷⁾ In view of the similarity of the physical pictures, it is not surprising that the present approach yields results of a similar form; however, we are able to express mixture properties in terms of collision integrals (rather than the experimental viscosities and thermal conductivities of the pure components), and we do give a prescription for extending and (hopefully) improving these first approximations to the mixture transport coefficients.

Since the use of mean-free-path ideas has successfully been used in this paper to evaluate time-correlation function expressions for the transport coefficients of simple dilute gases, it is possible that this approach may prove useful for studying systems for which solutions of the kinetic equations (or perhaps even the equations themselves) are uncertain. These cases include

systems with internal degrees of freedom and gases in the regime where gas-wall collisions become important. Work is currently under way on these problems.

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