

Documentation for multicomponent solutions

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1 Introduction

The starting point for developing a kinetic model for multicomponent, high density mixtures is the same as that for the binary, single component case, with a minor modification. The Boltzmann equations for an N component mixture may be written as

$$\left[\frac{\partial}{\partial t} + \mathbf{u}_i \cdot \nabla + \left(\frac{\mathbf{F}_i}{m_i} \right) \cdot \frac{\partial}{\partial \mathbf{u}_i} \right] f_i = \sum_j J_{ij}(f_i f_j), \quad i = \{1, 2, \dots, N\} \quad (1.1)$$

where t is the time, \mathbf{u}_i is the velocity, \mathbf{F}_i is the sum of external forces, m_i is the mass and f_i is the velocity distribution function (vdf.) of species i . J_{ij} is the streaming operator which becomes

$$J_{ij}(f_i f_j) \equiv \int \int \int \chi_{ij}(\mathbf{r}, \mathbf{r} + \sigma_{ij} \hat{k}) f'_i(\mathbf{r}) f'_j(\mathbf{r} + \sigma_{ij} \hat{k}) - \chi_{ij}(\mathbf{r}, \mathbf{r} - \sigma_{ij} \hat{k}) f_i(\mathbf{r}) f_j(\mathbf{r} - \sigma_{ij} \hat{k}) b db d\epsilon d\mathbf{u}_j \quad (1.2)$$

where \hat{k} is the unit vector connecting the two particles, b is the impact parameter and ϵ is the angular coordinate in the plane of b . The prime in f'_i denotes functions of the post-collision velocities. In the same manner as for low-density mixtures, the streaming operator describes the rate of change in the vdf. of species i due to collisions with species j .

The modification when comparing to the low-density streaming operator is the introduction of the factor χ_{ij} , the pair distribution function of the particles, which modifies the probability of finding particles i and j at positions \mathbf{r}_i and \mathbf{r}_j . Furthermore, the vdf. of particle j in the integral of Equation (1.2) is evaluated at $\mathbf{r} \pm \sigma_{ij} \hat{k}$ rather than at \mathbf{r} . Here, σ_{ij} is taken to be the distance between the centre of mass of the particles "at contact". For hard spheres, this definition is unproblematic but for particles interacting with some realistic potential the definition of being "at contact" is slightly less clear. For now, σ_{ij} may be regarded as a parameter in the range of the molecular sizes, that is independent of particle velocity and position.

Following the Enskog solution method,^[1] de Haro et al. find that a first approximation to the vdf. may be written as

$$f_i^{(1)} = f_i^{(0)} [1 + \Phi_i] \quad (1.3)$$

where

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp[-\mathcal{U}_i^2] \quad (1.4)$$

is the Maxwell distribution function, with the peculiar velocity $\mathbf{U}_i \equiv \mathbf{u}_i - \mathbf{u}^m$ defined relative to the *centre of mass* velocity \mathbf{u}^m and the dimensionless peculiar velocity defined as $\mathcal{U}_i^2 \equiv \frac{m_i}{2k_B T} U_i$. n_i is used to denote the particle density of species i .

Equivalently to the low-density case, $f_i^{(0)}$ satisfies the conservation equations of mass, energy and momentum exactly. That is,

$$\begin{aligned} \int f_i^{(0)} d\mathbf{u}_i &= n_i, \quad \forall i \\ \sum_i \int f_i^{(0)} m_i \mathbf{u}_i d\mathbf{u}_i &= \rho \mathbf{u}^m \\ \sum_i \int f_i^{(0)} \frac{m_i}{2} \mathbf{U}_i^2 d\mathbf{u}_i &= \frac{3}{2} n k_B T \end{aligned} \quad (1.5)$$

where ρ denotes the mass density of the mixture. Thus, for all $r > 0$ we can require that

$$\begin{aligned} \int f_i^{(r)} d\mathbf{u}_i &= 0, \quad \forall i \\ \sum_i \int f_i^{(r)} m_i \mathbf{u}_i d\mathbf{u}_i &= 0 \\ \sum_i \int f_i^{(r)} \frac{m_i}{2} \mathbf{U}_i^2 d\mathbf{u}_i &= 0. \end{aligned} \quad (1.6)$$

The equation of conservation of momentum is obtained by multiplying Equation (1.1) by $m_i \mathbf{u}_i$. Reordering this equation and inserting for $f_i^{(0)}$, one can identify the hydrostatic pressure as

$$p = p^k + p^\phi, \quad p^k = n k_B T, \quad p^\phi = \frac{2\pi}{3} n^2 k_B T \sum_i \sum_j x_i x_j \sigma_{ij}^3 \chi_{ij} \quad (1.7)$$

where x_i denotes the mole fraction of species i .

In determining the first order approximation to the vdf. it is found that Φ_i is of the form

$$\Phi_i = -\frac{1}{n} \mathbf{\Lambda}_i \nabla \ln T - \frac{1}{n} \mathbf{B}_i : \nabla \mathbf{u}^m + \frac{1}{n} H_i \nabla \cdot \mathbf{u}^m - \frac{1}{n} \sum_j \mathbf{D}_i^{(j)} \mathbf{d}'_j \quad (1.8)$$

where \mathbf{d}'_j is defined by

$$\mathbf{d}_i = \sum_{j \neq i} \omega_j \mathbf{d}'_i - \omega_i \mathbf{d}'_j \quad (1.9)$$

with ω_i denoting the weight fraction of species i and

$$\mathbf{d}_i = -\frac{\rho_i}{\rho n k_B T} \left[\nabla p + \sum_j \rho_j \left(\frac{\mathbf{F}_i}{m_i} - \frac{\mathbf{F}_j}{m_j} \right) \right] + \sum_j x_i \left(\delta_{i,j} + \frac{4\pi}{3} n_j M_{ij} \sigma_{ij}^3 \chi_{ij} \right) \nabla \ln T + \frac{x_i}{k_B T} \nabla_T \mu_j \quad (1.10)$$

where $\delta_{i,j}$ is the Kronecker delta and $M_{ij} = \frac{m_i}{m_i + m_j}$. The final term, the gradient in chemical potential at constant temperature may be rewritten as

$$\frac{x_i}{k_B T} \nabla_T \mu_i = \frac{x_i}{k_B T} \sum_j \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T, n_{k \neq j}} \nabla n_j \quad (1.11)$$

yielding

$$\mathbf{d}_i = -\frac{\rho_i}{\rho n k_B T} \left[\nabla p + \sum_j \rho_j \left(\frac{\mathbf{F}_i}{m_i} - \frac{\mathbf{F}_j}{m_j} \right) \right] + \sum_j x_i \left(\delta_{i,j} + \frac{4\pi}{3} n_j M_{ij} \sigma_{ij}^3 \chi_{ij} \right) \nabla \ln T + \frac{1}{n} E_{ij} \nabla n_j \quad (1.12)$$

where one should recall that n_i denotes the particle *density* of component i .

The response functions $\mathbf{\Lambda}_i$, \mathbf{B}_i , H_i and $\mathbf{D}_i^{(j)}$ are related to the thermal conductivity, shear viscosity, bulk viscosity and diffusion coefficient of the mixture. In the same manner as for a dilute mixture, one may determine the transport coefficients by writing the response functions as polynomial expansions in the Sonine polynomials, and requiring that these expansions obey the constraints posed by the summational invariants.

In the following sections the resulting equations for the transport coefficients, and their relation to the fluxes will be given. In the case of diffusion, the matter of how the diffusion coefficient should be defined will be addressed.

2 Diffusion

The molar flux of species i in the centre-of-mass frame of reference is related to the vdf. as

$$\mathbf{J}_i^{(n,m)} = n_i (\bar{\mathbf{u}}_i - \mathbf{u}^m) = \int f_i \mathbf{U}_i d\mathbf{u}_i. \quad (2.1)$$

The diffusive response functions $\mathbf{D}_i^{(j)}$ are written as the Sonine polynomial expansions

$$\mathbf{D}_i^{(j)} = \frac{m_i}{2k_B T} \sum_{p=0}^{\infty} d_{i,j}^{(p)} S_{3/2}^{(p)}(\mathcal{U}^2) \quad (2.2)$$

At constant temperature, the integral of Equation (2.1) may be evaluated in terms of the $d_{i,j}^{(r)}$ expansion coefficients as

$$\mathbf{J}_i^{(n,m)} = -\frac{x_i}{2} \sum_j d_{i,j}^{(0)} \mathbf{d}_j \quad (2.3)$$

where \mathbf{d}_j may be appropriately simplified in the absence of a temperature gradient.

This section will first describe the equations that must be solved to determine the expansion coefficients of the diffusive response function, then the relationship between the diffusive fluxes and driving forces is discussed. Finally, several ways of defining the diffusion coefficient in a mixture are introduced, and explicit expressions relating the diffusion coefficients to the expansion coefficients are given.

2.1 Determining the expansion coefficients

Using the orthogonality properties of the Sonine polynomials and inserting this expansion into the constraints posed by the summational invariants, one finds that the expansion coefficients must satisfy

$$\begin{aligned} \sum_{j=1}^s \sum_{q=0}^N \Lambda_{ij}^{pq} d_{j,k}^{(q)} &= \frac{8}{25k_B} \left(\delta_{i,k} - \frac{\rho_i}{\rho} \right) \delta_{p,0}, & \begin{cases} i = \{2, 3, \dots, s\} \\ p = \{0, 1, \dots, N\} \\ k = \{1, 2, \dots, s\} \end{cases} \\ \sum_{j=1}^s \sum_{q=0}^N \Lambda_{1j}^{(pq)} d_{j,k}^{(q)} &= 0, & \begin{cases} k = \{1, 2, \dots, s\} \\ p = \{1, 2, \dots, s\} \end{cases} \\ \sum_{j=1}^s \frac{\rho_j}{\rho} d_{j,k}^{(0)} &= 0, & k = \{1, 2, \dots, s\} \end{aligned} \quad (2.4)$$

where Λ_{ij}^{pq} are given by

$$\Lambda_{ij}^{pq} = x_i x_j \chi_{ij} \left[S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2, S_{3/2}^{(p)}(\mathcal{U}_j^2) \mathcal{U}_j^2 \right]_{ij} + \delta_{i,j} x_i \sum_k x_k \chi_{ik} \left[S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2, S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2 \right]_{ik}. \quad (2.5)$$

The square bracket integrals may be written as linear combinations of the collision integrals. [2] Thompson et al. identify these integrals as

$$\begin{aligned} \left[S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2, S_{3/2}^{(p)}(\mathcal{U}_j^2) \mathcal{U}_j^2 \right]_{ij} &= 8 M_{ij}^{q+\frac{1}{2}} M_{ji}^{p+\frac{1}{2}} \sum_{\ell=1}^{\min[p,q]+1} \sum_{r=\ell}^{p+q+2-\ell} A_{pqr\ell} \Omega_{ij}^{(\ell)}(r) \\ \left[S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2, S_{3/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i^2 \right]_{ik} &= 8 \sum_{\ell=1}^{\min[p,q]+1} \sum_{r=\ell}^{p+q+2-\ell} A'_{pqr\ell} \Omega_{ik}^{(\ell)}(r). \end{aligned} \quad (2.6)$$

The set of equations (2.4) may be written as

$$\underline{D} \mathbf{d} = \boldsymbol{\delta} \quad (2.7)$$

where \underline{D} is a $(Ns^2 \times Ns^2)$ matrix consisting of the blocks

$$\underline{D} = \begin{bmatrix} \boldsymbol{\omega} \\ \underline{\Lambda}_1^{(p>0)} \\ \underline{\Lambda}_{i>1} \end{bmatrix} \quad (2.8)$$

with

$$\begin{aligned} \underline{\boldsymbol{\omega}} &= \begin{bmatrix} \boldsymbol{\omega}^{(1)} \\ \boldsymbol{\omega}^{(2)} \\ \vdots \\ \boldsymbol{\omega}^{(s)} \end{bmatrix} \\ \boldsymbol{\omega}^{(k)} &= (0 \quad \dots \quad \times Ns(k-1) \quad \dots \quad 0 \quad \omega_1 \quad \omega_2 \quad \dots \quad \omega_s \quad 0 \quad \dots \quad \times s(Ns - N(k-1) - 1) \quad \dots \quad 0) \end{aligned} \quad (2.9)$$

$$\underline{\mathbf{\Lambda}}_1^{(p>0)} = \begin{bmatrix} \mathbf{\Lambda}(1,1) \\ \mathbf{\Lambda}(1,2) \\ \vdots \\ \mathbf{\Lambda}(1,N) \\ \mathbf{\Lambda}(2,1) \\ \vdots \\ \mathbf{\Lambda}(s,N) \end{bmatrix},$$

$$\mathbf{\Lambda}(k,p) = (0 \quad \dots \quad \times Ns(k-1) \quad \dots \quad 0 \quad \Lambda_{11}^{p0} \quad \Lambda_{12}^{p0} \quad \dots \quad \Lambda_{1s}^{p0} \quad \Lambda_{11}^{p1} \quad \dots \quad \Lambda_{1s}^{pN} \quad 0 \quad \dots \quad \times Ns(s-k) \quad \dots \quad 0)$$

(2.10)

$$\underline{\mathbf{\Lambda}}_{i>1} = \begin{bmatrix} \underline{\mathbf{\Lambda}}_{k=1} & & & & \\ & \underline{\mathbf{\Lambda}}_{k=2} & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & \underline{\mathbf{\Lambda}}_{k=s} \end{bmatrix}$$

$$\underline{\mathbf{\Lambda}}_k = \begin{bmatrix} \underline{\mathbf{\Lambda}}_{i>1}^{(00)} & \underline{\mathbf{\Lambda}}_{i>1}^{(01)} & \dots & \underline{\mathbf{\Lambda}}_{i>1}^{(0N)} \\ \underline{\mathbf{\Lambda}}_{i>1}^{(10)} & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \underline{\mathbf{\Lambda}}_{i>1}^{(N0)} & \dots & \dots & \underline{\mathbf{\Lambda}}_{i>1}^{(NN)} \end{bmatrix}, \quad \underline{\mathbf{\Lambda}}_{i>0}^{(pq)} = \begin{bmatrix} \Lambda_{21}^{pq} & \Lambda_{22}^{pq} & \dots & \dots & \Lambda_{2s}^{pq} \\ \Lambda_{31}^{pq} & \ddots & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \Lambda_{s1}^{pq} & \dots & \dots & \Lambda_{s,(s-1)}^{pq} & \Lambda_{ss}^{pq} \end{bmatrix}$$

(2.11)

\mathbf{d} and $\boldsymbol{\delta}$ are given as

$$\mathbf{d} = \begin{pmatrix} d_{1,1}^{(0)} \\ d_{2,1}^{(0)} \\ \vdots \\ d_{s,1}^{(0)} \\ d_{1,1}^{(1)} \\ \vdots \\ d_{s,1}^{(1)} \\ \vdots \\ d_{s,1}^{(N)} \\ d_{1,2}^{(0)} \\ \vdots \\ d_{s,2}^{(N)} \\ \vdots \\ d_{s,s}^{(N)} \end{pmatrix}, \quad \boldsymbol{\delta} = -\frac{8}{25k_B} \begin{pmatrix} 0 \\ \vdots \\ \times Ns \\ \vdots \\ 0 \\ \boldsymbol{\delta}^{(1)} \\ \boldsymbol{\delta}^{(2)} \\ \vdots \\ \boldsymbol{\delta}^{(s)} \end{pmatrix}, \quad \boldsymbol{\delta}^{(k)} = \begin{pmatrix} \omega_2 \\ \vdots \\ \omega_{k-1} \\ \omega_k - 1 \\ \omega_{k+1} \\ \vdots \\ \omega_s \\ 0 \\ \vdots \\ \times (N-1)(s-1) \\ \vdots \\ 0 \end{pmatrix}$$

(2.12)

2.2 Flux-Force relations

Inserting the polynomial expansion of $\mathbf{D}_i^{(j)}$ into Equation (2.1) one finds that at uniform temperature and pressure, and in the absence of external forces

$$\begin{aligned}\mathbf{J}_i^{(n,m)} &= -\frac{x_i}{2} \sum_j d_{i,j}^{(0)} \mathbf{d}_j \\ &= -\frac{x_i}{2n} \sum_j d_{i,j}^{(0)} \sum_k E_{jk} \nabla n_k \\ &\equiv -\frac{x_i}{2n} \sum_k \nabla n_k \sum_j E_{jk} d_{i,j}^{(0)}\end{aligned}\tag{2.13}$$

where $E_{ij} \equiv \frac{n_i}{k_B T} \left(\frac{\partial \mu_i}{\partial n_j} \right)_{T, n_{k \neq j}}$.

At this point it should be noted that the driving forces \mathbf{d}_j are not independent, but satisfy the relation $\sum_j \mathbf{d}_j = 0$, following from the Gibbs-Duhem equation. Due to this dependency there are several manners in which one may identify the diffusion coefficient of a multicomponent mixture. Equation (2.13) will be the starting point from which the diffusion coefficient is related to the polynomial expansion coefficients. It is therefore convenient to denote

$$\mathbf{J}_i^{(n,m)} = - \sum_j D_{ij}^{(E,m)} \nabla n_j \tag{2.14}$$

where

$$D_{ij}^{(E,m)} \equiv \frac{x_i}{2n} \sum_k E_{kj} d_{i,k}^{(0)} \tag{2.15}$$

In order to identify the diffusion coefficient related to different driving forces, it may be useful to express $\mathbf{J}_i^{(n,m)}$ in terms of the mole fraction gradients ∇x_i , as these conveniently sum to zero. Taking

$$\begin{aligned}\nabla n_k &= n \nabla x_k + x_k \nabla n \\ &= n \nabla x_k + x_k \sum_\ell \left(\frac{\partial n}{\partial x_\ell} \right)_{T,p} \nabla x_\ell \\ &= n \nabla x_k + x_k \sum_\ell - \frac{\left(\frac{\partial p}{\partial x_\ell} \right)_{T,n}}{\left(\frac{\partial p}{\partial n} \right)_{T,\mathbf{x}}} \nabla x_\ell \\ &= n \nabla x_k + x_k \sum_\ell - \frac{\left(\frac{\partial T}{\partial x_\ell} \right)_{p,n}}{\left(\frac{\partial T}{\partial n} \right)_{p,\mathbf{x}}} \nabla x_\ell \\ &= \sum_\ell \left[n \delta_{k,\ell} - x_k \frac{\left(\frac{\partial p}{\partial x_\ell} \right)_{T,n}}{\left(\frac{\partial p}{\partial n} \right)_{T,\mathbf{x}}} \right] \nabla x_\ell \\ &\equiv \sum_\ell \vartheta_{k\ell} \nabla x_\ell\end{aligned}\tag{2.16}$$

where the final equality defines $\vartheta_{k\ell}$ and the equality on the fourth line can be derived by differentiating the total differential of density

$$dn = \left(\frac{\partial n}{\partial T} \right)_{p,\mathbf{x}} dT + \left(\frac{\partial n}{\partial p} \right)_{T,\mathbf{x}} dT + \sum_i \left(\frac{\partial n}{\partial x_i} \right)_{T,p} dx_i \tag{2.17}$$

with respect to x_i and n , and using the fact that $\left(\frac{\partial n}{\partial x_i}\right)_{p,n} = \left(\frac{\partial n}{\partial x_i}\right)_{T,n} = 0$ and $\left(\frac{\partial n}{\partial n}\right)_{p,\mathbf{x}} = \left(\frac{\partial n}{\partial n}\right)_{T,\mathbf{x}} = 1$. Inserting Equation (2.16) into Equation (2.13) yields

$$\begin{aligned}\mathbf{J}_i^{(n,m)} &= -\frac{x_i}{2n} \sum_k \sum_\ell \vartheta_{k\ell} \nabla x_\ell \sum_j E_{jk} d_{ij}^{(0)} \\ &= -\frac{x_i}{2n} \sum_\ell \nabla x_\ell \sum_k \vartheta_{k\ell} \sum_j E_{jk} d_{ij}^{(0)}.\end{aligned}\quad (2.18)$$

Alternatively, one may choose to express the flux using a set of independent gradients. Using the condition $\sum_j \mathbf{d}_j = 0$ to express ∇n_i as

$$\begin{aligned}\sum_j \mathbf{d}_j &= \sum_j \sum_k E_{jk} \nabla n_k = 0 \\ \nabla n_i \sum_j E_{ji} + \sum_{k \neq i} \nabla n_k \sum_j E_{jk} &= 0 \\ \nabla n_i &= -\sum_{k \neq i} \nabla n_k \frac{\sum_j E_{jk}}{\sum_j E_{ji}} \equiv -\sum_{k \neq i} \nabla n_k \frac{E'_k}{E'_i},\end{aligned}\quad (2.19)$$

where the final equality defines $E'_i = \sum_j E_{ji}$, and inserting into Equation (2.13) one arrives at

$$\begin{aligned}\mathbf{J}_i^{(n,m)} &= -\frac{x_i}{2n} \sum_k \nabla n_k \sum_j E_{jk} d_{ij}^{(0)} \\ &= -\frac{x_i}{2n} \left(\nabla n_i \sum_j E_{ji} d_{ij}^{(0)} + \sum_{k \neq i} \nabla n_k \sum_j E_{jk} d_{ij}^{(0)} \right) \\ &= -\frac{x_i}{2n} \sum_{k \neq i} \nabla n_k \sum_j (E_{jk} - E_{ji} \frac{E'_k}{E'_i}) d_{ij}^{(0)}.\end{aligned}\quad (2.20)$$

As shown elsewhere,^[3] the molar fluxes in the centre of mass FoR can be translated to another frame of reference B via the matrix transformation

$$\mathbf{J}^{(B)} = \underline{\Psi}^{B,m} \mathbf{J}^{(m)} \quad (2.21)$$

where

$$\psi_{ij}^{Bm} = \delta_{i,j} - x_i \left(\frac{b_j}{b} - \frac{M_j b_\ell}{b M_\ell} \right) \quad (2.22)$$

where $\delta_{i,j}$ is the Kronecker delta, x_i denotes the mole fraction of species i , M_j is the molar mass of species j , $b = \left(\frac{\partial B}{\partial n}\right)_{T,p,\mathbf{x}}$ is the molar value of the extensive property B , $b_j \equiv \left(\frac{\partial B}{\partial n_j}\right)_{T,p,n_{k \neq j}}$ is the partial molar value of B with respect to species j and ℓ denotes an arbitrary component.

Note that because ℓ denotes an arbitrary component

The vector $\mathbf{J}^{(B)}$ is

$$\mathbf{J}^{(B)} = \begin{pmatrix} J_1^B \\ J_2^B \\ \vdots \\ J_s^B \end{pmatrix} \quad (2.23)$$

and equivalent for $\mathbf{J}^{(m)}$.

This transformation can also be used to translate the "apparent" diffusion coefficients between different frames of reference, as is discussed in the following section.

2.3 Defining the diffusion coefficients

The diffusion coefficients of a mixture may be defined through the relationship between the fluxes and driving forces in a mixture. In this section Equation (2.14), describing the relationship between the molar flux in the centre of mass FoR and the molar density gradients, will be related to other flux-force relationships through which the diffusion coefficients are commonly defined.

2.3.1 Binary mixtures

The molar flux in a binary mixture is often described by Ficks law in the centre-of-moles frame of reference. This is convenient in the case of fairly dilute mixtures in which equimolar counter diffusion applies. Ficks law for a binary mixture reads

$$\mathbf{J}_1^{(n,n)} = -D_{12}^{\text{Fick}} \nabla n_1 \quad (2.24)$$

where the superscript (n, n) indicates that the flux is in the molar basis, in the centre-of-moles FoR. Translating the fluxes of Equation (2.14) to the centre of moles frame of reference yields

$$\begin{pmatrix} \mathbf{J}_1^{(n,n)} \\ \mathbf{J}_1^{(n,n)} \end{pmatrix} = -\underline{\Psi}^{(n,m)} \underline{\mathbf{D}}^{(E,m)} \begin{pmatrix} \nabla n_1 \\ \nabla n_2 \end{pmatrix} \equiv -\underline{\mathbf{D}}^{(E,n)} \begin{pmatrix} \nabla n_1 \\ \nabla n_2 \end{pmatrix}. \quad (2.25)$$

where the final equality defines $\underline{\mathbf{D}}^{(E,n)} \equiv \underline{\Psi}^{(n,m)} \underline{\mathbf{D}}^{(E,m)}$. By Equation (2.19)

$$\nabla n_2 = -\frac{E'_1}{E'_2} \nabla n_1 \quad (2.26)$$

such that

$$\mathbf{J}_1^{(n,n)} = -D_{11}^{(E,n)} \nabla n_1 - D_{12}^{(E,n)} \nabla n_2 = \left(D_{12}^{(E,n)} \frac{E'_1}{E'_2} - D_{11}^{(E,n)} \right) \nabla n_1. \quad (2.27)$$

Thereby, the Fickean diffusion coefficient in the molar basis is identified as

$$D_{12}^{\text{Fick}} = D_{12}^{(E,n)} \frac{E'_1}{E'_2} - D_{11}^{(E,n)}. \quad (2.28)$$

2.3.2 Multicomponent mixtures

de Haro et al. define the diffusion coefficient through a multicomponent generalization of Ficks law in the centre of mass FoR

$$\mathbf{J}_i^{(n,m)} = \frac{1}{m_i} \sum_{j \neq i} D_{ij}^{\text{fick}} m_j \nabla n_j. \quad (2.29)$$

This expression has the advantage of reducing to the commonly used expression

$$\mathbf{J}_i^{(n,m)} = -D_{12} \nabla n_1 \quad (2.30)$$

in the case of a binary mixture. Comparing Equation (2.29) to (2.20) one finds that

$$D_{ij}^{\text{fick}} = -\frac{x_i m_i}{2n m_j} \sum_j (E_{jk} - E_{ji} \frac{E'_k}{E'_i}) d_{ij}^{(0)}. \quad (2.31)$$

An alternative to the generalized Fickean diffusion coefficient is the Maxwell-Stefan diffusion coefficient for multicomponent mixtures. It is defined by

$$\nabla x_i = -\sum_{j \neq i} \frac{x_i x_j}{D_{ij}^{M.S.}} (\bar{\mathbf{u}}_i - \bar{\mathbf{u}}_j) \quad (2.32)$$

As shown by

For a realistic mixture, it is of interest to separate the factors E_{ij} , which may be computed from an equation of state (EoS) from the polynomial expansion coefficients $d_{i,j}^{(0)}$ which can be computed from kinetic theory without requiring an accurate equation of state. Writing the fluxes as

$$\mathbf{J}^{(n,m)} = \underline{\mathbf{D}}^{kin} \underline{\mathbf{\Gamma}} \nabla \mathbf{n} \quad (2.33)$$

and comparing to Equation (2.13), one finds that this separation can be achieved by using

$$\underline{\mathbf{D}}^{kin} = -\frac{1}{2n} \begin{bmatrix} x_1 d_{1,1}^{(0)} & x_2 d_{1,2}^{(0)} & \dots & x_1 d_{1,s}^{(0)} \\ x_1 d_{2,1}^{(0)} & x_2 d_{2,2}^{(0)} & & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ x_1 d_{s,1}^{(0)} & x_2 d_{s,2}^{(0)} & \dots & x_s d_{s,s}^{(0)} \end{bmatrix}, \quad \underline{\mathbf{\Gamma}} = \begin{bmatrix} E_{11} & E_{12} & \dots & E_{1s} \\ E_{21} & E_{22} & & \vdots \\ \vdots & \vdots & \ddots & \vdots \\ E_{s1} & E_{s2} & \dots & E_{ss} \end{bmatrix} \quad (2.34)$$

One should note that these matrices are not invertible and that the coefficients do not reduce to the Fickian diffusion coefficients in the case of a binary mixture. This formulation is still convenient, as it allows one to transform the coefficients directly to another frame of reference B by the transformation

$$\begin{aligned} \mathbf{J}^{((B))} &= \underline{\Psi}^{B,m} \mathbf{J}^{(n,m)} \\ &= \underline{\Psi}^{B,m} \underline{\mathbf{D}}^{kin} \underline{\mathbf{\Gamma}} \nabla \mathbf{n} \\ &= \underline{\mathbf{D}}^{kin,B} \underline{\mathbf{\Gamma}} \nabla \mathbf{n} \\ \underline{\mathbf{D}}^{kin,B} &\equiv \underline{\Psi}^{B,m} \underline{\mathbf{D}}^{kin} \end{aligned} \quad (2.35)$$

where $\underline{\mathbf{D}}^{kin,B}$ is the apparent kinetic diffusion coefficient matrix in the B FoR. This may then be transformed as desired by the same procedure as that used to arrive at Equation (2.31) if one wishes to express the fluxes as a function of only independent gradients.

3 Thermal diffusion

Reiterating that the flux of species i in the centre of mass frame of reference is given as

$$\mathbf{J}_i^{(n,m)} = n_i (\bar{\mathbf{u}}_i - \mathbf{u}^m) = \int f_i \mathbf{U}_i d\mathbf{u}_i. \quad (3.1)$$

Investigate now the thermal response functions Λ_i , which are expanded in the Sonine polynomials as

$$\Lambda_i = -\frac{m_i}{2k_B T} \sum_{p=0}^{\infty} a_i^{(p)} S_{3/2}^{(p)}(\mathcal{U}^2) \quad (3.2)$$

This section will first describe how the expansion coefficients $a_i^{(p)}$ are determined, before relating the coefficients of Equation (3.11) to the thermal diffusion coefficient (D_T). The relationship to the thermal diffusion ratio (k_T), thermal diffusion factor (α_T) and Soret coefficient (S_T) are covered at the end of the section.

3.1 Determining the expansion coefficients

In order to satisfy the constraints posed by the summational invariants, the expansion coefficients $a_i^{(p)}$ must satisfy

$$\begin{aligned} \sum_i \omega_i a_i^{(0)} &= 0 \\ \sum_j \sum_q \Lambda_{1j}^{(pq)} a_j^{(q)} &= \frac{4}{5k_B} x_1 K_1 \delta_{p1}, & p = \{1, 2, \dots, N\} \\ \sum_j \sum_q \Lambda_{ij}^{(pq)} a_j^{(q)} &= \frac{4}{5k_B} x_i K_i \delta_{p1}, & \begin{cases} i = \{2, 3, \dots, s\} \\ p = \{0, 1, \dots, N\} \end{cases} \end{aligned} \quad (3.3)$$

where ω_i denotes the weight fraction of species i , and $\Lambda_{ij}^{(pq)}$ are given by Equation (2.5). This set of Equations may be written in matrix form in a manner analogous to that in Section 2.1,

$$\underline{\mathbf{A}} \mathbf{a} = \boldsymbol{\lambda} \quad (3.4)$$

where $\underline{\mathbf{A}}$ is a $Ns \times Ns$ matrix consisting of the blocks

$$\underline{\mathbf{A}} = \begin{bmatrix} \boldsymbol{\omega} \\ \underline{\mathbf{A}}_1^{(p>0)} \\ \underline{\mathbf{A}}_{i>1} \end{bmatrix} \quad (3.5)$$

where

$$\boldsymbol{\omega} = (\omega_1 \quad \omega_2 \quad \dots \quad \omega_s \quad 0 \quad \dots \quad \times s(N-1) \quad \dots \quad 0) \quad (3.6)$$

$$\underline{\mathbf{A}}_1^{(p>0)} = \begin{bmatrix} \Lambda_1^{(0)} & \Lambda_1^{(1)} & \dots & \Lambda_1^{(N)} \end{bmatrix}, \quad \Lambda_1^{(q)} = \begin{bmatrix} \Lambda_{11}^{(1q)} & \Lambda_{12}^{(1q)} & \dots & \Lambda_{1s}^{(1q)} \\ \Lambda_{11}^{(2q)} & \Lambda_{12}^{(2q)} & \dots & \Lambda_{1s}^{(2q)} \\ \vdots & \vdots & \ddots & \vdots \\ \Lambda_{11}^{(Nq)} & \Lambda_{12}^{(Nq)} & \dots & \Lambda_{1s}^{(Nq)} \end{bmatrix} \quad (3.7)$$

$$\underline{\mathbf{A}}_{i>1} = \begin{bmatrix} \underline{\mathbf{A}}_{i>1}^{(00)} & \underline{\mathbf{A}}_{i>1}^{(01)} & \dots & \underline{\mathbf{A}}_{i>1}^{(0N)} \\ \underline{\mathbf{A}}_{i>1}^{(10)} & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \underline{\mathbf{A}}_{i>1}^{(N0)} & \dots & \dots & \underline{\mathbf{A}}_{i>1}^{(NN)} \end{bmatrix}, \quad \underline{\mathbf{A}}_{i>0}^{(pq)} = \begin{bmatrix} \Lambda_{21}^{pq} & \Lambda_{22}^{pq} & \dots & \dots & \Lambda_{2s}^{pq} \\ \Lambda_{31}^{pq} & \ddots & & & \vdots \\ \vdots & & \ddots & & \vdots \\ \Lambda_{s1}^{pq} & \dots & \dots & \Lambda_{s,(s-1)}^{pq} & \Lambda_{ss}^{pq} \end{bmatrix} \quad (3.8)$$

\mathbf{a} and $\boldsymbol{\lambda}$ are given as

$$\mathbf{a} = \begin{pmatrix} a_1^{(0)} \\ a_2^{(0)} \\ \vdots \\ a_s^{(0)} \\ a_1^{(1)} \\ \vdots \\ a_s^{(N)} \end{pmatrix}, \quad \boldsymbol{\lambda} = \frac{4}{5k_B} \begin{pmatrix} 0 \\ x_1 K_1 \\ 0 \\ \vdots \\ \times(N-2) \\ \vdots \\ 0 \\ \mathbf{K}_2 \\ \vdots \\ \mathbf{K}_s \end{pmatrix}, \quad \mathbf{K}_i = \begin{pmatrix} 0 \\ \vdots \\ \times(i-1) \\ \vdots \\ 0 \\ x_i K_i \\ 0 \\ \vdots \\ \times(N-i) \\ \vdots \\ 0 \end{pmatrix} \quad (3.9)$$

3.2 Force-Flux relations

In the absence of a pressure gradient and external forces, the flux of species i in the center of mass frame of reference may be expressed as

$$\mathbf{J}_i^{(n,m)} = - \sum_{j \neq i} D_{ij}^{Fick} \frac{m_j}{m_i} \nabla n_j - \frac{\rho D_i^T}{m_i} \nabla \ln T. \quad (3.10)$$

Where D_i^T are the thermal diffusion coefficients. Evaluating the integral of Equation (3.1) to acquire an expression for the flux in terms of the expansion coefficients yields

$$\mathbf{J}_i^{(n,m)} = \frac{x_i}{2} \left[a_i^{(0)} \nabla \ln T - \sum_j d_{i,j}^{(0)} \mathbf{d}_j \right] \quad (3.11)$$

Inserting the definition of \mathbf{d}_j from Equation (1.10) with $\nabla p = \mathbf{F}_i = 0 \forall i$, Equation (3.11) becomes

$$\begin{aligned} \mathbf{J}_i^{(n,m)} &= \frac{x_i}{2} \left[a_i^{(0)} \nabla \ln T - \sum_j d_{i,j}^{(0)} \sum_k x_j \left(\delta_{j,k} + \frac{4\pi}{3} n_k M_{jk} \sigma_{jk}^3 \chi_{jk} \right) \nabla \ln T - \frac{1}{n} E_{jk} \nabla n_k \right] \\ &= \frac{x_i}{2} \left[a_i^{(0)} - \sum_j d_{i,j}^{(0)} \sum_k x_j \left(\delta_{j,k} + \frac{4\pi}{3} n_k M_{jk} \sigma_{jk}^3 \chi_{jk} \right) \right] \nabla \ln T - \frac{x_i}{2n} \sum_j d_{i,j}^{(0)} \sum_k E_{jk} \nabla n_k \end{aligned} \quad (3.12)$$

In order to compare Equations (3.10) and (3.12) the gradient ∇n_i must be eliminated from the rightmost summation in Equation (3.12). Using the condition $\sum_k \mathbf{d}_k = 0$, and denoting $b_{ij} \equiv \frac{4\pi}{3} n_j M_{ij} \sigma_{ij}^3 \chi_{ij}$

$$\begin{aligned} \mathbf{d}_i &= - \sum_{k \neq i} \mathbf{d}_k \\ \sum_j x_i (\delta_{i,j} + b_{ij}) \nabla \ln T + \frac{1}{n} E_{ij} \nabla n_j &= - \sum_{k \neq i} \sum_j x_k (\delta_{k,j} + b_{ij}) \nabla \ln T + \frac{1}{n} E_{kj} \nabla n_j \\ \frac{E_{ii}}{n} \nabla n_i + \frac{1}{n} \sum_{j \neq i} E_{ij} \nabla n_j &+ \sum_j x_i (\delta_{i,j} + b_{ij}) \nabla \ln T = - \sum_{k \neq i} \left\{ \frac{E_{ki}}{n} \nabla \ln n_i + \frac{1}{n} \sum_{j \neq i} E_{kj} \nabla n_j \right. \\ &\quad \left. + \sum_j x_k (\delta_{k,j} + b_{kj}) \nabla \ln T \right\} \\ \frac{1}{n} \sum_k E_{ki} \nabla n_i &= - \sum_k \left\{ \frac{1}{n} \sum_{j \neq i} E_{kj} \nabla n_j + x_k \sum_j (\delta_{k,j} + b_{kj}) \nabla \ln T \right\} \\ \nabla n_i &= - \sum_{j \neq i} \frac{E'_j}{E'_i} \nabla n_j - \sum_k \frac{n_k}{E'_i} \sum_j (\delta_{k,j} + b_{kj}) \nabla \ln T \end{aligned} \quad (3.13)$$

where the final equality is acquired by inverting the summation over k and j , and using $E'_i \equiv \sum_j E_{ji}$. Inserting this expression back into Equation (3.12) and collecting the terms related to each of the gradients

yields

$$\begin{aligned}
\mathbf{J}_i^{(n,m)} &= \frac{x_i}{2} \left[a_i^{(0)} - \sum_j d_{i,j}^{(0)} \sum_k x_j (\delta_{j,k} + b_{jk}) \right] \nabla \ln T \\
&\quad - \frac{x_i}{2n} \sum_j d_{i,j}^{(0)} \left[-E_{ji} \left(\sum_{k \neq i} \frac{E'_k}{E'_i} \nabla n_k + \sum_k \frac{n_k}{E'_i} \sum_\ell (\delta_{k,\ell} + b_{k\ell}) \nabla \ln T \right) + \sum_{k \neq i} E_{jk} \nabla n_k \right] \\
&= \frac{x_i}{2} \left[a_i^{(0)} + \sum_j d_{i,j}^{(0)} \sum_k x_k \left(\frac{E_{ji}}{E'_i} - \delta_{k,j} \right) \sum_\ell (\delta_{k,\ell} + b_{k\ell}) \right] \nabla \ln T \\
&\quad - \frac{x_i}{2n} \sum_{k \neq i} \nabla n_k \sum_j d_{i,j}^{(0)} \left(E_{jk} - E_{ji} \frac{E'_k}{E'_i} \right)
\end{aligned} \tag{3.14}$$

Comparing Equation (3.11) and (3.14) we can identify

$$\begin{aligned}
D_i^T &= -\frac{m_i x_i}{2\rho} \left[a_i^{(0)} + \sum_j d_{i,j}^{(0)} \sum_k x_k \left(\frac{E_{ji}}{E'_i} - \delta_{k,j} \right) \sum_\ell (\delta_{k,\ell} + b_{k\ell}) \right] \\
&= \frac{m_i x_i}{2\rho} \left[-a_i^{(0)} + \sum_j d_{i,j}^{(0)} \sum_k x_k \left(\delta_{k,j} - \frac{E_{ji}}{E'_i} \right) \sum_\ell (\delta_{k,\ell} + b_{k\ell}) \right]
\end{aligned} \tag{3.15}$$

3.3 Various measures of thermal diffusion

Measuring the thermal diffusion coefficient D_i^T is not necessarily trivial. Therefore, other measures of thermal diffusion and the relationship between them are presented here. We define the Soret coefficients ($S_{T,i}$) and thermal diffusion factors ($\alpha_{T,i}$) as

$$S_{T,i} \equiv \frac{\nabla x_i}{x_i(1-x_i)\nabla T}, \quad \mathbf{J}_j = 0 \quad \forall j, \quad \alpha_{T,i} \equiv T S_{T,i}, \tag{3.16}$$

Where the lacking superscript on \mathbf{J} is intentional, as if all fluxes vanish in one frame of reference the same is true in all other frames of reference, by the transformation in Equation (2.21).

The thermal diffusion ratio, we define by the condition

$$\mathbf{J}_i^{(n,m)} = 0 \quad \forall i \quad \implies \quad \nabla n_i = -n_i k_{T,i} \nabla \ln T, \quad \forall i \tag{3.17}$$

Inserting this definition into Equation (3.10) yields a set of equations defining $k_{T,i}$

$$\sum_{j \neq i} D_{ij} k_{T,j} \equiv \rho D_i^T, \quad \forall i. \tag{3.18}$$

Rewriting the definition of $k_{T,i}$ in terms of the mole fraction gradients, one can relate $k_{T,i}$ to $S_{T,i}$ through the set of equations

$$\begin{aligned}
\nabla n_i &= -n_i k_{T,i} \nabla \ln T \\
x_i \nabla n + n \nabla x_i &= -\frac{n_i k_{T,i}}{T} \nabla T \\
x_i \left[\left(\frac{\partial n}{\partial T} \right)_{p,\mathbf{x}} \nabla T + \sum_j \left(\frac{\partial n}{\partial x_j} \right)_{T,p} \nabla x_j \right] + n \nabla x_i &= -\frac{n_i k_{T,i}}{T} \nabla T \\
-\frac{x_i T}{n_i} \left(\frac{\partial n}{\partial T} \right)_{p,\mathbf{x}} + \sum_j \left[n \delta_{i,j} + \left(\frac{\partial n}{\partial x_j} \right)_{T,p} \right] x_j (1-x_j) S_{T,j} &= k_{T,i}.
\end{aligned} \tag{3.19}$$

Alternatively, starting from Equation (3.12) and setting $J_i = 0$, the Soret coefficients may be related directly to the Sonine polynomial expansion coefficients through the set of equations

$$\begin{aligned} \sum_{\ell} S_{T,\ell} \sum_j \sum_k d_{i,j}^{(0)} E_{jk} \left[n\delta_{\ell,k} + x_k \left(\frac{\partial n}{\partial x_{\ell}} \right)_{T,p} \right] x_{\ell}(1-x_{\ell}) \\ = \sum_j \sum_k d_{i,j}^{(0)} E_{jk} x_k \left(\frac{\partial n}{\partial T} \right)_{p,\mathbf{x}} - \frac{n}{T} \left[a_i^{(0)} - \sum_j d_{i,j}^{(0)} \sum_k x_j \left(\delta_{j,k} + \frac{4\pi}{3} n_k M_{jk} \sigma_{jk}^3 \chi_{jk} \right) \right] \end{aligned} \quad (3.20)$$

4 Thermal Conductivity

The heat flux in the centre of mass frame of reference is related to the vdf. as

$$\mathbf{J}_q = \sum_i \int f_i \frac{m_i}{2} \mathbf{U}_i^2 d\mathbf{u}_i \quad (4.1)$$

Having obtained expressions for the thermal- and diffusive response functions, $\mathbf{\Lambda}_i$ and $\mathbf{D}_i^{(j)}$ in the previous sections this integral may be evaluated to yield

$$\begin{aligned} \mathbf{J}_q = & -\frac{5k_B T}{4n} \sum_i K_i x_i \left(a_i^{(1)} \nabla \ln T - \sum_j d_{i,j}^{(1)} \mathbf{d}_j \right) \\ & - \frac{4k_B T}{3} \sum_i \sum_j \left(\frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{\frac{1}{2}} \frac{n_i n_j \sigma_{ij}^4 \chi_{ij}}{m_i + m_j} \nabla \ln T \\ & + k_B T \sum_i \sum_j \frac{2\pi}{3} n_j \sigma_{ij}^3 (M_{ij} - M_{ji}) \chi_{ij} \mathbf{J}_i^{(n,m)} \\ & + \frac{5k_B T}{2} \sum_i \left(1 + \sum_j \frac{2\pi}{3} n_j \sigma_{ij}^3 \chi_{ij} \right) \frac{m_i}{m_j} \mathbf{J}_i^{(n,m)}. \end{aligned} \quad (4.2)$$

In the absence of a mass flux, Fourier's law applies and we have

$$\mathbf{J}_q = -\lambda \nabla T \quad (4.3)$$

where λ is the conductivity. When all mass fluxes vanish in the presence of a temperature gradient, the molar density gradients in \mathbf{d}_i may be replaced by the thermal diffusion ratios, such that

$$\begin{aligned} \mathbf{d}_i &= \sum_j x_j (\delta_{i,j} + b_{ij} - k_{T,i} E_{ji}) \nabla \ln T, \quad \mathbf{J}_k^{(n,m)} = 0 \quad \forall \quad k \\ &\equiv \sum_j d_j^{th} \nabla \ln T, \end{aligned} \quad (4.4)$$

where the second equality defines d_j^{th} . Furthermore, because all mass fluxes have vanished, these d_j^{th} must satisfy

$$\sum_j d_{i,j}^{(0)} d_j^{th} = a_i^{(0)} \quad (4.5)$$

as is seen by setting the left hand side of Equation (3.11) to zero. Comparing Equations (4.2) and (4.3) we identify the thermal conductivity as

$$\lambda = -\frac{5k_B T}{4n} \sum_i K_i x_i \left(a_i^{(1)} - \sum_j d_{i,j}^{(1)} d_j^{th} \right) - \frac{4k_B T}{3} \sum_i \sum_j \left(\frac{2\pi m_i m_j k_B T}{m_i + m_j} \right)^{\frac{1}{2}} \frac{n_i n_j \sigma_{ij}^4 \chi_{ij}}{m_i + m_j} \quad (4.6)$$

5 Viscosity

The flux of momentum \underline{P} is related to the velocity distribution function as

$$\underline{P} = \sum_i \int f_i m_i \mathbf{U}_i d\mathbf{u}_i. \quad (5.1)$$

The hydrodynamic response functions \underline{B}_i and H_i may be written as the polynomial expansions

$$B_i = \frac{m_i}{2k_B T} \sum_{r=0}^{\infty} b_i^{(r)} S_{5/2}^{(r)}(\mathcal{U}^2), \quad H_i = \sum_{r=0}^{\infty} h_r^{(0)} S_{1/2}^{(r)}(\mathcal{U}^2) \quad (5.2)$$

where B_i is defined by $\underline{B}_i \equiv B_i (\mathbf{U}_i \mathbf{U}_i - \frac{1}{3} U_i^2 \mathbf{I})$. Inserting these expansions into Equation (5.1), and applying the conservation law for momentum yields a set of equations for the expansion coefficients as

$$\sum_{j=1}^s \sum_{q=0}^N B_{ij}^{(pq)} b_j^{(q)} = \frac{2}{k_B T} x_i K'_i \delta_{p,0}, \quad \begin{cases} i = \{1, 2, \dots, s\} \\ p = \{0, 1, \dots, N\} \end{cases} \quad (5.3)$$

where

$$K'_i = 1 + \frac{8\pi n}{15} \sum_j x_j M_{ji} \sigma_{ij}^3 \chi_{ij} \\ B_{ij}^{(pq)} = \frac{2}{5k_B T} \left\{ x_i x_j \left[S_{5/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i \overset{\circ}{\mathcal{U}}_i, S_{5/2}^{(q)}(\mathcal{U}_j^2) \mathcal{U}_j \overset{\circ}{\mathcal{U}}_j \right]_{ij} \right. \\ \left. + \delta_{i,j} \sum_k x_i x_k \left[S_{5/2}^{(p)}(\mathcal{U}_i^2) \mathcal{U}_i \overset{\circ}{\mathcal{U}}_i, S_{5/2}^{(q)}(\mathcal{U}_i^2) \mathcal{U}_i \overset{\circ}{\mathcal{U}}_i \right]_{ik} \right\} \quad (5.4)$$

with

$$\mathcal{U}_i \overset{\circ}{\mathcal{U}}_i \equiv \mathcal{U} \mathcal{U} - \frac{1}{3} \mathcal{U}^2 \mathbf{I}. \quad (5.5)$$

These bracket integrals are exactly the ones identified by Thompson et al. as linear combinations of the collision integrals.^[4]

5.1 Determining the expansion coefficients

5.2 Flux force relations

5.3 Viscosity in terms of the expansion coefficients

Comparing Equations ... and ... one can identify the shear viscosity as

$$\eta = \frac{k_B T}{2} \sum_i K'_i x_i b_i^{(0)} + \frac{4}{15} \sqrt{2\pi k_B T} \sum_i \sum_j \sqrt{\frac{m_i m_j}{m_i + m_j}} n_i n_j \sigma_{ij}^4 \chi_{ij} \quad (5.6)$$

6 Contact diameters

The "contact diameter", σ_{ij} has been mentioned several times thus far, and has been taken to be some distance in the range of the particle sizes. In the case of additive hard spheres, the contact diameter can unambiguously be defined as the distance between the centre of mass of the two particles at contact. However, for Mie particles this definition is not equally straight forward. In this section, various ways of defining the contact diameter, and the inherent underlying assumptions behind the different definitions will be discussed.

Firstly, it is worth mentioning that applying the multicomponent, density corrected solutions proposed by de Haro et al. to Mie fluids implies the assumption that the contact diameters are independent of particle velocities at collision. This assumption is necessary due to the fact that the integral of Equation (1.2) is one over the velocity space. The contact diameters are permitted to be functions of the temperature, and thereby the mean velocities, as well as density and composition but must be constant for all particles in a given state.

One could, in principle, define the contact diameters as some function of the velocities, but this would severely limit the possibility of utilising previously obtained results from the literature. Therefore, such an approach has not been attempted here.

When defining the contact diameters of Mie particles, we note the two roles this distance plays. The first is describing the covolume of the mixture, and the modified probability of finding two particles at contact through the radial distribution function "at contact". The second is describing the instantaneous transfer of energy and momentum from one particle to the other when particles collide. This effect manifests itself as the second terms in the expressions for the conductivity and viscosity, which depends on the density, contact diameters and rdf. but not on the polynomial expansion coefficients. Because the contact diameter plays two distinctly different roles, it is not necessarily so that the length one should use in these two roles must be the same.

To evaluate the radial distribution function "at contact" a highly convenient choice of the contact diameter is the Mie parameter σ_{ij} . This allows one to directly apply the expressions proposed by Lafitte et al. for the rdf. at contact.^[5] This formulation of the rdf. at contact has been shown to give accurate predictions of thermodynamic properties of fluids, and the associated distance is therefore likely to give a good representation of the covolume of the mixture. Therefore, it is believed that using σ_{ij} as the contact diameter when computing the rdf. at contact is not only a convenient choice, but also a choice that allows accurate representation of the modified probability of contact between particles due to volume exclusion.

Regarding the second property described by the contact diameter, the instantaneous transfer of energy and momentum at the moment of collision, a distance more directly related to the collision dynamics was chosen. Firstly, note that the equilibrium vdf. given in Equation (1.4) does not depend on the contact diameters. We regard a colliding pair of particles, and define the contact diameter as the average distance of closest approach (R) during collision where the particles repel each other (e.g. collisions where $\theta < \frac{\pi}{2}$). Further, we compute this average for a mixture at equilibrium, when $f_i = f_i^{(0)}$. The contact diameter is then given by

$$\bar{R}_{ij} = \int_0^\infty \int_0^{b'} R_{ij}(g_{ij}, b) db dg_{ij} \quad (6.1)$$

where g_{ij} is the relative speed of the colliding pair and b' is the solution to the equation

$$\theta_{ij}(b'; g_{ij}) = 0. \quad (6.2)$$

This integral is somewhat computationally expensive to evaluate, but may be simplified by noting that $R(g_{ij}; b)$ is reasonably symmetric about $g = \bar{g}$, the average relative speed, as shown in Figure 6.1. Due to this symmetry, a good approximation to the integral of Equation (6.1) is given by

$$\bar{R}_{ij} = \int_0^{\bar{b}'} R_{ij}(b; \bar{g}_{ij}) db \quad (6.3)$$

with \bar{b}' given by

$$\theta_{ij}(\bar{b}'; \bar{g}_{ij}) = 0. \quad (6.4)$$

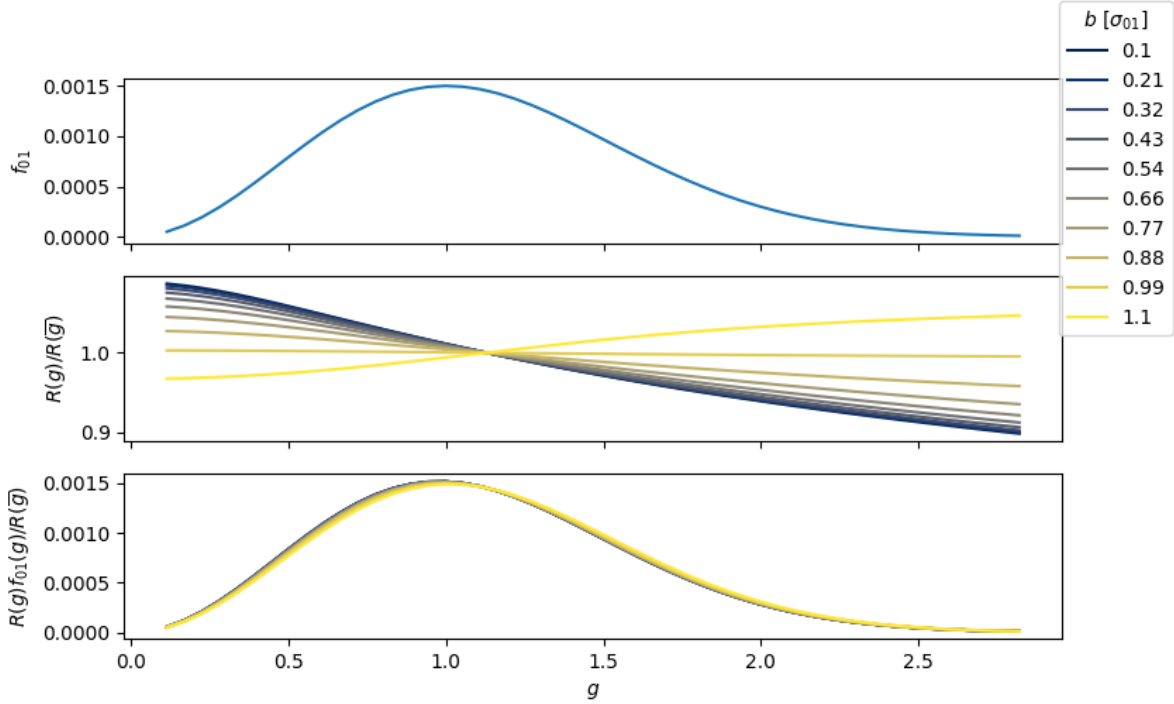


Figure 6.1: The distance of closest approach as a function of dimensionless relative velocity g and impact parameter b at $T = 500$ K

This integral was evaluated using a six-point Gauss-Legendre quadrature, after investigating the convergence behaviour of the quadrature and finding that this was sufficient to achieve a relative precision of $\approx 10^{-8}$.

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