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General Calculation of the Collision Integral for the Linearized Boltzmann Transport Equation

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We develop and describe a general method for evaluating collision integrals in the linearized Boltzmann transport equation which eliminates the necessity to repeat similar integration steps for each force law. Integrations not dependent on scattering cross-section variables have been carried out once and for all. The two mathematical innovations which facilitate these general integrations are (i) the development of an expansion of the Burnett function $X_{NML}(\mathbf{x} + \mathbf{y})$ into products of Burnett functions of argument $\mathbf{x}$ with other functions; and (ii) the use of representations of the full rotation group to transform from space-fixed axes to axes aligned with the relative velocity vector of colliding atoms. The relations so derived allow rapid evaluation of the collision integral from a knowledge of the scattering cross section.

KEY WORDS: Boltzmann transport equation; collision integral; Burnett function.

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1. INTRODUCTION

The solution of the Boltzmann transport equation to obtain transport coefficients is normally carried out by linearization and evaluation of the so-called collision integrals.[1] Traditionally the collision integrals are performed for each proposed interparticle force law. The development of a general method which eliminates the necessity to repeat similar integration steps for each force law would seem desirable.

In this paper the integrations which do not depend on scattering cross-section variables, namely the relative speed of colliding atoms and the angle through which the relative velocity vector is rotated, are carried out once and for all. The two mathematical innovations which facilitate these general integrations are (i) the development of an expansion of the Burnett function $X_{NLM}(\mathbf{x} + \mathbf{y})$ into products of Burnett functions of argument $\mathbf{x}$ with other functions; and (ii) the use of properties of the full rotation group to transform from space-fixed axes to axes aligned with the relative velocity vector of colliding atoms. The relations so derived allow rapid evaluation of the collision integral from a knowledge of the scattering cross section. Recently[2] collision integrals have been presented in terms of summations of powers of cosines. A more convenient form in terms of orthogonal polynomials is now given.

In Section 2 the problem is defined employing terms common to previous papers. Certain mathematical preliminaries relating to properties of Burnett functions are derived in Section 3. The general expression for collision integral matrix elements for a gas mixture is deduced in Section 4 and in Section 5 the pure gas result together with the hard sphere interaction example are given.

2. THE MATRIX ELEMENTS OF THE LINEARIZED COLLISION OPERATOR

The kinetic theory of an ideal monatomic gas mixture is described by the one-particle distribution functions $f_i(\mathbf{r}, \mathbf{v}_i, t)$, where $f_i(\mathbf{r}, \mathbf{v}_i, t)\, d\mathbf{r}\, d\mathbf{v}_i$ is the number of atoms of kind i with position coordinates in the range $d\mathbf{r}$ about $\mathbf{r}$ and velocity coordinates in the range $d\mathbf{v}_i$ about $\mathbf{v}_i$ at time t.

The Boltzmann equation for the time evolution of $f_i(\mathbf{r}, \mathbf{v}_i, t)$ in the absence of external forces is

$$\begin{aligned}[(\partial/\partial t) + \mathbf{v}_i\cdot(\partial/\partial\mathbf{r})]f_i(\mathbf{r}, \mathbf{v}_i, t) &= \sum_j \int d^3\mathbf{v}_j \int d^2\Omega'\, u\sigma(u, \alpha)[f_i(\mathbf{r}, \mathbf{v}_i', t)f_j(\mathbf{r}, \mathbf{v}_j', t) \\ &\quad - f_i(\mathbf{r}, \mathbf{v}_i, t)f_j(\mathbf{r}, \mathbf{v}_j, t)] \qquad (1)\end{aligned}$$

The right-hand side is the collision term and includes contributions from the collision of an atom of kind i with its own kind as well as with all others; it specifically excludes inelastic collisions or collisions involving chemical reactions. Before collision the relative velocity of the ith to the jth atom is given by

$$\mathbf{u} = \mathbf{v}_i - \mathbf{v}_j$$

and has magnitude u. Since the consequence of the elastic collision is the production of i and j atoms with velocities $\mathbf{v}_i'$ and $\mathbf{v}_j'$, respectively, conservation of momentum and energy ensures that u is also the magnitude of the relative velocity after collision. (Primes are used here and in that which follows to denote quantities appropriate to the atoms after collision.) The collision cross section $\sigma(u, \alpha)$ depends on the relative speed u of the atoms and the angle α through which the relative velocity is rotated into the element of solid angle $d^2\Omega' = \sin\alpha \, d\alpha \, d\phi$. Here ϕ is the azimuth angle of the relative velocity after collision $\mathbf{u}'$ with respect to a set of axes with z direction aligned with the direction of the vector $\mathbf{u}$. It follows that the total cross section is given by

$$\sigma_{\text{tot}}(u) = \int d^2\Omega' \, \sigma(u, \alpha)$$

It is convenient to define the collision operator

$$J_{ij}(f, g) = \pi^{3/2}(\mu_{ij}/kT)^{1/2}(n_i n_j)^{-1} \int d^3\mathbf{v}_j \int d^2\Omega' \times u\sigma(u, \alpha)[f_i(\mathbf{r}, \mathbf{v}_i', t)g_j(\mathbf{r}, \mathbf{v}_j', t) - f_i(\mathbf{r}, \mathbf{v}_i, t)g_j(\mathbf{r}, \mathbf{v}_j, t)] \tag{2}$$

where the reduced mass μ_{ij} is defined by

$$\mu_{ij} = m_i m_j/(m_i + m_j)$$

In these expressions m_i (m_j) is the mass and n_i (n_j) is the equilibrium number density in position space of atoms of the ith (jth) kind. The Boltzmann equation (1) can then be written as

$$[(\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r})]f_i(\mathbf{r}, \mathbf{v}_i, t) = \sum_j \pi^{-3/2}(kT/\mu_{ij})^{1/2} n_i n_j J_{ij}(f, f) \tag{3}$$

The equilibrium distribution function is given by

$$f_{0i}(\mathbf{r}, \mathbf{v}_i, t) = n_i(m_i/2\pi kT)^{3/2} \exp(-m_i v_i^2/2kT) = f_{0i}(\mathbf{v}_i) \tag{4}$$

say, where k is Boltzmann's constant and T is the absolute temperature. It follows that

$$n_i^{-1} \int d^3\mathbf{v}_i f_{0i}(\mathbf{v}_i) = 1 \tag{5}$$

The equilibrium distribution function (4) renders each side of the Boltzmann equation (3) zero.

A small-amplitude disturbance from equilibrium can be represented by the distribution function

$$f_i(\mathbf{r}, \mathbf{v}_i, t) = f_{0i}(\mathbf{v}_i)[1 + h_i(\mathbf{r}, \mathbf{v}_i, t)] \tag{6}$$

Substitution of this expression in (3) yields

$$\begin{aligned} f_{0i}(\mathbf{v}_i)[(\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r})]h_i(\mathbf{r}, \mathbf{v}_i, t) \\ = \sum_j \pi^{-3/2}(kT/\mu_{ij})^{1/2} n_i n_j [J_{ij}(f_0, f_0) + J_{ij}(f_0, f_0 h) \\ + J_{ij}(f_0 h, f_0) + J_{ij}(f_0 h, f_0 h)] \end{aligned} \tag{7}$$

Using the definitions of $f_{0i}(\mathbf{r}, \mathbf{v}_i, t)$ [Eq. (4)] and the collision operator (2), it is a consequence of energy conservation that

$$J_{ij}(f_0, f_0) = 0$$

The term $J_{ij}(f_0 h, f_0 h)$ has an integrand quadratic in the small disturbance factor $h(\mathbf{r}, \mathbf{v}, t)$ and is therefore neglected in the linear approximation. The linearized Boltzmann equation is then

$$\begin{aligned} f_{0i}(\mathbf{v}_i)[(\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r})]h_i(\mathbf{r}, \mathbf{v}_i, t) \\ = \sum_j \pi^{-3/2}(kT/\mu_{ij})^{1/2} n_i n_j [J_{ij}(f_0, f_0 h) + J_{ij}(f_0 h, f_0)] \end{aligned} \tag{8}$$

The solution of this equation by the Chapman–Enskog method[1] involves expansion of the functions $h_i(\mathbf{r}, \mathbf{v}_i, t)$ in terms of the normalized Burnett functions $X_{NLM}(\boldsymbol{\xi}_i)$,[3] viz.

$$h_i(\mathbf{r}, \boldsymbol{\xi}_i, t) = \sum_{NLM} \alpha^i_{NLM}(\mathbf{r}, t) X_{NLM}(\boldsymbol{\xi}_i) \tag{9}$$

where

$$X_{NLM}(\boldsymbol{\xi}_i) = [2N!/(N + L + \tfrac{1}{2})!]^{1/2} \xi_i^L L_N^{L+1/2}(\xi_i^2) Y_{LM}(\hat{\xi}_i) \tag{10}$$

In these equations the dimensionless velocity $\boldsymbol{\xi}_i$ is defined by

$$\boldsymbol{\xi}_i = (m_i/2kT)^{1/2} \mathbf{v}_i \tag{11}$$

which magnitude ξ_i, $Y_{LM}(\hat{\xi}_i)$ is the spherical harmonic, where $\hat{\xi}_i$ denotes the spherical coordinate angles which the vector $\boldsymbol{\xi}_i$ makes with fixed axes; and $L_N^{L+1/2}(\xi_i^2)$ is the associated Laguerre polynomial defined by

$$L_n^{\alpha}(x) = \sum_{m=0}^{n} \frac{(-1)^m (n + \alpha)!}{m!\,(m + \alpha)!\,(n - m)!} x^m \tag{12}$$

Making the substitution (9) for $h_i(r, \xi_i, t)$ in (8) then yields

$$\sum_{N'L'M'} f_{0i}(\mathbf{v}_i)X_{N'L'M'}(\boldsymbol{\xi}_i)[(\partial/\partial t) + \mathbf{v}_i \cdot (\partial/\partial \mathbf{r})]\alpha^i_{N'L'M'}(\mathbf{r}, t)$$
$$= \sum_j \pi^{-3/2}(kT/\mu_{ij})^{1/2} n_i n_j \sum_{N'L'M'} [\alpha^j_{N'L'M'} J_{ij}(f_0, f_0 X_{N'L'M'})$$
$$+ \alpha^i_{N'L'M'} J_{ij}(f_0 X_{N'L'M'}, f_0)] \tag{13}$$

A set of equations for the coefficients $\alpha^i_{NLM}(\mathbf{r}, t)$ can then be obtained by multiplying each side of (13) by $X^*_{NLM}(\boldsymbol{\xi}_i)$, the complex conjugate Burnett function, and integrating over all $\mathbf{v}_i$. The resulting equation can be written in terms of dimensionless velocities $\boldsymbol{\xi}_i$ and dimensionless relative velocities $\boldsymbol{\gamma}$, where

$$\boldsymbol{\gamma} = (\mu_{ij}/2kT)^{1/2}(\mathbf{v}_i - \mathbf{v}_j) \tag{14}$$

of magnitude γ:

$$\sum_{N'L'M'} \int d^3\xi_i \exp(-\xi_i^2) X^*_{NLM}(\boldsymbol{\xi}_i) X_{N'L'M'}(\boldsymbol{\xi}_i)$$
$$\times [(\partial/\partial t) + (2kT/m)^{1/2} \boldsymbol{\xi}_i \cdot \nabla]\alpha^i_{N'L'M'}(\mathbf{r}, t)$$
$$= \sum_j (kT/\mu_{ij})^{1/2} n_j \sum_{N'L'M'} [\alpha^j_{N'L'M'}(\mathbf{r}, t)\langle iNLM|C_1|jN'L'M'\rangle$$
$$+ \alpha^i_{N'L'M'}(\mathbf{r}, t)\langle iNLM|C_2|iN'L'M'\rangle] \tag{15}$$

In this equation the matrix elements of the linearized collision operators are defined as

$$\langle iNLM|C_1|jN'L'M'\rangle$$
$$= \int d^3\mathbf{v}_i X^*_{NLM}(\boldsymbol{\xi}_i) J_{ij}(f_0, f_0 X_{N'L'M'})$$
$$= \sqrt{2}\pi^{-3/2} \int d^3\xi_i \int d^3\xi_j \int d^2\Omega' \gamma\sigma(\gamma, \alpha)$$
$$\times \exp(-\xi_i^2 - \xi_j^2) X^*_{NLM}(\boldsymbol{\xi}_i)[X_{N'L'M'}(\boldsymbol{\xi}_j') - X_{N'L'M'}(\boldsymbol{\xi}_j)] \tag{16}$$

and

$$\langle iNLM|C_2|iN'L'M'\rangle$$
$$= \int d^3\mathbf{v}_i X^*_{NLM}(\boldsymbol{\xi}_i) J_{ij}(f_0 X_{N'L'M'}, f_0)$$
$$= \sqrt{2}\pi^{-3/2} \int d^3\xi_i \int d^3\xi_j \int d^2\Omega' \gamma\sigma(\gamma, \alpha) \exp(-\xi_i^2 - \xi_j^2) X^*_{NLM}(\boldsymbol{\xi}_i)$$
$$\times [X_{N'L'M'}(\boldsymbol{\xi}_i') - X_{N'L'M'}(\boldsymbol{\xi}_i)] \tag{17}$$

where use has been made of the energy conservation property for elastic collisions

$$\xi_i^2 + \xi_j^2 = \xi_i'^2 + \xi_j'^2 \tag{18}$$

It is apparent that (16) and (17) are both eightfold integrals: three components of $\boldsymbol{\xi}_i$, three components of $\boldsymbol{\xi}_j$, and two angles in the integration over Ω'. The dynamics of the collision enters only via the cross section $\sigma(\gamma, \alpha)$, which is a function of two variables. It should therefore be possible to perform six of the eight integrations once and for all, explicitly, without reference to the functional form of the cross section $\sigma(\gamma, \alpha)$. The remaining two integrations over γ and α are the only ones which, in principle, require knowledge of the dynamics, rather than merely the kinematics, of the collision.

The aim of this paper is to carry out this program in detail and the resulting expressions (70) and (74) involve only two-fold integrals $I_{\lambda s}$ defined by (71). The coefficients of the $I_{\lambda s}$ are reduced explicitly to known quantities such as the Clebsch-Gordan coefficients.

3. MATHEMATICAL PRELIMINARIES

The reduction of the matrix elements (16) and (17) to a form involving twofold integration requires development of special identities involving Burnett functions. These will be derived in this section. However, it is first necessary to reduce the number of vector variables appearing in the matrix element integrals from three, namely $\boldsymbol{\xi}_i$, $\boldsymbol{\xi}_j$, and $\boldsymbol{\gamma}$, to two which are independent. It will then be clear which are the required Burnett function properties.

3.1. Velocity Coordinate Transformation

In the form given by (16) and (17) the matrix elements depend on $\boldsymbol{\xi}_i$ and $\boldsymbol{\xi}_j$ explicitly through $\boldsymbol{\gamma}$, which is a linear combination of them. Introduction of another variable vector, the dimensionless center of mass velocity $\boldsymbol{\chi}$, where

$$\boldsymbol{\chi} = [2kT(m_i + m_j)]^{-1/2}(m_i\mathbf{v}_i + m_j\mathbf{v}_j) \tag{19}$$

allows the matrix elements to be rewritten in terms of $\boldsymbol{\chi}$ and $\boldsymbol{\gamma}$ only. From (11), (14), and (19) it follows that

$$\boldsymbol{\xi}_i = m_{ij}^{1/2}\boldsymbol{\chi} + m_{ji}^{1/2}\boldsymbol{\gamma} \tag{20}$$

and

$$\boldsymbol{\xi}_j = m_{ji}^{1/2}\boldsymbol{\chi} - m_{ij}^{1/2}\boldsymbol{\gamma} \tag{21}$$

where

$$m_{ij} = m_i/(m_i + m_j) \tag{22}$$

$$\xi_i^2 + \xi_j^2 = \gamma^2 + \chi^2 \tag{23}$$

$$d^3\boldsymbol{\xi}_i\, d^3\boldsymbol{\xi}_j = d^3\boldsymbol{\gamma}\, d^3\boldsymbol{\chi} \tag{24}$$

$$\boldsymbol{\chi} = \boldsymbol{\chi}' \qquad \text{(conservation of momentum)} \tag{25}$$

$$\gamma = \gamma' \qquad \text{(conservation of energy)} \tag{26}$$

The matrix elements are then

$$\begin{aligned}\langle iNLM|C_1|jN'L'M'\rangle &= \sqrt{2}\pi^{-3/2}\int d^3\boldsymbol{\gamma}\int d^3\boldsymbol{\chi}\int d^2\Omega'\,\gamma\sigma(\gamma,\alpha)\exp(-\gamma^2-\chi^2)\\ &\times X^*_{NLM}(m_{ij}^{1/2}\boldsymbol{\chi}+m_{ji}^{1/2}\boldsymbol{\gamma})[X_{N'L'M'}(m_{ji}^{1/2}\boldsymbol{\chi}-m_{ij}^{1/2}\boldsymbol{\gamma}')\\ &- X_{N'L'M'}(m_{ji}^{1/2}\boldsymbol{\chi}-m_{ij}^{1/2}\boldsymbol{\gamma})]\end{aligned} \tag{27}$$

and

$$\begin{aligned}\langle iNLM|C_2|iN'L'M'\rangle &= \sqrt{2}\pi^{-3/2}\int d^3\boldsymbol{\gamma}\int d^3\boldsymbol{\chi}\int d^2\Omega'\,\gamma\sigma(\gamma,\alpha)\exp(-\gamma^2-\chi^2)\\ &\times X^*_{NLM}(m_{ij}^{1/2}\boldsymbol{\chi}+m_{ji}^{1/2}\boldsymbol{\gamma})[X_{N'L'M'}(m_{ij}^{1/2}\boldsymbol{\chi}+m_{ji}^{1/2}\boldsymbol{\gamma}')\\ &- X_{N'L'M'}(m_{ij}^{1/2}\boldsymbol{\chi}+m_{ji}^{1/2}\boldsymbol{\gamma})]\end{aligned} \tag{28}$$

The fundamental property of Burnett functions which enables the center-of-mass integration to be evaluated in these expressions is the orthogonality condition (all identities assumed in this section are given in Ref. 4),

$$\int d^3\mathbf{x}\,\exp(-x^2)X^*_{nlm}(\mathbf{x})X_{n'l'm'}(\mathbf{x}) = \delta_{nn'}\,\delta_{ll'}\,\delta_{mm'} \tag{29}$$

This identity has immediate application in evaluating the first term on the left-hand side of (15). However, for (27) and (28) only after expanding a Burnett function of the form $X_{NLM}(\mathbf{x}+\mathbf{y})$ does one obtain the corresponding matrix element integral

$$A(a, nlm; b, n'l'm') = \int d^3\mathbf{x}\,\exp(-x^2)X^*_{nlm}(a\mathbf{x})X_{n'l'm'}(b\mathbf{x}) \tag{30}$$

Such an integral is then immediately evaluated with the help of (29) and an expansion for $X_{nlm}(a\mathbf{x})$ in terms of Burnett functions with argument $\mathbf{x}$.

The key to this development lies in the establishment, in the next subsection, of a generating function for Burnett functions from which an expression for $X_{NLM}(\mathbf{x}+\mathbf{y})$ is deduced in Section 3.3. In Section 3.4, $X_{nlm}(a\mathbf{x})$ is expanded, allowing the evaluation in Section 3.5 of $A(a, nlm; b, n'l'm')$.

3.2. A Generating Function for Burnett Functions

The generating function is deduced from the following identities[4]:

$$\exp(i\mathbf{k}\cdot\mathbf{s}) = \sum_{l=0}^{\infty} i^l[4\pi(2l+1)]^{1/2}(\pi/2ks)^{1/2}J_{l+1/2}(ks)\,Y_{l0}(\theta) \tag{31}$$

where $\cos\theta = \mathbf{k}\cdot\mathbf{s}/ks$;

$$Y_{l0}(\theta) = [4\pi/(2l+1)]^{1/2}\sum_{m=-l}^{l} Y^*_{lm}(\hat{k})\,Y_{lm}(\hat{s}) \tag{32}$$

and

$$\frac{\exp(z)J_\alpha[2(tz)^{1/2}]}{(tz)^{\alpha/2}} = \sum_{n=0}^{\infty}\frac{L_n{}^\alpha(t)z^n}{(n+\alpha)!} \tag{33}$$

The definition of $J_\nu(x)$ is

$$J_\nu(x) = (x/2)^\nu\sum_{j=0}^{\infty}[(-1)^j/j!\,(j+\nu)!](x/2)^{2j} \tag{34}$$

Setting $\alpha = l + \frac{1}{2}$, $\sqrt{z} = k/2$, and $\sqrt{t} = s$ in (33), then substituting (33) and (32) into (31) yields

$$\exp(i\mathbf{k}\cdot\mathbf{s} + \tfrac{1}{4}k^2) = 2\pi^{3/2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{n=0}^{\infty}\frac{i^l(k/2)^{2n+l}s^l}{(n+l+\frac{1}{2})!}L_n^{l+1/2}(s^2)\,Y^*_{lm}(\hat{k})\,Y_{lm}(\hat{s}) \tag{35}$$

Making the substitution

$$k = -2ix$$

in (35) and then interchanging $\mathbf{x}$ and $\mathbf{s}$ leads to

$$\exp(2\mathbf{x}\cdot\mathbf{s} - s^2) = (2\pi^3)^{1/2}\sum_{l=0}^{\infty}\sum_{m=-l}^{l}\sum_{n=0}^{\infty}(-1)^n\frac{X_{nlm}(\mathbf{x})}{[n!\,(n+l+\frac{1}{2})!]^{1/2}}s^{2n+l}\,Y^*_{lm}(\hat{s}) \tag{36}$$

where the Burnett function definition (10) has been incorporated.

Equation (36) shows that $\exp(2\mathbf{x}\cdot\mathbf{s} - s^2)$ is a generating function for the Burnett functions $X_{nlm}(\mathbf{x})$: The Burnett functions appear as coefficients in an expansion of the exponential as a triple power series in the components of the vector $\mathbf{s}$, i.e., as a series with terms like $(s_1)^{V_1}(s_2)^{V_2}(s_3)^{V_3}$, where the terms of same degree, $V_1 + V_2 + V_3 = 2n + l$, have been arranged together into solid harmonics.

3.3. An Expansion of $X_{NLM}(x + y)$

The existence of the generating function (36) indicates that this expansion can be effected with the help of the identity

$$\exp[2(\mathbf{x}+\mathbf{y})\cdot\mathbf{s} - s^2] = \exp(2\mathbf{y}\cdot\mathbf{s})\exp(2\mathbf{x}\cdot\mathbf{s} - s^2) \tag{37}$$

An expansion for $\exp(2\mathbf{y}\cdot\mathbf{s})$ follows from setting $ik = 2y$ in (31), and substituting (32) and (34) into (31):

$$\exp(2\mathbf{y}\cdot\mathbf{s}) = 2\pi^{3/2} \sum_{\lambda=0}^{\infty} \sum_{\nu=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \frac{(ys)^{2\nu+\lambda}}{\nu!\,(\nu+\lambda+\frac{1}{2})!} Y_{\lambda\mu}^{*}(\hat{s}) Y_{\lambda\mu}(\hat{y}) \tag{38}$$

It is now possible to compare left and right sides of (37) making the substitutions (36) and (38). The order of summations in these two expressions can be changed: This is a direct consequence of the absolute and uniform convergence of identities (33), (34), and (36). Thus, both left and right sides of (37) can be expressed as series in terms of $s^{2N+L} Y_{LM}^{*}(\hat{s})$, the coefficients of which can be compared. This leads immediately to an expression for $X_{NLM}(\mathbf{x} + \mathbf{y})$ in terms of $X_{nlm}(\mathbf{x})$, as will now be shown.

The product of (36) and (38) is simplified with the help of the relation[5]

$$Y_{lm}^{*}(\hat{s}) Y_{\lambda\mu}^{*}(\hat{s}) = \sum_{L,M} \left[\frac{(2l+1)(2\lambda+1)}{4\pi(2L+1)}\right]^{1/2} (l\lambda 00|l\lambda L0)(l\lambda m\mu|l\lambda LM) Y_{LM}^{*}(\hat{s}) \tag{39}$$

where the allowed values of L are those satisfying

$$\begin{aligned} |\lambda - L| &\leqslant l \leqslant \lambda + L \\ |l - L| &\leqslant \lambda \leqslant l + L \\ |l - \lambda| &\leqslant L \leqslant l + \lambda \end{aligned} \tag{40}$$

the allowed values of M are given by

$$M = m + \mu \tag{41}$$

and $(l\lambda m\mu|l\lambda LM)$ is the Clebsch–Gordan coefficient,[6] sometimes written as $S_{Lm\mu}^{(l\lambda)}$.[5] Combining (36), (38), and (39) then leads to

$$\begin{aligned} &\exp(2\mathbf{s}\cdot\mathbf{y}) \exp(2\mathbf{x}\cdot\mathbf{s} - s^2) \\ &= \pi(2\pi^3)^{1/2} \sum_{\lambda\nu\mu} \sum_{lmn} \sum_{LM} (-1)^n \frac{y^{(2\nu+\lambda)}}{\nu!\,(\nu+\lambda+\frac{1}{2})!} \frac{X_{nlm}(\mathbf{x})}{[n!\,(n+l+\frac{1}{2})!]^{1/2}} \\ &\quad \times (l\lambda 00|l\lambda L0)(l\lambda m\mu|l\lambda LM) Y_{\lambda\mu}(\hat{y}) s^{(2n+l+2\nu+\lambda)} Y_{LM}^{*}(\hat{s}) \end{aligned} \tag{42}$$

subject to the above constraints on L and M values.

From (36) it follows that

$$\begin{aligned} &\exp[2(\mathbf{x}+\mathbf{y})\cdot\mathbf{s} - s^2] \\ &= (2\pi^3)^{1/2} \sum_{LMN} (-1)^N \frac{X_{NLM}(\mathbf{x}+\mathbf{y})}{[N!\,(N+L+\frac{1}{2})!]^{1/2}} s^{2N+L} Y_{LM}^{*}(\hat{s}) \end{aligned} \tag{43}$$

Equating coefficients of $s^{2N+L} Y_{LM}^{*}(s)$ in expressions (42) and (43) yields finally

$$\begin{aligned} X_{NLM}(\mathbf{x}+\mathbf{y}) = \sum_{lmn} \sum_{\lambda\nu\mu} &\frac{\langle \nu\lambda n l \| D \| NL \rangle}{[n!\,(n+l+\frac{1}{2})!]^{1/2}} \\ &\times (l\lambda m\mu|l\lambda LM) y^{(2\nu+\lambda)} Y_{\lambda\mu}(\hat{y}) X_{nlm}(\mathbf{x}) \end{aligned} \tag{44}$$

where

$$\langle \nu\lambda nl \| D \| NL \rangle = (-1)^{N+n}\pi\left[\frac{(2l+1)(2\lambda+1)}{2L+1}\right]^{1/2}\frac{[N!\,(N+L+\frac{1}{2})!]^{1/2}}{\nu!\,(\nu+\lambda+\frac{1}{2})!}(l\lambda 00|l\lambda L0) \quad (45)$$

and where L, M and N values are subject to the constraints (40), (41), and

$$2(n+\nu)+l+\lambda = 2N+L \quad (46)$$

3.4. An Expansion of $X_{nlm}(ax)$

From the definition (10) it follows that

$$X_{nlm}(a\mathbf{x}) = \left[\frac{2n!}{(n+l+\frac{1}{2})!}\right]^{1/2}(ax)^l L_n^{l+1/2}(a^2x^2)\,Y_{lm}(\theta,\phi) \quad (47)$$

An identity exists[4] for simplifying the argument of the associated Laguerre polynomial, viz.

$$L_n^{\alpha}(\lambda x^2) = \sum_{k=0}^{n}\frac{(n+l+\frac{1}{2})!}{k!\,(n-k+l+\frac{1}{2})!}\lambda^{n-k}(1-\lambda)^k L_{n-k}^{l+\frac{1}{2}}(x^2) \quad (48)$$

Thus, with $\lambda = a^2$ and $\alpha = l + \frac{1}{2}$, (48) allows us to rewrite (47) as

$$X_{nlm}(a\mathbf{x}) = [2n!\,(n+l+\tfrac{1}{2})!]^{1/2}a^l \times \sum_{k=0}^{n}\frac{a^{2(n-k)}(1-a^2)^k}{k!\,(n-k+l+\frac{1}{2})!}x^l L_{n-k}^{l+\frac{1}{2}}(x^2)\,Y_{lm}(\theta,\phi) \quad (49)$$

Application of the Burnett function definition (10) to this equation produces the required identity

$$X_{nlm}(a\mathbf{x}) = [n!\,(n+l+\tfrac{1}{2})!]^{1/2}a^l \times \sum_{k=0}^{n}\frac{a^{2(n-k)}(1-a^2)^k}{k!\,[(n-k)!\,(n-k+l+\frac{1}{2})!]^{1/2}}X_{n-k,l,m}(\mathbf{x}) \quad (50)$$

3.5. The Evaluation of $A(a, nlm; b, n'l'm')$

The defining integral (31) for $A(a, nlm; b, n'l'm')$ can now be evaluated using (50) and the orthogonality condition (29). For a and b real the integral is then

$$A(a, nlm; b, n'l'm') = \delta_{ll'}\,\delta_{mm'}\,[n!\,n'!\,(n+l+\tfrac{1}{2})!\,(n'+l'+\tfrac{1}{2})!]^{1/2}a^l b^{l'} \times \sum_{k=0}^{n}\sum_{k'=0}^{n'}\delta_{n-k,n'-k'} \times \frac{a^{2(n-k)}(1-a^2)^k b^{2(n'-k')}(1-b^2)^{k'}}{k!\,k'!\,[(n-k)!\,(n'-k')!\,(n-k+l+\frac{1}{2})!\,(n'-k'+l'+\frac{1}{2})!]^{1/2}} \quad (51)$$

It is convenient to set

$$n - k = K = n' - k'$$

so that K can take values between zero and the minimum of n and n'. Equation (51) finally becomes

$$A(a, nlm; b, n'l'm') = \delta_{ll'}\,\delta_{mm'}[n!\,n'!\,(n + l + \tfrac{1}{2})!\,(n' + l + \tfrac{1}{2})!]^{1/2} \times (ab)^l(1 - a^2)^n(1 - b^2)^{n'} f^l_{nn'}\left(\frac{ab}{[(1 - a^2)(1 - b^2)]^{1/2}}\right) \tag{52}$$

where

$$f^l_{nn'}(u) = \sum_{K=0}^{\min(n,n')} \frac{u^{2K}}{(n - K)!\,(n' - K)!\,K!\,(K + l + \tfrac{1}{2})!} \tag{53}$$

Two special cases of this relation will be useful in the next section: The first is that for which

$$1 - a^2 = b^2 \tag{54}$$

so that (52) reduces to

$$A_1(a, nlm; b, n'l'm') = \delta_{ll'}\,\delta_{mm'}[n!\,n'!\,(n + l + \tfrac{1}{2})!\,(n' + l + \tfrac{1}{2})!]^{1/2} \times a^{2n'+l}b^{2n+l}f^l_{nn'}(1) \tag{55}$$

and the second is that for which

$$a^2 = b^2 = 1 - c^2 \tag{56}$$

so that (52) reduces to

$$A(a, nlm; a, n'l'm') = \delta_{ll'}\,\delta_{mm'}\,[n!\,n'!\,(n + l + \tfrac{1}{2})!\,(n' + l + \tfrac{1}{2})!]^{1/2} \times a^{2l}c^{2(n+n')}f^l_{nn'}\left(\frac{a^2}{1 - a^2}\right) \tag{57}$$

4. EVALUATION OF THE MATRIX ELEMENTS

The matrix elements of the linearized collision operators can now be evaluated using the results of Section 3.

4.1. $\langle iNLM|C_1|jN'L'M'\rangle$

From (27) the Burnett functions for this matrix element can be written as

$$X_{NLM}(m_{ij}^{1/2}\boldsymbol{\chi} + m_{ji}^{1/2}\boldsymbol{\gamma}) = \sum_{lmn}\sum_{\lambda\nu\mu} \frac{\langle\nu\lambda nl\|D\|NL\rangle}{[n!\,(n + l + \tfrac{1}{2})!]^{1/2}}\,(l\lambda m\mu|l\lambda LM)(m_{ji}^{1/2}\gamma)^{2\nu+\lambda} \times Y_{\lambda\mu}(\hat{\gamma})X_{nlm}(m_{ij}^{1/2}\boldsymbol{\chi}) \tag{58}$$

and

$$X_{N'L'M'}(m_{ji}^{1/2}\boldsymbol{\chi} - m_{ij}^{1/2}\boldsymbol{\gamma}')$$
$$= \sum_{l'm'n'} \sum_{\lambda'\nu'\mu'} \frac{\langle \nu'\lambda'n'l' \| D \| N'L' \rangle}{[n'!\,(n' + l' + \frac{1}{2})!]^{1/2}} (l'\lambda'm'\mu' | l'\lambda'L'M')$$
$$\times (m_{ij}^{1/2}\gamma)^{2\nu'+\lambda'} Y_{\lambda'\mu'}(-\hat{\gamma}') X_{n'l'm'}(m_{ji}^{1/2}\boldsymbol{\chi}) \tag{59}$$

The third Burnett function involved is the same as (59) but with $\boldsymbol{\gamma}$ replacing $\boldsymbol{\gamma}'$.

Inspection of (58) and (59) shows that when they are substituted in the matrix element equation (27), the $\boldsymbol{\chi}$ integral can be performed immediately. Using (55) and the fact that $m_{ij} = 1 - m_{ji}$, it is given by

$$\int d^3\boldsymbol{\chi}\, \exp(-\chi^2) X_{nlm}(m_{ij}^{1/2}\boldsymbol{\chi}) X_{n'l'm'}(m_{ji}^{1/2}\boldsymbol{\chi})$$
$$= \delta_{ll'}\, \delta_{mm'}\, [n!\, n'!\, (n + l + \tfrac{1}{2})!\, (n' + l' + \tfrac{1}{2})!]^{1/2} m_{ij}^{n'+l/2} m_{ji}^{n+l/2} f_{nn'}^{l}(1) \tag{60}$$

Thus (27) becomes

$$\langle iNLM | C_1 | jN'L'M' \rangle$$
$$= \sqrt{2}\pi^{-3/2} \sum_{lmn} \sum_{\lambda\nu\mu} \sum_{l'm'n'} \sum_{\lambda'\nu'\mu'} \delta_{ll'}\, \delta_{mm'}\, \langle \nu\lambda nl \| D \| NL \rangle$$
$$\times \langle \nu'\lambda'n'l' \| D \| N'L' \rangle (l\lambda m\mu | l\lambda LM)(l'\lambda'm'\mu' | l'\lambda'L'M')$$
$$\times m_{ij}^{\nu'+n'+(\lambda 1/2)+(l/2)} m_{ji}^{\nu+n+(\lambda/2)+(l/2)} f_{nn'}^{l}(1) \int d^3\boldsymbol{\gamma} \int d^2\Omega'\, \sigma(\gamma, \alpha)$$
$$\times \exp(-\gamma^2) \gamma^{[2(\nu+\nu')+\lambda+\lambda'+1]} Y_{\lambda\mu}^{*}(\hat{\gamma})$$
$$\times [(-1)^{\lambda'} Y_{\lambda'\mu'}(\hat{\gamma}') - (-1)^{\lambda} Y_{\lambda\mu}(\hat{\gamma})] \tag{61}$$

where the spherical harmonic property $Y_{\lambda'\mu'}(-\hat{\gamma}') = (-1)^{\lambda'} Y_{\lambda'\mu'}(\hat{\gamma}')$ has been used.

The remaining integrals are evaluated most simply by transforming all quantities from a coordinate system defined relative to the space-fixed z axis to one defined relative to the initial relative velocity or $\hat{\gamma}$ direction. The element of solid angle $d\Omega' = \sin\alpha\, d\alpha\, d\phi$ is already so defined: The angles (α, ϕ) denote the direction of $\boldsymbol{\gamma}'$ in this system.

Under such a transformation $Y_{\lambda'\mu'}(\hat{\gamma}')$ can be expanded as[5]

$$Y_{\lambda'\mu'}(\hat{\gamma}') = \sum_{\mu''} D_{\mu''\mu'}^{\lambda'}(R)\, Y_{\lambda'\mu''}(\alpha, \phi) \tag{62}$$

where $D_{\mu''\mu'}^{\lambda}(R)$ is the $\mu''\mu'$ matrix element of the irreducible representation $D^{\lambda'}(R)$ of the rotation group for the rotation R that sends the direction $\hat{\gamma}$ into the space-fixed z axis. It follows that

$$D_{0\mu'}^{\lambda'}(R) = \left(\frac{4\pi}{2\lambda' + 1}\right)^{1/2} Y_{\lambda'\mu'}(\hat{\gamma}) \tag{63}$$

In the new coordinate system, the ϕ integration of (61) then only involves

$$\int d\phi \; Y_{\lambda'\mu''}(\alpha, \phi) = 2\pi \, \delta_{\mu''0} \; Y_{\lambda'0}(\alpha, 0) \tag{64}$$

so that by (62)–(64)

$$\int d\phi \; Y_{\lambda'\mu''}(\hat{\gamma}') = 2\pi P_\lambda(\cos\alpha) \, Y_{\lambda'\mu'}(\hat{\gamma}) \tag{65}$$

where

$$P_\lambda(\cos\alpha) = \left(\frac{4\pi}{2\lambda + 1}\right)^{1/2} Y_{\lambda 0}(\alpha) \tag{66}$$

is the Legendre polynomial in $\cos \alpha$.

Incorporating (65) and the orthogonality property of spherical harmonics, viz.

$$\int d^2\Omega \; Y_{\lambda'\mu'}(\hat{\gamma}) \, Y_{\lambda\mu}(\hat{\gamma}) = \delta_{\mu\mu'} \, \delta_{\lambda\lambda'} \tag{67}$$

into the angle integrations of (61) yields

$$\begin{aligned} &\int d^2\Omega \int d^2\Omega' \; \sigma(\gamma, \alpha) \, Y^*_{\lambda\mu}(\hat{\gamma})[(-1)^{\lambda'} Y_{\lambda'\mu'}(\hat{\gamma}') - (-1)^\lambda Y_{\lambda\mu}(\hat{\gamma})] \\ &\qquad = -\delta_{\mu\mu'} \, \delta_{\lambda\lambda'} \, 2\pi(-1)^\lambda \int_0^\pi d\alpha \, (\sin\alpha)\sigma(\gamma, \alpha)[1 - P_\lambda(\cos\alpha)] \end{aligned} \tag{68}$$

The delta functions $\delta_{\mu\mu'}$, $\delta_{\lambda\lambda'}$, $\delta_{ll'}$, $\delta_{mm'}$ then allow use of the property of Clebsch–Gordan coefficients[6] that

$$\sum_{m,\mu} (l\lambda m\mu | l\lambda LM)(l\lambda m\mu | l\lambda L'M') = \delta_{LL'} \, \delta_{MM'} \tag{69}$$

Finally, substitution of (68) and (69) in (61) yields

$$\langle iNLM | C_1 | jN'L'M' \rangle = -\delta_{LL'} \, \delta_{MM'} \sum_\lambda \sum_s K^{NN'L}_{\lambda s} I_{\lambda s} \tag{70}$$

where $s = \nu + \nu'$,

$$I_{\lambda s} = \int_0^\infty d\gamma \int_0^\pi d\alpha \, \exp(-\gamma^2) \gamma^{[2(\lambda + s) + 3]} \sigma(\gamma, \alpha)(\sin\alpha)[1 - P_\lambda(\cos\alpha)] \tag{71}$$

$$\begin{aligned} K^{NN'L}_{\lambda s} = {} & 2\sqrt{2}\pi^{-1/2}(-1)^\lambda \sum_\nu \sum_l \sum_{nn'} \langle \nu\lambda nl \| D \| NL \rangle \langle s - \nu, \lambda n'l \| D \| N'L \rangle \\ & \times m_{ij}^{(l/2) + n' + s - \nu + (\lambda/2)} m_{ji}^{(l/2) + n + \nu + (\lambda/2)} f^l_{nn'}(1) \end{aligned} \tag{72}$$

and, as defined by (53),

$$f^l_{nn'}(1) = \sum_{K=0}^{\min(n,n')} [(n - K)! \, (n' - K)! \, K! \, (K + l + \tfrac{1}{2})!]^{-1} \tag{73}$$

4.2. $\langle iNLM|C_2|iN'L'M'\rangle$

A similar analysis to that given above leads to

$$\langle iNLM|C_2|iN'L'M'\rangle = -\delta_{LL'}\,\delta_{MM'}\sum_{\lambda}\sum_{s} H_{\lambda s}^{NN'L} I_{\lambda s} \tag{74}$$

where $I_{\lambda s}$ is as defined in (71),

$$H_{\lambda s}^{NN'L} = 2\sqrt{2}\pi^{-1/2}\sum_{\nu}\sum_{l}\sum_{nn'}\langle \nu\lambda nl\|D\|NL\rangle\langle s-\nu,\,\lambda n'l\|D\|N'L\rangle \times m_{ij}^{l} m_{ji}^{n+n'+s+\lambda} f_{nn'}^{l}(m_i/m_j) \tag{75}$$

and

$$f_{nn'}^{l}(m_i/m_j) = \sum_{K=0}^{\min(n,n')} (m_i/m_j)^{2K}[(n-K)!\,(n'-K)!\,K!\,(K+l+\tfrac{1}{2})!]^{-1} \tag{76}$$

The absence of the factor $(-1)^{\lambda}$ in (75) in contrast to (72) is important since it leads to cancellations in the collision integral for like atoms.

5. MATRIX ELEMENTS FOR THE PURE GAS: HARD SPHERES

For a pure gas, in which only one kind of collision can occur, the right-hand side of (15) reduces to

$$\sum_{N'L'M'} (2kT)^{1/2} n_i \alpha_{N'L'M'}^{i}\langle NLM|C_i|N'L'M'\rangle$$

where

$$\langle NLM|C_i|N'L'M'\rangle = \langle iNLM|C_1|jN'L'M'\rangle_{m_i=m_j} + \langle iNLM|C_2|iN'L'M'\rangle_{m_i=m_j} \tag{77}$$

Such a collision between like atoms implies

$$m_{ij} = m_{ji} = \tfrac{1}{2}$$

$f_{nn'}^{l}(m_i/m_j)$ reduces to $f_{nn'}^{l}(1)$, and (77) becomes

$$\langle NLM|C_i|N'L'M'\rangle = -\delta_{LL'}\,\delta_{MM'}\sum_{\lambda=2,4,6,\ldots}\sum_{s} G_{\lambda s}^{NN'L} I_{\lambda s} \tag{78}$$

where

$$G_{\lambda s}^{NN'L} = 2^{3}(2\pi)^{-1/2}\sum_{\nu}\sum_{l}\sum_{n,n'} 2^{-(l+n+n'+s+\lambda)}\langle \nu\lambda nl\|D\|NL\rangle \times \langle s-\nu,\,\lambda n'l\|D\|N'L\rangle f_{nn'}^{l}(1) \tag{79}$$

Finally, the constraint (46) allows one to make the substitution

$$l + n + n' + s + \lambda = N + N' + L \tag{80}$$

so that

$$G_{\lambda s}^{NN'L} = 2^{-(N+N'+L-3)}(2\pi)^{-1/2} \sum_{\nu} \sum_{l} \sum_{n,n'} \langle \nu\lambda nl \| D \| NL \rangle$$
$$\times \langle s-\nu, \lambda n'l \| D \| N'L \rangle f_{nn'}^{l}(1) \tag{81}$$

Various features of expression (78) for the matrix element are important from the viewpoint of computation:

(a) Legendre polynomials are employed rather than the usual summations of powers of cosines.
(b) The matrix element is symmetric with respect to interchange of N and N'.
(c) L and L' must be equal for a nonzero result (see also Ref. 2).
(d) M and M' must be equal for a nonzero result, in which case the matrix element is independent of M (this is a special case of the Wigner–Eckart theorem).
(e) The $\lambda = 0$ term is always zero, so the summation over λ takes the values $\lambda = 2, 4, 6, \ldots$.

Point (e) taken in conjunction with the conditions (40) and (46) implies that the five matrix elements

$$\langle 000|C_i|N'L'M'\rangle, \quad \langle 100|C_i|N'L'M'\rangle, \quad \langle 01{-}1|C_i|N'L'M'\rangle,$$
$$\langle 011|C_i|N'L'M'\rangle, \quad \text{and} \quad \langle 010|C_i|N'L'M'\rangle$$

are zero for all (N', L', M'). These matrix elements are associated with the five basic hydrodynamic modes which persist in the long-wave limit.[(2)]

Values of the coefficient $G_{\lambda s}^{NN'L}$ have been computed for the cases where each of $L, N, N' \leqslant 9$.[2]

5.1. Hard Sphere Interaction

The example of the hard sphere interaction model is particularly simple. Using the cross section

$$\sigma(\gamma, \alpha) = a^2/4$$

where a is the sphere diameter, the expression (71) for $I_{\lambda s}$ reduces to

$$I_{\lambda s} = a^2(\lambda + s + 1)!/4$$

The matrix elements (78) for the cases where each of $L, N, N' \leqslant 9$ and with $a = 1$ have been computed. These results are consistent with those of Foch and Ford,[(2)] who calculated some of the ratios of matrix elements for the cases $L \leqslant 3$ and each of $N, N' \leqslant 4$.

[2] The results of this computation are stored in the Data Bank of the American Society for Information Science (ASIS).

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