Toward a Unified Theory of Isotropic Molecular Transport Phenomena

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Accurate models for multicomponent transport are a prerequisite for the design of many industrial processes and the interpretation of experiments. Present theories, stemming from the statistical-mechanics developments of Chapman–Enskog, Zhdanov–Kagan–Sazykin, and Bearman–Kirkwood are shown to apply only to systems with low shear. These theories are not able to describe gaseous counterdiffusion in capillaries, such as in the experiments of Remick and Geankoplis, and the salt diffusion experiment in a simple cylinder by Fick. A simple experiment shows that the irreversible thermodynamics approach by De Groot–Mazur and Hirschfelder–Curtiss–Bird provides inconsistencies. The cause for this is the common development of the theories as perturbations superposed on the mass-averaged velocity. A new solution to the Boltzmann equation is developed for monatomic dilute gases, based on nonequilibrium trial functions, in which the velocity distributions are centered around the averaged velocities of the individual species. In the resulting momentum balance, individual shear and convected momentum terms are present. Transport coefficients for pure monatomic gases are equal to those from classic theory; for mixtures of such gases new expressions are found that give an excellent description of experimental data. Based on these results, generalized versions of the transport equations are proposed, for dense media and liquids, and limit versions are presented. Important physical parameters are the partial viscosities. The applicability to the experimental situations above is demonstrated. The present theory offers the perspective of evaluating both concentration and velocity profiles, as well as temperature gradients, for individual species in three-dimensional space for molecular transport. Thus it provides a new basis for the modeling of multicomponent transport in a multitude of systems, such as in catalysts, adsorbents, membranes, CVD- and microreactors, but also for the classical problem of the circulation in Stefan tubes. In one of its limits, for long flat or cylindrical channels, it supports the earlier developed velocity profile model (VPM-1) for transport in pores. © 2004 American Institute of Chemical Engineers *AIChE J*, 51: 79–121, 2005
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Introduction

In the field of chemical engineering the theory of isotropic molecular diffusion, viscous shear, and heat conduction is generally accepted as mature. The very clear and systematic book of Bird et al.,[1] followed by many other excellent textbooks (Slattery,[2] Taylor and Krishna,[3] Lightfoot,[4] Cussler,[5] Deen,[6] Beek et al.,[7] Wesselingh and Krishna[8]), dedicates a considerable part to the phenomena themselves, but equal strength lies in the methodology of setting up differential balances and applying them to a host of engineering problems. Most of these nonturbulent problems are concerned with either

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single-component flow in various situations and geometries, with binary diffusion and diffusion–convection problems and heat transfer, also coupled to mass transfer. For most of the chemical engineers this is part of their heritage, and together with the material on boundary layer theory forms a basic toolbox, which has been put to good use innumerable times. For problems in heat conduction and Fickian diffusion in the main geometries for different boundary conditions, analytical solutions and the underlying mathematics are provided by the works of Carslaw and Jaeger,[9] Crank,[10] and Luikov.[11] For the basic foundation of the expressions of the laws of Fourier, Fick, and Newton in fluids, the textbook reader is referred to a classic work such as the Chapman–Enskog theory, laid down in Chapman and Cowling[12] (CC), and Hirschfelder et al.[13] (HCB).

In the previously mentioned transport phenomena textbooks multicomponent transport is also introduced, either on the basis of results from statistical mechanics, or those from irreversible thermodynamics. Notable is a special section on this by Lightfoot[4] in his pioneering work on transport phenomena in living systems. Recently special textbooks have been written about this subject, such as Taylor and Krishna[3] and Wesselingh and Krishna.[8] Also in textbooks about special application areas such as heterogeneous catalysis and adsorption considerable parts of the text are devoted to the description of (multicomponent) transport in porous media (for example, Jackson,[14] Cunningham and Williams,[15] Keil,[16] Wijngaarden et al.,[17] and Do[18]). Review papers have been published, such as the recent one by Krishna and Wesselingh[19] and Curtiss and Bird.[20] The theory presented on multicomponent diffusion is of considerable complexity. In part this is inherent complexity because of the larger number of components, and their possible thermodynamic interactions, and the reference material from statistical mechanics. The other factor is the confusion caused by special terminology (such as "diffusive flux"), by the language and concepts from irreversible thermodynamics (such as "Curie principle" and "entropy production"), and by additional phenomena to take into account such as slip phenomena in gases and thermal diffusion. In our view, confusion is also introduced by the lack of the well-known framework for "simple systems," as indicated above, in which one has a "point" equation, formulates a shell balance, and solves this using appropriate boundary conditions. On the contrary, fluxes and velocities appear in the text, and are sometimes changing from "point" character to area-averaged fluxes without a clear indication why this would be allowed. A central model for transport in porous media is the approach of the dusty gas model (DGM) of Mason et al.,[21] Mason and Malinauskas,[22] and Mason and Viehland.[23] In previous work[24] we have analyzed in some depth the derivations of the DGM, and showed that there are serious flaws in the derivation for both the gas-phase model[21] and the liquid-phase version.[23] For the transport in capillaries and in porous media, we have also presented novel models in the form of the binary friction model (BFM) and the velocity profile model (VPM-1).[24,25] The former was founded basically on engineers physical intuition, whereas the latter started with the formulation of a momentum balance for each species, in which a shear term was included depending on the divergence of the species velocity. Solving the differential equations for a capillary leads to the velocity profiles for each species. Subsequent integration over the pore cross-sectional area provides expressions for the averaged species fluxes. For a binary system the flux equations show that the BFM is supported by the velocity profile model.

In ample discussions with colleagues, several times the question was raised: "What is the 'real' Maxwell–Stefan equation?," especially related to teaching these matters. A good example of this is the discussion by Do[18] in his Appendix 8.5. In the present paper we intend to make our points more clear, and we attempt to establish on a fundamental level a modified basis for transport phenomena.

In the following we will try to formulate and resolve problems attached to the present state of the art in multicomponent transport. We will do this from the perspective of advanced "nuts-and-bolts" chemical engineers, who desire to make use of theoretical knowledge to be used as tools in a multitude of situations. We will start with considering some relatively simple systems, and show the problems involved with attempting to apply basic theory to them. The main problem will be shown to stem from the appearance of the mass-averaged velocity in several places in the base equations; this is caused by the choice of this velocity as the mathematical frame of reference. The confusion around the occurrence of the stress tensor in the momentum balance will be elucidated. The next section goes in depth into the derivation of the Chapman–Enskog theory, to show how their approximation method introduces the relevant problematic terms into the final equations. Also attention is paid to the equations resulting from Grad's 13-moment method, given that these were used as the basis for the DGM. In the same section we discuss some aspects of the Bearman–Kirkwood theory for liquid transport, and show where in this theory the same problems result. This is followed by a short discussion of the dusty gas model. Less known to chemical engineers are the specialized works in the field of statistical mechanics, some aimed at developing theory directly connected with the transport in channels or capillaries. Some of this work will be discussed in the subsequent section. After that, we present a new solution to the Boltzmann equation for dilute monatomic gases, as an alternative to the Chapman–Enskog theory. Based on this we propose related alternative equations for transport in dense media and liquids. Following this, we will apply the new equations to several well-known limit situations. It is shown that our new equations allow the standard solution methodology to be applied for all kinds of situations, including pores and the description of Fick's experiment.

It has been our experience that the literature from statistical mechanics is hard to master without formal education in this area. Because we want chemical engineers in the same situation to have a good view on our arguments, we decided to go into detail in some derivations more than in the usual papers for specialists in the area. For these specialists we present the derivation of the new approximate solution to the Boltzmann equation, also in detail, to enable critical review of all steps. Moreover, we hope to interest specialists in statistical mechanics into further research that will help chemical engineers. This is the reason that we also describe the engineering problems in some detail.

Some Consistency Problems in Diffusion

A consistent system: Taylor dispersion

Before going to the problems associated with diffusion in capillaries and pores, we want to consider the problem of Taylor dispersion in laminar flow in a long capillary. The mathematical solution devised by Taylor[26,27] is a very good

example of creative work that formed the basis of the classic chemical engineering framework. He first solved the equation of motion for steady laminar flow of a liquid, under the assumption of absence of radial flow, negligible entrance effects, constant temperature, negligible effect of convected momentum, constant density and viscosity, and no radial pressure gradients, and so from the Navier–Stokes equation remains

$$\eta \nabla^2 u_{c,x} = -\frac{dp}{dx} \tag{1}$$

Here $u_{c,x}$ is the mass-averaged velocity in the axial x-direction. The mass-averaged velocity is defined by

$$\rho \mathbf{u}_c = \sum_i \rho_i \overline{\mathbf{v}}_i = \sum_i \rho_i \mathbf{N}_i / c_i \tag{2}$$

Here we use the notation $\overline{\mathbf{v}}_i$ for the velocity of a component, averaged over its molecular velocity distribution, as will be discussed in more detail in a later section ("Analysis of the Classic Diffusion Equations").

For the divergence only the radial component remains, and so we have

$$\eta \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial u_{c,x}}{\partial r} \right) = -\frac{dp}{dx} \tag{3}$$

This is solved with the following boundary conditions

$$r = 0 \qquad \frac{\partial u_{c,x}}{\partial r} = 0 \tag{4a}$$

$$r = r_p \qquad u_{c,x} = 0 \tag{4b}$$

to result in the well-known Poiseuille parabolic velocity profile

$$u_{c,x} = -\frac{1}{4\eta} \frac{dp}{dx} \left[1 - \left(\frac{r}{r_p} \right)^2 \right] = \frac{1}{4\eta} \frac{\Delta p}{L} \left[1 - \left(\frac{r}{r_p} \right)^2 \right] \tag{5}$$

Integration gives the cross-sectional area-averaged velocity

$$\langle u_{c,x} \rangle = \frac{1}{\pi r_p^2} 2\pi \int_0^{r_p} r u_{c,x} dr = \frac{r_p^2}{8\eta} \frac{\Delta p}{L} \tag{6}$$

Superposed on this is now assumed the unsteady convection–diffusion equation for a tracer component a in the absence of chemical reaction

$$\frac{\partial c_a}{\partial t} = -(\nabla \cdot c_a \mathbf{u}_c) + (\nabla \cdot c_t D_{ab} \nabla x_a) \tag{7}$$

In our notation we use D_{ij} for the Fickian diffusion coefficient, and $\mathcal{D}_{ij}$ for the Maxwell–Stefan (MS) diffusion coefficients. The latter notation is chosen in accordance with the
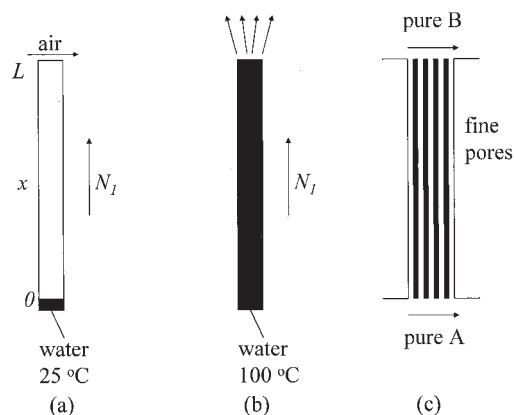

Figure 1. Representation of transport in three situations, leading to different ways of modeling, after Whitaker.[29,30]

classic texts on diffusion; in modern texts the symbol $Ð_{ij}$ is also used for the MS diffusivities.

Here Eq. 7 can be simplified to

$$\frac{\partial c_a}{\partial t} = -u_{c,x} \frac{\partial c_a}{\partial x} + D_{ab} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c_a}{\partial r} \right) + \frac{\partial^2 c_a}{\partial x^2} \right] \tag{8}$$

With a number of elegant simplifications, and a coordinate transformation for the tracer diffusion, Taylor obtained the approximate analytical equation for the concentration distribution. Several authors have used these results in measuring diffusion coefficients, as we also have in our own laboratory.[28] Without going into further detail about the solution, we see that here first a momentum balance is solved for the liquid as a whole, after which a diffusion–convection equation is solved for the tracer. The result is quite satisfactory.

Gas diffusion in tubes and pores

Whitaker[29,30] drew attention to the problem of the Stefan tube, and more generally to the fact that depending on the context students and academics intuitively choose a way of formulating the transport mathematically. In Figure 1 some of his discussed ideas are shown. In Figure 1a, the chemical engineers reflex is to state: "This is a Stefan diffusion problem," and a simple steady-state diffusion equation is acquired from Bird et al.[1] (Table 17.8-2, p. 537)

$$N_1 = N_t x_1 - c_t D_{12} \frac{dx_1}{dx} \tag{9}$$

which then is solved, assuming no dependency of the water vapor (1) flux on the radial coordinate, and stagnant air (2), leading to

$$N_1 = c_t D_{12} \frac{x_{1,0} - x_{1,L}}{L(1 - x_1)_{\ln}} \tag{10}$$

in which $(1 - x_1)_{\ln}$ is the logarithmic average of the air mole fraction (Bird et al.[1]; p. 548). In Figure 1b one is tempted to
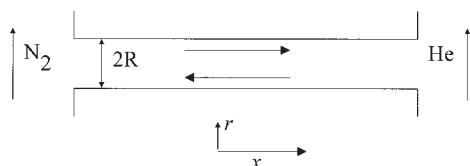
Figure 2. Schematic representation of counterdiffusion experiment of He and N$_2$, in capillaries of 39.1 μm diameter and 9.6 mm length, at 300 K, by Remick and Geankoplis.[38]

formulate a momentum balance, which after integration for a thin tube would result in a Hagen–Poiseuille expression. Often wall-slip is neglected, and so the same boundary equations as in Eq. 3 are used. The difference here with the Taylor example is that the expansion of the gas upon passage through the tube is taken into account, which leads to

$$\langle \rho u_c \rangle = \frac{\rho_0 + \rho_L}{2} \frac{r_p^2 \Delta p}{8 \eta L} \qquad (11)$$

and so here momentum transfer is chosen as a model.

Confronted with the situation as in Figure 1c many students will go to a textbook on multicomponent transport, and will try to find an answer by using the dusty gas model, or a simpler lumped-parameter equation. The point made by Whitaker is that apparently there is no common framework in education that would automatically set readers on the trail of a momentum balance. Earlier, the fact that in the Stefan problem there is a net flow, and thus there should be a momentum balance included in the treatment, was also recognized by other authors, such as Heinzelmann et al.,[31] Rao and Bennett,[32] and Meyer and Kostin.[33] The first two papers approach the momentum balance by directly assuming a parabolic velocity profile, and subsequently solving the diffusion–convection equation in a manner similar to that devised by Taylor. Meyer and Kostin solved the coupled equations for momentum transfer and diffusion in both the radial and the axial directions, for a wide slim tube of rectangular cross section. For the momentum balance they used the steady-state Navier–Stokes equation for the mass-averaged velocity. This was coupled to the fluxes through Eq. 2. By application of boundary conditions such as zero flux through the vessel walls, and a zero velocity for both components at the walls, they solved the problem numerically. From their results it is clear that the "stagnant" air is in fact circulating, a phenomenon earlier suggested by Rao and Bennett. In our own recent work on the velocity profile model we came to similar conclusions from a different set of equations, although we took wall-slip into account.[25] Whitaker[34] derived a criterion to estimate when the approximation of a virtually flat velocity profile is justified. His starting point is the species momentum balance, which in the absence of chemical reaction can be written as

$$\rho_i \left(\frac{\partial \overline{\mathbf{v}}_i}{\partial t} + \overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i \right) = -\nabla p_i + \rho_i \hat{\mathbf{F}}_i + \nabla \cdot \boldsymbol{\pi}_i + p \sum_{j=1}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i) \qquad (12)$$

in which he does not give a further expression for the partial stress tensor $\boldsymbol{\pi}_i$. He comments that in principle there are $n - 1$ independent species equations, and the nth equation is that for the momentum of the mixture as a whole

$$\rho \left(\frac{\partial \mathbf{u}_c}{\partial t} + \mathbf{u}_c \cdot \nabla \mathbf{u}_c \right) = -\nabla p + \sum_{i=1}^{n} \rho_i \hat{\mathbf{F}}_i + \nabla \cdot \boldsymbol{\pi} \qquad (13)$$

where the total stress tensor is given by

$$\boldsymbol{\pi} = \sum_{i=1}^{n} \left[\boldsymbol{\pi}_i - \rho_i \overline{(\mathbf{v}_i - \mathbf{u}_c)(\mathbf{v}_i - \mathbf{u}_c)} \right] \qquad (14)$$

He did not solve the equations, but made order-of-magnitude estimates to find the criterion for the traditional Stefan diffusion equation to hold in close approximation

$$\frac{\eta \mathscr{D}_{wa}}{4 p r_p^2} \ll x_a \qquad (15)$$

Let us now consider the counterdiffusion of two ideal gases in a thin, long capillary. Experiments for binary mixtures have been reported by Graham,[35] Kramers and Kistemaker,[36] Waldmann and Schmitt,[37] and Remick and Geankoplis.[38] The latter reported experimental flux data through a bundle of capillaries, for a setup in which on each side nearly pure gases were present at equal pressures, as indicated in Figure 2. In Figure 3 their results are presented as velocities, at the point where the mole fractions are equal, in dependence on the total pressure. For the formulation of a detailed model, it would seem logical to use the foregoing methodology, and thus first solve the equation for the mass-averaged velocity and, subsequently, solve the equation for the individual components. The experiments were performed under steady state, one may assume that the con-
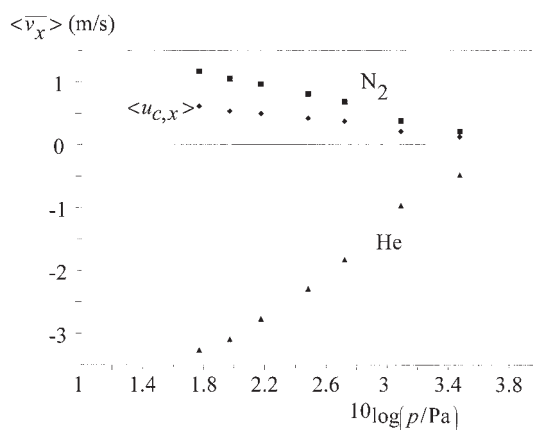

Figure 3. Velocities of both components, and mass-averaged velocity, deduced from experimental data of Remick and Geankoplis,[38] evaluated at 50 mol %.

vected momentum is small, and there are no external forces. This would lead to the equation for the mixture

$$-\nabla p + \nabla \cdot \boldsymbol{\pi} \approx 0 \qquad (16)$$

and because the process is isobaric, we have

$$\nabla \cdot \boldsymbol{\pi} \approx 0 \qquad (17)$$

To find the differential equation for the mass-averaged velocity, one needs an expression for $\boldsymbol{\pi}$. From the Chapman–Enskog approach, as will be discussed in more detail in a later section, it follows that

$$\boldsymbol{\pi} = -2\eta_t \mathbf{S} \qquad (18)$$

with $\mathbf{S}$ the rate-of-deformation tensor

$$\mathbf{S} = \frac{1}{2}\left[\nabla \mathbf{u}_c + (\nabla \mathbf{u}_c)^T - \frac{2}{3}(\nabla \cdot \mathbf{u}_c)\mathbf{I}\right] \qquad (19)$$

For convenience, expressions for the component of $\mathbf{S}$ in Cartesian and cylindrical coordinate systems are given in Appendix A.

In the absence of radial transport, Eq. 17 becomes

$$-\eta \frac{1}{r}\frac{d}{dr}\left(r \frac{du_{c,x}}{dr}\right) = 0 \qquad (20)$$

Simple integration then leads to

$$u_{cx} = c_1 = \text{constant} \qquad (21)$$

If one would apply no-slip boundary conditions

$$r = r_p \qquad u_{cx} = 0 \qquad (22)$$

one would directly obtain the following result

$$u_{cx} = c_1 = 0 \qquad (23)$$

A more realistic boundary condition could be the Maxwell-slip condition[24,39]

$$r = r_p \qquad \overline{\nu_{i,x}} = -G_i \frac{d\nu_{i,x}}{dr}\bigg|_{r=r_p} \qquad (24)$$

For the binary system here we would have

$$\rho_1 \overline{\nu_{1,x}} + \rho_2 \overline{\nu_{2,x}} = \rho c_1$$
$$\rho_1 \frac{d\overline{\nu_{1,x}}}{dr} + \rho_2 \frac{d\overline{\nu_{2,x}}}{dr} = 0 \qquad (25)$$

However, in the absence of radial partial pressure gradients, we have from Eq. 12
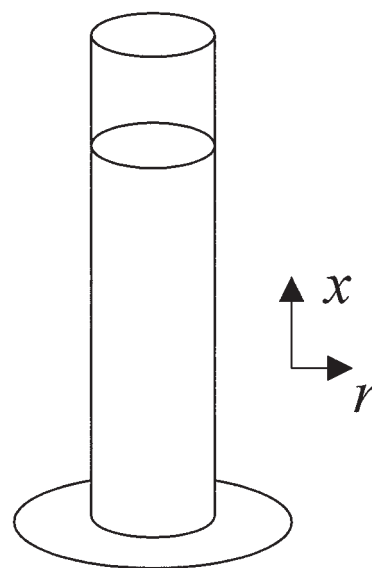

Figure 4. Schematic representation of one of the experimental setups of Fick[40] for the study of diffusion in aqueous salt solutions.

$$\frac{n_1 n_2}{n^2 \mathscr{D}_{12}}\left(\frac{d\nu_{1,x}}{dr} - \frac{d\nu_{2,x}}{dr}\right) = 0 \qquad (26)$$

and so

$$\frac{d\overline{\nu_{1,x}}}{dr} = \frac{d\overline{\nu_{2,x}}}{dr} = 0 \qquad (27)$$

and through Eq. 24

$$\overline{\nu_{1,x}} = \overline{\nu_{2,x}} = 0 \qquad (28)$$

also leading to zero mass-averaged velocity. This is clearly in contradiction with the experimental observations.

Here we conclude that the methodology, which works well for the Taylor dispersion method, seems to work well for the Stefan problem but does not work for the Remick and Geankoplis type of experiment. As we will discuss in the section on "Other Approaches from Statistical Mechanics," another kind of approach from statistical mechanics would be to directly derive an approximate solution for a tube. As will be clear from that section, this approach does not help us engineers very much.

In the section "Analysis of the Classic Diffusion Equations" we will discuss the various forms in which the momentum balance (Eq. 12) appears, as derived from statistical mechanics.

How to describe Fick's experiment

As a next, subtle example we may take one of the experiments of Fick,[40] the diffusion of salt (1) in water (2) in a cylindrical vessel, which is illustrated in Figure 4. The first Fick's law is expressed as

$$N_1 = -D_{12} \frac{dc_1}{dx} \tag{29}$$

Let us first tackle this problem with the diffusion Eq. 9

$$N_1 = N_t x_1 - c_t D_{12} \frac{dx_1}{dx} \tag{9}$$

Often it is stated that one needs to assume a contant molar density to transform Eq. 9 to Eq. 29. Less known is that the assumption of negligible volume contraction is sufficient. Then the following would hold

$$N_1 \bar{V}_1 + N_2 \bar{V}_2 = 0 \tag{30}$$

and also

$$c_1 \bar{V}_1 + c_2 \bar{V}_2 = 1 \tag{31}$$

This leads to

$$c_t \frac{dx_1}{dx} = c_t \left(\frac{1}{c_t} - \frac{c_1}{c_t^2} \frac{dc_t}{dc_1} \right) \frac{dc_1}{dx}$$

$$= c_t \left[\frac{1}{c_t} - \frac{c_1}{c_t^2} \left(1 - \frac{\bar{V}_1}{\bar{V}_2} \right) \right] \frac{dc_1}{dx} = \frac{1}{c_t \bar{V}_2} \frac{dc_1}{dx}$$

$$\langle N_1 \rangle - \langle N_t \rangle x_1 = \langle N_1 \rangle \left[1 - \left(1 - \frac{\bar{V}_1}{\bar{V}_2} \right) \frac{c_1}{c_t} \right] = \frac{1}{c_t \bar{V}_2} \langle N_1 \rangle$$

$$\tag{32}$$

and so Eq. 29 follows.

In words Eq. 30 states that the volume-averaged velocity is equal to zero. Because of the changes in density, however, this means that the mass-averaged velocity is not equal to zero.

Now let us consider the momentum balance. Bearman and Kirkwood[41] arrived from statistical mechanics to the following system of equations

$$\frac{\partial \rho_i \bar{v}_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_c \mathbf{u}_c) = \eta_i \nabla^2 \mathbf{u}_c + (\varphi_i + \eta_i/3) \nabla \nabla \cdot \mathbf{u}_c$$

$$- c_i \nabla_T \mu_i - \sum_{j=1}^{n} c_i R_{ij} \mathbf{j}_j - c_i R_{i0} \mathbf{q} + c_i \mathbf{F}_i \tag{33a}$$

$$\mathbf{q} = -\lambda \kappa T \nabla \ln T + \sum_{j=1}^{n} Q_j^* \mathbf{j}_j \tag{33b}$$

with

$$\mathbf{j}_i = c_i (\bar{v}_i - \mathbf{u}_c) \tag{34}$$

Here the φ_i and η_i are partial bulk and dynamic viscosities, respectively; the summation gives the values for the mixture as a whole.

They also show that in summing over all components the following Navier–Stokes equation is obtained

$$\rho \frac{\partial \mathbf{u}_c}{\partial t} + (\nabla \cdot \rho \mathbf{u}_c \mathbf{u}_c) = -\nabla p + \eta_t \nabla^2 \mathbf{u}_c$$

$$+ (\varphi + \eta/3) \nabla \nabla \cdot \mathbf{u}_c + \sum_{i=1}^{n} c_i \mathbf{F}_i \tag{35}$$

If we neglect bulk viscosity, and consider transport only in the x-direction, from Eq. 35 it follows that

$$\frac{dp}{dx} + \rho g - \frac{1}{r} \frac{\partial}{\partial r} \left(r \eta \frac{\partial u_{c,x}}{\partial r} \right) = 0 \tag{36}$$

The pressure gradient is balanced by the hydrostatic pressure, and so this would lead to

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \eta \frac{\partial u_{c,x}}{\partial r} \right) = 0 \tag{37}$$

Solving this with a no-slip condition at the wall would lead to a zero mass-averaged velocity, which is in conflict with experimental observation.

The next question is how to obtain Eq. 9 from the Bearman and Kirkwood equations. Again, neglecting bulk viscosity and the absence of temperature gradients, and negligible inertial effects are assumed. Equation 33a can then be written for transport in the x-direction as

$$c_i \nabla_T \mu_i = \eta_i \nabla^2 u_{c,x} - \sum_{j=1}^{n} c_i R_{ij} j_{j,x} + c_i F_{i,x} \tag{38}$$

or, alternatively, as shown by Mason and Viehland,[23] as

$$\sum_{j=1}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} (\bar{v}_{i,x} - \bar{v}_{j,x}) = -\frac{x_i}{RT} \nabla_T \mu_i + \frac{\eta_i}{c_t RT} \nabla^2 u_{c,x} + \frac{x_i}{RT} F_{i,x}$$

$$\tag{39}$$

or in terms of fluxes

$$\sum_{j=1}^{n} \frac{N_i x_j - N_j x_i}{c_t \mathscr{D}_{ij}} = -\frac{x_i}{RT} \nabla_T \mu_i + \frac{\eta_i}{c_t RT} \nabla^2 u_{c,x} + \frac{x_i}{RT} F_{i,x} \tag{40}$$

Here we have a generalized driving force, and so this type of equation is known as the "generalized Stefan–Maxwell equation."

For a component in a liquid the driving force is expressed as

$$\frac{x_i}{RT} \frac{d\mu_i}{dx} \bigg|_T = \frac{x_i}{RT} \frac{d\mu_i}{dx} \bigg|_{P,T} + \frac{x_i \bar{V}_i}{RT} \frac{dp}{dx}$$

$$= x_i \sum_{j=1}^{n-1} \frac{\partial \ln a_i}{\partial x_j} \frac{dx_j}{dx} + \frac{x_i \bar{V}_i}{RT} \frac{dp}{dx}$$

$$= \sum_{j=1}^{n-1} \left(x_i \frac{\partial \ln \gamma_i}{\partial x_j} + \delta_{ij} \right) \frac{dx_j}{dx} + \frac{x_i \bar{V}_i}{RT} \frac{dp}{dx} = \sum_{j=1}^{n-1} \Gamma_{ij} \frac{dx_j}{dx} + \frac{x_i \bar{V}_i}{RT} \frac{dp}{dx}$$

$$(41)$$

in which Γ_{ij} is Krishna's "thermodynamic factor." [42]

For a binary mixture we have

$$\frac{x_1}{RT} \frac{d\mu_1}{dx} \bigg|_T = \left(\frac{\partial \ln \gamma_1}{\partial x_1} + 1 \right) \frac{dx_1}{dx} + \frac{x_1 \bar{V}_1}{RT} \frac{dp}{dx} = \Gamma_{11} \frac{dx_1}{dx} + \frac{x_1 \bar{V}_1}{RT} \frac{dp}{dx}$$

$$(42)$$

Should we assume that Eq. 39 holds, and that the body force for component 1 can be written as

$$c_1 F_{1,x} = \rho_1 g \qquad (43)$$

it follows that Eq. 40 becomes

$$\frac{N_{1,x} x_2 - N_{2,x} x_1}{\mathcal{D}_{12}} = -c_t \Gamma_{11} \frac{dx_1}{dx} + \frac{1}{RT} (\rho_1 - c_1 \bar{V}_1 \rho) g \quad (44)$$

The last term within brackets is equal to zero only if the partial molar volumes of the components are equal, and so the density is constant. In that case it follows that

$$N_{1,x} = (N_{1,x} + N_{2,x}) x_1 - c_t \mathcal{D}_{12} \Gamma_{11} \frac{dx_1}{dx} = N_{t,x} x_1 - c_t \mathcal{D}_{12} \frac{dx_1}{dx}$$

$$(45)$$

in which the Fickian diffusion coefficient $\mathcal{D}_{12}$ is coupled to the Maxwell–Stefan diffusion coefficient $\mathcal{D}_{12}$ by the well-known Darken relation[43,43]:

$$D_{12} = \mathcal{D}_{12} \Gamma_{11} \qquad (46)$$

However, this means that the same set of relationships that leads to the zero mass-averaged velocity also leads to Eq. 9, which together with our physical intuition of a zero volume-averaged velocity leads to a nonzero mass-averaged velocity. Also we need to assume a constant density to obtain the simplified diffusion equation from the general Bearman–Kirkwood equations. So we have an internal discrepancy here.

One may ask why to go through such troubles, given that the experiment is clearly a diffusion experiment. However, the foregoing shows that there are internal inconsistencies in the description of a very simple experiment. Although practical chemical engineers can readily find their way with the diffusion Eq. 9, it means that things are getting pretty confusing when the experimental situation is more complicated, such as in pressure-driven flow of a mixture through a pore in a membrane. The foregoing shows that we may expect to have at least some troubles in applying the results of the Bearman–Kirkwood
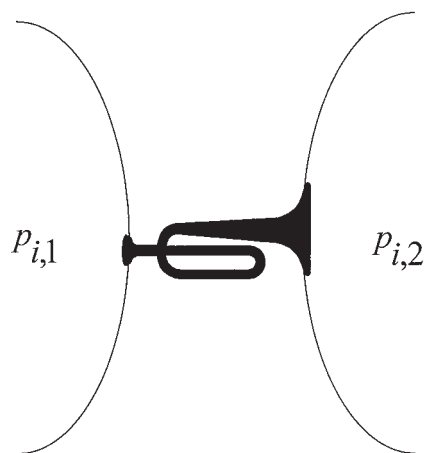

Figure 5. Schematic representation of transport through an object of complicated shape, with two openings.

theory. We will come back to the theory in the section on "Analysis of the Classic Diffusion Equations."

Irreversible thermodynamics and the meso-trumpet

Let us imagine that we want to calculate the multicomponent transport in a novel very small instrument of a trumpet shape, such as sketched in Figure 5. Let it be so small and the circumstances such that there occurs no turbulence. In view of the experience in the foregoing example, we decide to investigate this through the framework of irreversible thermodynamics. We agree with the statement of Cussler[5] that "the theory is quite intimidating," and will show that in the form most well known to our profession there are some serious problems. First, however, we want to approach the problem from the physical angle, in terms of system definition. On both open sides we prescribe a set of partial pressures, and we assume the given temperature, the absence of external forces, and a fully prescribed geometry. Should we build and operate the instrument, then we can in principle sample both the species velocities and partial pressures at each point in space. This means that in principle we can know all species fluxes and partial pressures, and consequently also species velocity gradients in all directions. Going one step further, it seems logical to assume that within the instrument for a given set of conditions, only one single set of species velocities (and gradients) and partial pressures will develop in the steady state, even if we do not perform measurements. It also is logical that if for each species the local velocities and partial pressures are fixed, then the mixture velocity, its gradients, and the total pressure are also fixed.

Let us now review some of the results of "IT," in the form as presented in HCB[13] and by Lightfoot,[4] followed by many others in the textbooks well known to us (Bird et al.[1]; Chapter 24).

The starting point is the entropy production, moving with the mass-averaged velocity:

$$\rho T \frac{D\hat{S}}{Dt} = -T\nabla \cdot \left[(\mathbf{q}/T) - \sum_{i=1}^{n} \mathbf{j}_i \mu_i / M_i T \right] - \mathbf{q} \cdot \nabla \ln T$$

$$- \sum_{i=1}^{n} \mathbf{j}_i \cdot \left[T\nabla \left(\frac{\mu_i}{TM_i} \right) - \mathbf{F}_i^m \right] + \boldsymbol{\pi} : \nabla \mathbf{u}_c - \sum_{i=1}^{n} \mu_i R_{\nu i} \quad (47)$$

De Groot and Mazur[44] derived that the Curie principle holds, stating that there is no coupling between the mass and heat fluxes and forces, which are of order 1 (vectorial) and the flux and force in the viscous dissipation term, which are of order 2 (tensorial). The stress tensor is defined here identical to Eq. 18.

The definition of forces and fluxes in several treatments is very confusing, as criticized by Truesdell.[45] He also strongly criticized the lack of fundamental background of the Curie principle, and showed that this principle cannot be found in the original paper by Curie.[46] The mass-transfer force in the above equation is given by[4]

$$\boldsymbol{\Lambda}_i = \nabla_{T,p} \frac{\mu_i}{M_i} + \frac{\bar{V}_i}{M_i} \nabla p - \hat{\mathbf{F}}_i \quad (48)$$

An arbitrary step is now made by addition of a term, $1/\rho(-\nabla p + \sum_{i=1}^{n} \rho_i \hat{\mathbf{F}}_i)$, to these forces, for "convenience," and for the fluxes the choice is made to take the velocities. Retaining the mass fluxes, a similar addition is made by Curtiss and Bird.[47] This leads then to the equivalence

$$\sum_{i=1}^{n} (\mathbf{j}_i \cdot \boldsymbol{\Lambda}_i) = \sum_{i=1}^{n} \left(\mathbf{j}_i \cdot \left[\boldsymbol{\Lambda}_i - \frac{1}{\rho} \nabla p + \sum_{k=1}^{n} \omega_k \hat{\mathbf{F}}_k \right] \right)$$

$$= \sum_{i=1}^{n} \left((\bar{\mathbf{v}}_i - \mathbf{u}_c) \cdot \left[\rho_i \boldsymbol{\Lambda}_i - \frac{\rho_i}{\rho} \nabla p + \rho_i \sum_{k=1}^{n} \omega_k \hat{\mathbf{F}}_k \right] \right)$$

$$= \sum_{i=1}^{n} [(\bar{\mathbf{v}}_i - \mathbf{u}_c) \cdot cRT\mathbf{d}_i] \quad (49)$$

$$\sum_{i=1}^{n} (\mathbf{j}_i \cdot \boldsymbol{\Lambda}_i) = \sum_{i=1}^{n} [(\bar{\mathbf{v}}_i - \mathbf{u}_c) \cdot cRT\mathbf{d}_i] \quad (50)$$

with the "diffusional driving forces" (Bird et al.[1]; p. 766):

$$cRT\mathbf{d}_i \equiv c_i \nabla_{T,p} \mu_i + (c_i \bar{V}_i - \omega_i)\nabla p - \rho_i \left(\hat{\mathbf{F}}_i - \sum_{k=1}^{n} \omega_k \hat{\mathbf{F}}_k \right) \quad (51)$$

This is in our view an arbitrary construct to obtain the analog of the driving force as developed in kinetic theory of dilute gases, as we will see in the next section.

The following expression is subsequently developed:

$$\mathbf{d}_i = \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} (\bar{\mathbf{v}}_j - \bar{\mathbf{v}}_i) - \frac{B_{i0}}{c_t RT} [\mathbf{q}^{(c)} + \mathbf{q}^{(x)}] \quad (52)$$

If we do not make the addition, we end with the simpler formulation

$$\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} (\bar{\mathbf{v}}_j - \bar{\mathbf{v}}_i) - \frac{B_{i0}}{c_t RT} [\mathbf{q}^{(c)} + \mathbf{q}^{(x)}]$$

$$= \frac{1}{c_t RT} [c_i \nabla \mu_i |_{T,p} + c_i \bar{V}_i \nabla p - \rho_i \hat{\mathbf{F}}_i] \quad (53)$$

From the momentum balance for the fluid as a whole, it follows that

$$cRT\mathbf{d}_i \equiv c_i \nabla_{T,p} \mu_i + c_i \bar{V}_i \nabla p - \rho_i \hat{\mathbf{F}}_i + \rho_i \frac{D\mathbf{u}_c}{Dt} - \frac{\rho_i}{\rho} \nabla \cdot \boldsymbol{\pi} \quad (54)$$

So, even in steady diffusion, the addition has included the stress tensor in the driving force, and so effectively a coupling is present between the unequal order tensors. This, together with our physical argument at the start of this section, shows that once again we have a problem of internal inconsistency with the above formulation. In addition, the arguments about the formal number of independent diffusion coefficients and the use of arbitrary reference velocities make the treatment virtually incomprehensible even for advanced readers.

Analysis of the Classic Diffusion Equations

In the foregoing we found consistency problems within several classic theories. They were demonstrated by the behavior of the mass-averaged velocity in the examples of the Remick–Geankoplis experiment and the Fick experiment, and by basic physical reasoning for the meso-trumpet. What we will show in this section is that this is a direct consequence of the choice of the mass-averaged velocity as a reference frame, which has profound consequences for all further approximations and introduced definitions.

The shape of the Chapman–Enskog, Hirschfelder–Curtiss–Bird, and Zhdanov–Kagan–Sazykin equations for dilute monatomic gases

One of the classical diffusion equations is the result of the Chapman–Enskog (CE) approach.[12] For a dilute mixture of monatomic gases they obtained an approximate solution of the linearized Boltzmann equation, by means of a series expansion of the velocity distributions in Sonine polynomials. We will discuss some of the details in the next paragraph. In terms of the species momentum balance their equation reads

$$\sum_j \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} (\bar{\mathbf{v}}_i - \bar{\mathbf{v}}_j) = -\mathbf{d}_i - \left[\sum_j \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} \left(\frac{D_i^T}{n_i m_i} - \frac{D_j^T}{n_j m_j} \right) \right] \nabla \ln T$$

$$(55)$$

with the "driving force"

$$\mathbf{d}_i \equiv \nabla\left(\frac{n_i}{n}\right) + \left(\frac{n_i}{n} - \frac{n_i m_i}{\rho}\right)\nabla \ln p - \left(\frac{n_i m_i}{p\rho}\right)\left(\frac{\rho}{m_i}\mathbf{X}_i - \sum_j n_j\mathbf{X}_j\right)$$

(56)

In Eq. 55, the Chapman–Enskog momentum balance for component i, for dilute gases, to the terms shown in Eq. 56 in $\mathbf{d}_i$, as mechanisms are ascribed[1]: concentration diffusion, pressure diffusion, and forced diffusion, to which in Eq. 55 thermal diffusion is added. Also quoted is the momentum balance for the mixture as a whole:

$$\rho \frac{\partial \mathbf{u}_c}{\partial t} + \rho \mathbf{u}_c \cdot \nabla \mathbf{u}_c + \nabla \cdot \boldsymbol{\pi} = -\nabla p + \sum_{j=1}^{n} n_j\mathbf{X}_j$$

(57)

in which the stress tensor, assuming ideal gas behavior, can be written as

$$\boldsymbol{\pi} = \sum_{j=1}^{n} \boldsymbol{\pi}_j = -2\mathbf{S} \sum_{j=1}^{n} \eta_j = -2\eta_t\mathbf{S}$$

(58)

with $\mathbf{S}$ given by Eq. 19.

In Eq. 57 for steady state the first term is dropped, whereas for many processes the second term, the convected momentum, may be neglected. Under these circumstances Eq. 57 reduces to

$$\nabla \cdot \boldsymbol{\pi} = -\nabla p + \sum_{j=1}^{n} n_j\mathbf{X}_j$$

(59)

This means that $\mathbf{d}_i$ can also be written as

$$\mathbf{d}_i = \nabla\left(\frac{n_i}{n}\right) + \frac{n_i}{n}\nabla \ln p + \frac{n_i m_i}{p\rho}\nabla \cdot \boldsymbol{\pi} - \frac{n_i}{p}\mathbf{X}_i$$

$$= \frac{1}{p}\nabla p_i + \frac{n_i m_i}{p\rho}\nabla \cdot \boldsymbol{\pi} - \frac{n_i}{p}\mathbf{X}_i \quad (60)$$

and so one could also view the driving force to be built up of a partial pressure gradient, a contribution of the overall shear force, and the external force on i.

Grad[48] developed another approximation to the velocity distribution functions through his method of moments. Based on the 13-moment result, Zhdanov et al.[49] (ZKS) derived an expression for the momentum balance, which was formulated by Zhdanov[50] as

$$\sum_{j=1}^{n} \frac{n_i n_j kT}{n_t \mathcal{D}_{ij}}(\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i) = \nabla p_i + (\nabla \cdot \boldsymbol{\pi}_i) - n_i\mathbf{X}_i$$

(61)

in which the elements of the stress tensor $\boldsymbol{\pi}_i$ are given by

$$\boldsymbol{\pi}_{i,kl} = -2\eta_i \varepsilon_{kl}$$

(62)

and

$$\varepsilon_{kl} = \frac{\partial u_{c,k}}{\partial x_l} + \frac{\partial u_{c,l}}{\partial x_k} - \frac{2}{3}(\nabla \cdot \mathbf{u}_c) \qquad x_{j,k,l} = x, y, z \quad (63)$$

Zhdanov[50] also states that the thermal diffusion term $-\sum_{j=1}^{n} x_i x_j \alpha_{ij}\nabla \ln T$ can be added to the right-hand side of Eq. 61. Inspection of the ZKS paper shows that there must have been a typing error in the equivalent of Eq. 63 because the stress tensor would become a factor 2 too high. In the notation they used, the rate-of-deformation tensor should be half of that in Eq. 63 (see also the comparable Eq. 19 in the Chapman–Enskog development).

Next to Mason et al.[21] (MME) in their development of the dusty gas model, Zhdanov and Roldughin[50,51] also used Eq. 61 as the starting point in their study of the transport in capillaries.

The MME paper essentially is devoted to two tasks. One is the derivation of the transport equation itself, and the other is the accurate calculation of the transport coefficients by including second-order effects. Because these two lines of work are followed simultaneously, the tractability of the paper is very difficult to chemical engineers. For clarity we present the equations here with the second-order corrections included in the coefficients. Also we have removed the factor 2 in the stress tensor, correcting the mistake mentioned above. Their starting equation, again the species momentum balance, for transport in the x-direction, for the present application may then be quoted as

$$\sum_{j=1}^{n} \frac{1}{n_t^2 \mathcal{D}_{ij}}(n_j J_{i,x} - n_i J_{j,x}) = -\frac{1}{p}\left(\frac{\partial p_i}{\partial x} - \frac{\rho_i}{\rho}\frac{\partial p}{\partial x}\right)$$

$$+ \frac{1}{p}\left(n_i X_{i,x} - \frac{\rho_i}{\rho}\sum_{j=1}^{n} n_j X_{j,x}\right) - \sum_{j=1}^{n} x_i x_j \alpha_{ij}\frac{\partial \ln T}{\partial x}$$

$$+ \frac{1}{p}\left(\eta_i - \frac{\rho_i}{\rho}\eta_t\right)\left(\frac{\partial \varepsilon_{xx}}{\partial x} + \frac{\partial \varepsilon_{xy}}{\partial y} + \frac{\partial \varepsilon_{xz}}{\partial z}\right) \quad (64)$$

In the transition from Eq. 61 the equalities $p = n_t kT$ and $J_{i,x} = n_i \overline{v}_{i,x}$ have been used. For the isothermal steady motion of the gas as a whole, they also provide the following equation (again corrected for the factor 2):

$$\eta_t\left(\frac{\partial \varepsilon_{xx}}{\partial x} + \frac{\partial \varepsilon_{xy}}{\partial y} + \frac{\partial \varepsilon_{xz}}{\partial z}\right) = \frac{\partial p}{\partial x} - \sum_{j=1}^{n} n_j X_{j,x}$$

(65)

From this it follows that

$$\frac{\rho_i}{\rho}\frac{\partial p}{\partial x} - \frac{\rho_i}{\rho}\sum_{j=1}^{n} n_j X_{j,x} + \frac{\rho_i}{\rho}\eta_t\left(\frac{\partial \varepsilon_{xx}}{\partial x} + \frac{\partial \varepsilon_{xy}}{\partial y} + \frac{\partial \varepsilon_{xz}}{\partial z}\right) = 0 \quad (66)$$

and so we could simplify Eq. 64 to

$$\sum_{j=1}^{n} \frac{1}{n_t^2 \mathcal{D}_{ij}} \left(n_j J_{i,x} - n_i J_{j,x} \right) = -\frac{1}{p} \frac{\partial p_i}{\partial x} + \frac{1}{p} n_i X_{i,x}$$

$$- \sum_{j=1}^{n} x_i x_j \alpha_{ij} \frac{\partial \ln T}{\partial x} + \frac{1}{p} \eta_i \left(\frac{\partial^2 u_{c,x}}{\partial x^2} + \frac{\partial^2 u_{c,x}}{\partial y^2} + \frac{\partial^2 u_{c,x}}{\partial z^2} \right) \quad (67)$$

In terms of the species velocities the following expression is now obtained

$$\sum_{j=1}^{n} \frac{n_i n_j}{n^2 \mathcal{D}_{ij}} \left(\overline{\nu_{i,x}} - \overline{\nu_{j,x}} \right) = -\frac{1}{p} \frac{\partial p_i}{\partial x} + \frac{1}{p} n_i X_{i,x} - \sum_{j=1}^{n} x_i x_j \alpha_{ij} \frac{\partial \ln T}{\partial x}$$

$$+ \frac{1}{p} \eta_i \left(\frac{\partial^2 u_{c,x}}{\partial x^2} + \frac{\partial^2 u_{c,x}}{\partial y^2} + \frac{\partial^2 u_{c,x}}{\partial z^2} \right) \quad (68)$$

The Chapman–Enskog Eq. 55 can be written, using Eqs. 19 and 60, for the x-direction

$$\sum_{j=1}^{n} \frac{n_i n_j}{n^2 \mathcal{D}_{ij}} \left(\overline{\nu_{i,x}} - \overline{\nu_{j,x}} \right) = -\frac{1}{p} \frac{\partial p_i}{\partial x} + \frac{1}{p} n_i X_{i,x} - \sum_{j=1}^{n} \frac{n_i n_j}{n^2 D_{ij}} \left(\frac{D_i^T}{n_i m_i} \right.$$

$$\left. - \frac{D_j^T}{n_j m_j} \right) \frac{\partial \ln T}{\partial x} + \frac{1}{p} \frac{\rho_i}{\rho} \eta_t \left(\frac{\partial^2 u_{c,x}}{\partial x^2} + \frac{\partial^2 u_{c,x}}{\partial y^2} + \frac{\partial^2 u_{c,x}}{\partial z^2} \right) \quad (69)$$

The difference is the viscous shear term, given that $\eta_i \neq (\rho_i/\rho)\eta_t$. For unidirectional isothermal transport, in the absence of external forces, we have Eq. 20 for the mixture as a whole. This shows again that for isobaric counterdiffusion the mass-averaged velocity would be equal to 0, by means of the integration and boundary conditions as shown in the previous section. Thus it follows that the set of Eqs. 65 and 68 cannot realistically describe isobaric counterdiffusion, and thus cannot be expected to give a good description of more complicated phenomena.

Summary of the derivation of the Chapman–Enskog and Hirschfelder–Curtiss–Bird equations for dilute monatomic gases

Both methods start with the Boltzmann equation[52]:

$$\frac{\partial f_i}{\partial t} + (\mathbf{v}_i \cdot \nabla f_i) + \frac{1}{m_i} \left(\mathbf{X}_i \cdot \frac{\partial f_i}{\partial \mathbf{v}_i} \right)$$

$$= \sum_j \int \int \int (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_j \quad (70)$$

with the notation

$$\frac{\partial}{\partial \mathbf{v}} = \mathbf{e}_1 \frac{\partial}{\partial \nu_x} + \mathbf{e}_2 \frac{\partial}{\partial \nu_y} + \mathbf{e}_3 \frac{\partial}{\partial \nu_z} \quad (71)$$

and

$$\int \ldots d\mathbf{v} = \int \int \int \ldots d\nu_x d\nu_y d\nu_z \quad (72)$$

Also we can use the notation

$$\mathcal{D} f_i = \sum_j J(f_i, f_j) \quad (73)$$

with

$$\mathcal{D} f_i \equiv \frac{\partial f_i}{\partial t} + (\mathbf{v}_i \cdot \nabla f_i) + \frac{1}{m_i} \left(\mathbf{X}_i \cdot \frac{\partial f_i}{\partial \mathbf{v}_i} \right) \quad (74)$$

and

$$J(f_i, f_j) \equiv \int \int \int (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_j \quad (75)$$

Here $g_{ij} \equiv |\mathbf{v}_i - \mathbf{v}_j|$, and the integration over $b \, db \, d\varepsilon$ represents the frequency of collisions between a molecule i and all molecules j, within a velocity range $d\mathbf{v}_j$ for a given velocity difference before collision $\mathbf{g}_{ij} \equiv \mathbf{v}_i - \mathbf{v}_j$. The velocity distributions of i and j before a collision are denoted by f_i and f_j, and those after a collision by f_i' and f_j'. Thus $J(f_i, f_j)$ represents the rate of change in the distribution function f_i through the collisions with component j. (Note also that i–i collisions are taken into account.) In a collision between two molecules the following invariants hold

$$m_i' = m_i \qquad m_j' = m_j \quad (76)$$

$$m_i \mathbf{v}_i' + m_j \mathbf{v}_j' = m_i \mathbf{v}_i + m_j \mathbf{v}_j \quad (77)$$

$$\frac{1}{2} m_i \nu_i'^2 + \frac{1}{2} m_j \nu_j'^2 = \frac{1}{2} m_i \nu_i^2 + \frac{1}{2} m_j \nu_j^2 \quad (78)$$

One of the key factors in the developed approximate solution is the equilibrium solution, for which

$$\int \int \int (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_j = 0 \quad (79)$$

In the classic texts, starting from Boltzmann's H-theorem it is shown that this is a linear combination of the collision invariants

$$\ln f_i^0 = \alpha_{i,1} + \boldsymbol{\alpha}_{i,2} \cdot m_i \mathbf{v}_i + \alpha_{i,3} \frac{1}{2} m_i \nu_i^2 \quad (80)$$

in which $\alpha_{i,1}$ and $\alpha_{i,3}$ are constants, and $\boldsymbol{\alpha}_{i,2}$ is a vector constant, all to be determined.

This is equivalent to

$$\ln f_i^0 = \alpha_{i,1}' + \boldsymbol{\alpha}_{i,2}' \cdot m_i(\mathbf{v}_i - \mathbf{v}_{ref}) + \alpha_{i,3}' \frac{1}{2} m_i(\mathbf{v}_i - \mathbf{v}_{ref})^2 \quad (81)$$

The constants are determined from the following equations

$$\int f_i d\mathbf{v}_i = n_i \quad (82)$$

$$\int \mathbf{v}_i f_i d\mathbf{v}_i = n_i \overline{\mathbf{v}}_i \quad (83)$$

and also follows directly

$$\int (\mathbf{v}_i - \mathbf{v}_{ref}) f_i d\mathbf{v}_i = n_i(\overline{\mathbf{v}}_i - \mathbf{v}_{ref}) \quad (84)$$

A third integral yields

$$\frac{1}{2} m_i \int (\mathbf{v}_i - \mathbf{v}_{ref})^2 f_i d\mathbf{v}_i$$

$$= \frac{1}{2} n_i m_i \overline{v_i^2} - n_i m_i \overline{\mathbf{v}}_i \cdot \mathbf{v}_{ref} + \frac{1}{2} n_i m_i v_{ref}^2 \quad (85)$$

Summation over all components gives

$$\sum_i \frac{1}{2} m_i \int (\mathbf{v}_i - \mathbf{v}_{ref})^2 f_i d\mathbf{v}_i = \sum_i \frac{1}{2} n_i m_i \overline{v_i^2} - \rho \mathbf{u}_c \cdot \mathbf{v}_{ref} + \frac{1}{2} \rho v_{ref}^2$$

$$(86)$$

For a mixture in motion, the CE and HCB approach is to define a temperature by averaging the squared velocity fluctuations with respect to the mass-averaged velocity

$$\frac{3}{2} nkT = \sum_i \frac{1}{2} m_i \int (\mathbf{v}_i - \mathbf{u}_c)^2 f_i d\mathbf{v}_i = \sum_i \frac{1}{2} n_i m_i \overline{v_i^2} - \frac{1}{2} \rho u_c^2 \quad (87)$$

and so the thermal energy is considered as the difference between a "total" kinetic energy and a "translational" kinetic energy.

Adopting this temperature definition leads to the "equilibrium" velocity distribution for a gas mixture in motion

$$f_i^0 = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp \left(-\frac{m_i(\mathbf{v}_i - \mathbf{u}_c)^2}{2kT} \right) \quad (88)$$

To complete the basic equations, we write here the equations of change. In the derivations according to Chapman–Enskog and Hirschfelder et al. the so-called collisional invariants are introduced. These are denoted by the general symbol Ψ, which may be equal to $\Psi_i = 1, m_i \mathbf{v}_i, 1/2(m_i v_i^2)$, indicating the conservation of numbers, momentum, and kinetic energy upon collisions.

For such a quantity the general equation of change reads (HCB, Eq. 7.2-31, p. 460)

$$\frac{\partial (n_i \overline{\Psi}_i)}{\partial t} + (\nabla \cdot n_i \overline{\Psi_i \mathbf{v}_i}) - n_i \left[\frac{\partial (\overline{\Psi}_i)}{\partial t} + (\overline{\mathbf{v}_i \cdot \nabla \Psi_i}) + \left(\frac{\mathbf{X}_i}{m_i} \cdot \frac{\overline{\partial \Psi_i}}{\partial \mathbf{v}_i} \right) \right]$$

$$= \sum_j \int \int \int \int \Psi_i (f_i' f_j' - f_i f_j) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j \quad (89)$$

Application of this equation leads to the equations of change.
Equation of Continuity

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \overline{\mathbf{v}}_i) = 0 \quad (90)$$

Momentum Balance

$$m_i \frac{\partial n_i \overline{\mathbf{v}}_i}{\partial t} + \nabla \cdot (m_i n_i \overline{\mathbf{v}_i \mathbf{v}_i}) - n_i \mathbf{X}_i$$

$$= \sum_j m_i \int \int \int \int \mathbf{v}_i (f_i' f_j' - f_i f_j) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j \quad (91)$$

where the overbar denotes averaging over the distribution function of i

$$\overline{\mathbf{a}} \equiv \frac{1}{n_i} \int \mathbf{a} f_i d\mathbf{v}_i \quad (92)$$

where $\mathbf{a}$ is a tensor of order 0, 1, 2.
(Partial) Kinetic Energy Balance

$$\frac{1}{2} m_i \left[\frac{\partial (n_i v_i^2)}{\partial t} + (\nabla \cdot n_i \overline{v_i^2 \mathbf{v}_i}) - 2n_i \frac{\mathbf{X}_i}{m_i} \cdot \overline{\mathbf{v}}_i \right]$$

$$= \frac{1}{2} m_i \sum_j \int \int \int \int v_i^2 (f_i' f_j' - f_i f_j) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j \quad (93)$$

For the mixture as a whole addition leads to the following.
Equation of Continuity

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}_c) = 0 \quad (94)$$

given that $\rho \mathbf{u}_c = \sum_i n_i m_i \overline{\mathbf{v}}_i$.
Momentum Balance

$$\sum_i \left(m_i \frac{\partial n_i \mathbf{v}_i}{\partial t} + \nabla \cdot (m_i n_i \overline{\mathbf{v}_i \mathbf{v}_i}) - n_i \mathbf{X}_i \right) = 0 \quad (95)$$

Energy Balance

$$\sum_i \frac{1}{2} m_i \left[\frac{\partial (n_i v_i^2)}{\partial t} + (\nabla \cdot n_i \overline{v_i^2 \mathbf{v}_i}) - 2n_i \frac{\mathbf{X}_i}{m_i} \cdot \overline{\mathbf{v}}_i \right] = 0 \quad (96)$$

For the reference velocity now is chosen the mass-averaged velocity $\mathbf{u}_c$. In the notation of HCB,[13] they introduce the following:

The Peculiar Velocity

$$\mathbf{V}_i \equiv \mathbf{v}_i - \mathbf{u}_c \qquad (97)$$

The Diffusion Velocity

$$\overline{\mathbf{V}}_i = \overline{\mathbf{v}}_i - \mathbf{u}_c \qquad (98)$$

In the solution method a series of successive approximation methods is used. The velocity distribution function is expanded in a series as

$$f_i = f_i^{[0]} + f_i^{[1]} + f_i^{[2]} + \cdots \qquad (99)$$

We will not go into the mathematical background of the series development, but refer to the original texts here (CC, HCB, Ferziger and Kaper[53]). Also we will limit the discussion to the zero and first approximations. For the zero-order approximation is taken the equilibrium solution

$$f_i^{[0]} = f_i^0 = n_i \left(\frac{m_i}{2\pi kT} \right)^{3/2} \exp\left(-\frac{m_i(\mathbf{v}_i - \mathbf{u}_c)^2}{2kT} \right) \qquad (88)$$

Thus a local equilibrium around the mass-averaged velocity is assumed. For the first-order approximation is approached

$$\frac{\partial f_i^{[0]}}{\partial t} + (\mathbf{v}_i \cdot \nabla f_i^{[0]}) + \frac{1}{m_i} \left(X_i \cdot \frac{\partial f_i^{[0]}}{\partial \mathbf{v}_i} \right)$$
$$= \sum_j \left[J(f_i^{[0]}, f_j^{[1]}) + J(f_i^{[1]}, f_j^{[0]}) \right] \qquad (100)$$

The solution of Eq. 100 is now approached by a perturbation function:

$$f_i \approx f_i^{[0]}(1 + \phi_i) \qquad (101)$$

Substitution in the collision integral, and neglecting higher-order products, leads to

$$\sum_j \left[J(f_i^{[0]}, f_j^{[1]}) + J(f_i^{[1]}, f_j^{[0]}) \right] = \sum_j \int \int \int f_i^{[0]} f_j^{[0]}$$
$$\times (\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_j \qquad (102)$$

In the lefthand side of Eq. 100 the derivatives of $f_i^{[0]}$ appear, and they can be written as

$$\frac{\partial \ln f_i^{[0]}}{\partial t} = \frac{\partial \ln n_i}{\partial t} - \left(\frac{3}{2} - \frac{m_i(\mathbf{v}_i - \mathbf{u}_c)^2}{2kT} \right) \frac{\partial \ln T}{\partial t}$$
$$+ \frac{m_i}{kT} \frac{\partial \mathbf{u}_c}{\partial t} \cdot (\mathbf{v}_i - \mathbf{u}_c) \qquad (103)$$

$$\nabla \ln f_i^{[0]} = \nabla \ln n_i - \left(\frac{3}{2} - \frac{m_i(\mathbf{v}_i - \mathbf{u}_c)^2}{2kT} \right) \nabla \ln T$$
$$+ \frac{m_i}{kT} \nabla \mathbf{u}_c \cdot (\mathbf{v}_i - \mathbf{u}_c) \qquad (104)$$

$$\frac{\partial \ln f_i^{[0]}}{\partial \mathbf{v}_i} = -\frac{m_i}{kT} (\mathbf{v}_i - \mathbf{u}_c) \qquad (105)$$

The time derivatives are now eliminated using the equations of change for the mixture. The momentum balance for the mixture is written as

$$\frac{\partial \mathbf{u}_c}{\partial t} + (\mathbf{u}_c \cdot \nabla \mathbf{u}_c) = -\frac{1}{\rho} (\nabla \cdot \boldsymbol{\pi}) + \frac{1}{\rho} \sum_i n_i \mathbf{X}_i \qquad (106)$$

in which the stress tensor is defined as

$$\boldsymbol{\pi} = \sum_i \boldsymbol{\pi}_i = \sum_i n_i m_i \overline{\mathbf{V}_i \mathbf{V}_i} = \sum_i n_i m_i \overline{(\mathbf{v}_i - \mathbf{u}_c)(\mathbf{v}_i - \mathbf{u}_c)} \qquad (107)$$

The energy balance is expressed in terms of temperature by (HCB, p. 463)

$$\frac{3}{2} nk \left[\frac{\partial T}{\partial t} + (\mathbf{u}_c \cdot \nabla T) \right] = -(\nabla \cdot \mathbf{q}_{m,c}) - (\boldsymbol{\pi} : \nabla \mathbf{u}_c)$$
$$+ \sum_i n_i (\mathbf{X}_i \cdot \overline{\mathbf{V}}_i) + \frac{3}{2} kT \left(\nabla \cdot \sum_i n_i \overline{\mathbf{V}}_i \right) \qquad (108)$$

Here $\mathbf{q}_{m,c}$ is the (classic) molecular heat flux vector

$$\mathbf{q}_{m,c} = \sum_i \mathbf{q}_{i,m,c} = \sum_i \frac{1}{2} n_i m_i \overline{V_i^2 \mathbf{V}_i} \qquad (109)$$

The time-derivatives of n_i, T, and $\mathbf{u}_c$, following from the equations of change, are substituted in the derivatives of $f_i^{[0]}$, and the averaging of the various velocity terms is approached by averaging over $f_i^{[0]}$. In this approximation the stress tensor and the heat flux are reduced to

$$\boldsymbol{\pi}^{[0]} = p\mathbf{I}$$
$$\mathbf{q}_{m,c}^{[0]} = 0 \qquad (110)$$

An additional step is made by Chapman–Enskog, the introduction of the substantial derivative

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + (\mathbf{u}_c \cdot \nabla) \qquad (111)$$

and mass, momentum, and energy balances are written in terms of these derivatives. Because the mathematical result of the substitution of the time derivatives is the same as when one does not change to the substantial derivatives, we will not discuss this here further.

The resulting equation for the perturbation function is

$$f_i^{[0]}\left[\frac{n}{n_i}(\mathbf{V}_i \cdot \mathbf{d}_i) + (\mathbf{b}_i : \nabla \mathbf{u}_c) - \left(\frac{5}{2} - W_i^2\right)(\mathbf{V}_i \cdot \nabla \ln T)\right]$$

$$= \sum_j \int \int \int f_i^{[0]} f_j^{[0]}(\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_j \quad (112)$$

with $\mathbf{d}_i$ given by Eq. 56, and

$$\mathbf{b}_i = 2\left[\mathbf{W}_i\mathbf{W}_i - \frac{1}{3}W_i^2\mathbf{I}\right] \quad (113)$$

$$\mathbf{W}_i = \mathbf{V}_i\sqrt{\frac{m_i}{2kT}} \quad (114)$$

It is shown (CC, HCB) that the perturbation function must have the form

$$\phi_i = -(\mathbf{A}_i \cdot \nabla \ln T) - (\mathbf{B}_i : \nabla \mathbf{u}_c) + n \sum_j (\mathbf{C}_i^{(j)} \cdot \mathbf{d}_i) \quad (115)$$

given that the distribution function holds within their framework

$$\int f_i \, d\mathbf{v}_i = n_i \quad (116)$$

$$\sum_i m_i \int \mathbf{v}_i f_i \, d\mathbf{v}_i = \rho\mathbf{u}_c \quad (117)$$

$$\frac{1}{2}\sum_i m_i \int (\mathbf{v}_i - \mathbf{u}_c)^2 f_i \, d\mathbf{v}_i = \frac{3}{2}nkT \quad (118)$$

Because the equilibrium function $f_i^{[0]}$ already satisfies the above equations, there remain three auxiliary equations for the ϕ_i functions

$$\int f_i^{[0]}\phi_i \, d\mathbf{v}_i = 0 \quad (119)$$

$$\sum_i m_i \int \mathbf{v}_i f_i^{[0]}\phi_i \, d\mathbf{v}_i = 0 \quad (120)$$

$$\frac{1}{2}\sum_i m_i \int (\mathbf{v}_i - \mathbf{u}_c)^2 f_i^{[0]}\phi_i \, d\mathbf{v}_i = 0 \quad (121)$$

It is shown that the coefficients must satisfy the following relations

$$\mathbf{A}_i = \mathbf{W}_i A_i(W_i) \quad (122)$$

$$\mathbf{B}_i = \left\{\mathbf{W}_i\mathbf{W}_i - \frac{1}{3}W_i^2\mathbf{I}\right\}B_i(W_i) \quad (123)$$

$$\mathbf{C}_i^{(j)} = \mathbf{W}_i C_i^{(j)}(W_i) \quad (124)$$

The coefficients $\mathbf{B}_i$ in the above form do satisfy each of the auxiliary equations, whereas these equations pose for $\mathbf{A}_i$ and $\mathbf{C}_i^{(j)}$

$$\sum_i \sqrt{m_i} \int (\mathbf{A}_i \cdot \mathbf{W}_i) f_i^{[0]} d\mathbf{v}_i = 0 \quad (125)$$

$$\sum_i \sqrt{m_i} \int \{\mathbf{C}_i^{(j)} - \mathbf{C}_i^{(k)}\} \cdot \mathbf{W}_i) f_i^{[0]} d\mathbf{v}_i = 0 \quad (126)$$

Through extended mathematics the coefficients $\mathbf{A}_i$, $\mathbf{B}_i$, and $\mathbf{C}_i^{(j)}$ are determined, in their dependence on $\mathbf{W}_i$. Chapman–Enskog approach the coefficients as an infinite series of Sonine polynomials and find the solutions for the functions $A_i(W_i)$, $B_i(W_i)$, and $C_i(W_i)$ in the form of infinite matrices. By taking one or two elements of these matrices they end with finite approximations for the coefficients. HCB use a finite series of Sonine polynomials and a variational approach to find similar approximations. After this step, the processes of molecular diffusion, thermal diffusion, heat flow, and shear are considered more or less individually, and further mathematics leads to expressions of the diffusion coefficient, the thermal diffusion coefficient, the thermal conductivity, and the viscosity. The mathematics involved for the first three of these is quite complicated. In the results of this the transport coefficients are expressed in terms of the collision integrals $\Omega_{ij}^{(l,s)}$, which allow (numerical) evaluation of the coefficients for various models for the intermolecular potential. As indicated by CC and HCB, a further development in terms of $f_i^{[2]}$ gives only a small contribution to the values of the coefficients.

The shape of the "driving force" $\mathbf{d}_i$ is the consequence of the substitution of the derivatives for the mixture as a whole into the species momentum balances. Because the equation of the mixture as a whole is used in addition to the species equations, the consequence is that the $\mathbf{d}_i$ values are not independent, and so within this framework the following expression holds

$$\sum_i \mathbf{d}_i = 0 \quad (127)$$

This and the elimination of the integral parts by adding the momentum balance over all components lead to the very complicated inversions needed to transform the multicomponent "Fickian form" of the diffusion equation to the Maxwell–Stefan type (HCB, pp. 479–487). Assuming negligible acceleration and momentum convection, the species momentum balance is expressed as

$$\sum_j \frac{n_i n_j}{n^2 \mathcal{D}_{ij}}(\overline{\mathbf{v}}_i - \overline{\mathbf{v}}_j) = -\mathbf{d}_i - \left(\sum_j \frac{n_i n_j}{n^2 \mathcal{D}_{ij}}\left(\frac{D_i^T}{n_i m_i} - \frac{D_j^T}{n_j m_j}\right)\right)\nabla \ln T$$

$$(55)$$

and for the mixture as a whole

$$\rho \, \frac{\partial \mathbf{u}_c}{\partial t} + \rho \mathbf{u}_c \cdot \nabla \mathbf{u}_c + \nabla \cdot \boldsymbol{\pi} = -\nabla p + \sum_{j=1}^{n} n_j \mathbf{X}_j \quad (57)$$

with

$$\boldsymbol{\pi} = \sum_{j=1}^{n} \boldsymbol{\pi}_j = -2\mathbf{S} \sum_{j=1}^{n} \eta_j = -2\eta_t \mathbf{S} \quad (58)$$

with $\mathbf{S}$ given by Eq. 19.

The foregoing shows that the divergence of the mass-averaged velocity $\mathbf{u}_c$, as it occurs in Eqs. 57 and 19, is the result of the assumption that the velocity distribution functions of the components are in first approximation given by the equilibrium distributions, centered around $\mathbf{u}_c$. The dependency of the distribution functions on space and time coordinates occurs in the framework of these approximations only through the dependency of n_i, T, and $\mathbf{u}_c$ on space and time coordinates. This implies that in this approach the molecular transport phenomena can be evaluated only when the description of the mass-averaged velocity is known, and so the latter is regarded as a quantity independent of the molecular transport of the species. Regarding the example of the Remick and Geankoplis experiments, the individual species velocities are not small compared to the mass-averaged velocity, and the concept of a fluid flowing independently through space, with relatively small molecular transport variations superposed on it, breaks down.

The Bearman–Kirkwood approach for liquid transport

Bearman and Kirkwood[41] extended the single-component methodology of Irving and Kirkwood[54] to multicomponent systems. The present authors do not have enough working knowledge of the Liouville method to understand the derivation in detail. However, we attempt here to follow the main steps taken in the derivation, and illustrate some of the main features that lead to the shape of their final species momentum balance. In their section 2 on the phenomenological theory, they state: "The flow pattern is determined by specifying the local velocity $\bar{\mathbf{v}}_i$ of each component i. However, more convenient independent variables are the velocity $\mathbf{u}_c$ of the local center of mass and $\nu - 1$ of the diffusion currents $\mathbf{j}_i$." This means that their framework is basically the same as that of Chapman–Enskog, as discussed for dilute monatomic gases. In section 3 they start to develop the Liouville equation for the probability distribution function, for molecules with 3 degrees of translational freedom. In section 4 they develop the equations of transport through a theorem of Irving and Kirkwood, leading to the equation of continuity, and subsequently to the "hydrodynamical equations of motion." In their Eq. 4.7 they change from the velocity with respect to fixed coordinates, $\mathbf{p}_i/m_i$, to that with respect to the mass-averaged velocity, $(\mathbf{p}_i/m_i) - \mathbf{u}_c$. In their Eq. 4.21 they subsequently define a partial stress tensor $\boldsymbol{\sigma}_i$ as consisting of a kinetic contribution $(\boldsymbol{\sigma}_i)_k$, which is defined in terms of the peculiar velocity distribution, and an intermolecular force contribution $(\boldsymbol{\sigma}_i)_v$, which is defined in terms of the intermolecular potential V_{ki} and the pair corre-

lation function g_{ki} for molecules k and i. In section 5, they further develop the transport equations. Their method is to approach the molecular distribution functions by the sum of equilibrium terms and perturbation terms. For the equilibrium state they write the singlet density distribution in Eq. 5.2 as

$$\omega_i^{(1,0)}(\mathbf{p}_1, \mathbf{r}_1) = \frac{c_i(\mathbf{r}_1)}{(2\pi m_i kT)^{3/2}} \exp\left[-\frac{(\mathbf{p}_1 - m_i \mathbf{u}_c)^2}{2m_i kT}\right] \quad (128)$$

This is the equivalent of the velocity distribution function in the Chapman–Enskog dilute gas theory, and it is clear that this is also centered around the mass-averaged velocity. In the further development the customary "linearization" is applied, meaning that nonlinear terms in the diffusion velocity and temperature gradients, and higher-order spatial derivatives are discarded. In their Eq. 5.8 we see now that the result for the partial stress tensor becomes (using notation from their Eq. 2.7)

$$\boldsymbol{\sigma}_i = \left(\varphi_i - \frac{2}{3}\eta_i\right)\mathbf{I}\nabla \cdot \mathbf{u}_c + \eta_i[(\nabla \mathbf{u}_c) + (\nabla \mathbf{u}_c)^T] \quad (129)$$

The final Eq. 5.13 for the motion of component i reads

$$\frac{\partial \rho_i \mathbf{u}_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{u}_c \mathbf{u}_c) = \eta_i \nabla^2 \mathbf{u}_c + (\varphi_i + \eta_i/3)\nabla\nabla \cdot \mathbf{u}_c$$

$$- c_i \nabla_T \mu_i - \sum_{j=1}^{n} c_i R_{ij} \mathbf{j}_j - c_i R_{i0} \mathbf{q} + c_i \mathbf{F}_i \quad (33a)$$

The term with R_{ij} is of the Maxwell–Stefan form, as was later worked out further by Mason and Viehland.[23] In this species momentum balance we see clearly the presence of shear next to intermolecular friction, and external forces. Also we see that the shear term is characterized by partial dynamic and bulk viscosities η_i and φ_i, and that they depend on the gradients of the mass-averaged velocity. This is caused by the choice of the mass-averaged velocity as center of the singlet distribution function. In a later section we will touch upon the work of Snell et al.,[55] who made a similar derivation, but took the component average velocity as the center for the singlet distribution function.

Additional comments on the dusty gas model

As discussed above, the ZKS equation, which was the starting point for the development of the dusty gas model by Mason et al., leads to the result that the mass-averaged velocity would be zero for isobaric transport in a capillary. This was also observed by Jackson,[14] who decided that there was probably something wrong, but that the DGM was the only model available whose final equations seemed to describe several phenomena quite well. Mason et al. probably were also troubled by such matters, without mentioning it explicitly. The gist of their lengthy argumentation is that in the approximations used, the equation for a species and for the mixture as a whole are coupled only because the local composition depends on the individual species motions, and influences the mixture viscous transport because the transport coefficients depend on compo-

sition. Both Mason et al. and Zhdanov and Roldughin now avoid this difficulty by eliminating the divergence; they perform the backsubstitution in terms of the total pressure gradient and obtain the equivalent of

$$\sum_{j=1}^{n} \frac{n_i n_j}{n^2 \mathcal{D}_{ij}} (\overline{v_{i,x}} - \overline{v_{j,x}}) = -\frac{1}{p} \frac{dp_i}{dx} + \frac{1}{p} \frac{\eta_i}{\eta_t} \frac{dp}{dx} \tag{130}$$

or in terms of (molecular) fluxes

$$\sum_{j=1}^{n} \frac{1}{n^2 \mathcal{D}_{ij}} (n_j J_{i,x} - n_i J_{j,x}) = -\frac{1}{p} \frac{dp_i}{dx} + \frac{1}{p} \frac{\eta_i}{\eta_t} \frac{dp}{dx} \tag{131}$$

Here it is assumed that there are no radial (partial) pressure gradients. As we write the equation here in terms of velocities, it is clear that through this substitution the problem is not solved, but is only masked. MME then make their famous statement that the fluxes occurring in Eqs. 126 are only "diffusive fluxes," and that there should be added a "viscous contribution"

$$J_i = J_i^D + x_i J_{visc} \tag{132}$$

This statement follows nowhere from the basic theory. The next step is using the "masked" Eq. 131 to switch the "point" fluxes to cross-section–averaged fluxes, without explicitly mentioning this. This can be justified only if the species velocities would not vary over the cross section, and again there is no physical justification for this. This is followed by the argument that the "viscous flux" should obey a Darcy-type equation. MME argue that solution of the equivalent of Eq. 65 would lead to a Darcy-type equation

$$\langle u_{c,x} \rangle = -\frac{K}{\eta} \frac{dp}{dx} \tag{133a}$$

and for the viscous flux they write the equivalent of

$$J_{visc} = n \langle u_c \rangle \tag{133b}$$

Apparently they have not taken into account wall-slip phenomena. They also introduce the dust as a component $(n + 1)$ into Eq. 131, by adding on the left side a Maxwell–Stefan diffusion term for the dust, and on the right side the drag force, which corresponds to Eq. 133. By means of the addition of the "diffusive" and "viscous" fluxes, they obtain their final equation, which can be written as

$$\sum_{j=1}^{n} \frac{n_i n_j}{n^2 \mathcal{D}_{ij}} (\overline{v_{i,x}} - \overline{v_{j,x}}) + \frac{n_i \overline{v_{i,x}}}{n D_{iK}} - \frac{n_i u_{c,x}}{n D_{iK}} = -\frac{1}{p} \frac{dp_i}{dx} + \frac{1}{p} n_i X_{i,x} \tag{134}$$

Here they have defined

$$D_{iK} \equiv \mathcal{D}_{id}/x_d \tag{135}$$

In earlier work we have presented our criticism in detail.[24] We showed that the "dust Knudsen" term is equal to the viscous pressure drop according to the Darcy equation. With the manipulated Eq. 134 the flow of a single component would result in the well-known two-term slip-flow equation

$$\langle u_x \rangle = -\left(D^K + \frac{Kp}{\eta}\right) \frac{1}{p} \frac{dp}{dx} \tag{136}$$

which is in direct conflict with Eq. 133a, which was used as input to the same model. As we showed, in the DGM for liquids, errors are also present, and it would for the transport of a single liquid component lead to an equation of the form of Eq. 136, while starting with the Darcy Eq. 133a.

Here we will show some further inconsistencies within the model. Let us consider the mass-averaged velocity for isothermal flow through a capillary, in the absence of external forces. Solution of the momentum balance as it follows from Eq. 65, under the assumption of zero-velocity at the wall, gives

$$\langle u_{c,x} \rangle = -\frac{r_p^2}{8\eta} \frac{dp}{dx} = -\frac{B_o}{\eta} \frac{dp}{dx} \tag{137}$$

By definition

$$\langle u_{c,x} \rangle = \sum_{j=1}^{n} \omega_j v_{j,x} = \sum_{j=1}^{n} \omega_j \frac{N_{j,x}}{c_j} \tag{2}$$

and if the additivity of fluxes would hold, we would obtain

$$\langle u_{c,x} \rangle = \sum_{j=1}^{n} \omega_j \frac{N_{j,x}^D}{c_j} + \sum_{j=1}^{n} \omega_j \frac{x_j N_{visc,x}}{c_j}$$

$$= \sum_{j=1}^{n} \omega_j \frac{N_{j,x}^D}{c_j} + N_{visc,x} \frac{1}{c_t} \sum_{j=1}^{n} \omega_j$$

$$= \sum_{j=1}^{n} \omega_j \frac{N_{j,x}^D}{c_j} - \frac{B_o}{\eta} \frac{dp}{dx} = \sum_{j=1}^{n} \omega_j \frac{N_{j,x}^D}{c_j} + \langle u_{c,x} \rangle \tag{138}$$

and so the mass-averaged diffusive velocity would equal zero, as it would also for nonisobaric transport

$$\langle u_{c,x}^D \rangle = \sum_{j=1}^{n} \omega_j \frac{N_{j,x}^D}{c_j} = 0 \tag{139}$$

For a binary system without body forces Eq. 134 leads to

$$N_{1,x}^D = -\frac{D_1^K c_t \mathcal{D}_{12}}{x_1 D_2^K + x_2 D_1^K} \left(\frac{1}{p} \frac{dp_1}{dx} + \frac{x_1 D_2^k}{p \mathcal{D}_{12}} \frac{dp}{dx}\right) \tag{140}$$

and a similar one for component 2. For isobaric transport we find

$$N_{1,x}^D = -\frac{D_1^K c_t \mathcal{D}_{12}}{x_1 D_2^K + x_2 D_1^K} \frac{dx_1}{dx} \qquad (141)$$

$$N_{2,x}^D = -\frac{D_2^K}{D_1^K} N_{1,x}^D \qquad (142)$$

$$\langle u_{c,x}^D \rangle = \omega_1 \frac{N_{1,x}^D}{c_1} + \omega_2 \frac{N_{2,x}^D}{c_2} = N_{1,x}^D \left(\frac{\omega_1}{c_1} - \frac{\omega_2}{c_2} \right) \qquad (143)$$

which is generally in contradiction with Eq. 139. It means that by the introduction of the viscous and diffusive fluxes somewhere an internal inconsistency has crept in, and at least that the final result is in conflict with the original equations.

Our conclusion here is that the approximations contained in the ZKS approach, as was the case for the Chapman–Enskog approach, do lead to a momentum balance for the mixture, which would predict a zero mass-averaged velocity for isobaric, isothermal diffusion, contrary to experimental observation. The developments made by Mason et al. for the dusty gas model can be seen as an attempt to repair this flaw. However, they do not follow from first principles, thus leading to arbitrary change in the momentum balance and to an internally inconsistent model.

Other Approaches from Statistical Mechanics

The partial molecular stress tensor according to Snell, Aranow, and Spangler

Snell et al.[55] considered the same dense systems as Bearman and Kirkwood,[41] for isothermal situations. They aimed their treatment at incorporation of the individual species velocities, and so their Eq. 4.5 for the singlet distribution function is centered around the average velocity of component i

$$\omega_i^{(1,0)}(\mathbf{p}_1, \mathbf{r}_1) = \frac{c_i(\mathbf{r}_1)}{(2\pi m_i kT)^{3/2}} \exp\left[-\frac{(\mathbf{p}_1 - m_i \bar{\mathbf{v}}_i)^2}{2m_i kT} \right] \qquad (144)$$

It is remarkable that in the development of their Eq. 2.1 they first set the same step as BK, the addition and subtraction of the mass-averaged velocity $\mathbf{u}_c$. After that they develop their equation for the kinetic part of the partial stress tensor by adding and subtracting the species average velocity $\bar{\mathbf{v}}_i$. Their final result is

$$\frac{\partial \rho_i \bar{\mathbf{v}}_i}{\partial t} = \nabla \cdot [\mathbf{H}_i - \boldsymbol{\kappa}_i^o - \rho_i(\bar{\mathbf{v}}_i \mathbf{u}_c + \mathbf{u}_c \bar{\mathbf{v}}_i - \mathbf{u}_c \mathbf{u}_c)]$$

$$+ c_i \sum_{k=1}^{\nu} \xi_{ik} c_k (\bar{\mathbf{v}}_k - \bar{\mathbf{v}}_i) + c_i \mathbf{F}_i - c_i \nabla \mu_i \qquad (145)$$

with

$$\mathbf{H}_i = c_i \sum_{k=1}^{\nu} \left[\left(\phi_{ik} - \frac{2}{3} \eta_{ik} \right) \mathbf{I} \nabla \cdot c_k \bar{\mathbf{v}}_k + \eta_{ik}[(\nabla c_k \bar{\mathbf{v}}_k) + (\nabla c_k \bar{\mathbf{v}}_k)^T] \right] \qquad (146)$$

and

$$\boldsymbol{\kappa}_i^o = \rho_i(\bar{\mathbf{v}}_i - \mathbf{u}_c)(\bar{\mathbf{v}}_i - \mathbf{u}_c) \qquad (147)$$

Without going into further derivation of this, one can recognize terms with convected momentum, the Maxwell–Stefan friction term, external forces, and the gradient of the chemical potential. The main difference with the Bearman–Kirkwood result is the formulation of the shear term; here the gradients of the species velocities (multiplied by their concentrations) appear. As we will discuss later, this reflects a substantial difference with the theories in which the mass-averaged velocity gradients are considered as shear components. Unfortunately, this approach has not made a breakthrough, and certainly has disappeared from the view of chemical engineers.

A much more limited approach for a binary system was made by Hamel.[56] He started from the Boltzmann equation, and assumed that the velocity distribution of a component i would be a perturbation of the Maxwellian distribution, centered around the component velocity $\bar{\mathbf{v}}_i$, and with individual temperature T_i. He continued with the derivation for Maxwellian inverse fifth-power-law molecules, and derived expressions for the differences in species temperatures, especially for molecules with strongly different masses. The main results are different forms for the approximations of the collision integral J_i, as defined in the previous section. He did not present transport phenomena equations.

Theories developed for channels and capillaries

Several researchers have been concerned with derivations from statistical mechanics directly for channels or capillaries. Shendalman[57] developed approximate solutions through the BGK-model, which was formulated by Bhatnagar et al.[58] in their consideration of plasmas. He considers steady, isothermal, binary diffusion in long cylinders neglecting end effects, without external forces. For the velocity distribution a trial function is posed

$$f_i = n_i(x) \left[\left(\frac{m_i}{2kT} \right)^{3/2} \exp\left(-\frac{m_i v_i^2}{2kT} \right) - h_{i,S} \right] \qquad (148)$$

and

$$n_i \equiv n_i(x) \lfloor 1 - g_{i,S}(r) \rfloor \qquad (149)$$

The perturbation functions $h_{i,S}$ and $g_{i,S}(r)$ are developed further, and the final solution is found by the Bubnov–Galerkin variational method. Shendalman considers two trial functions for the axial velocity of the components. One is a flat velocity profile over the radius, the second a parabolic profile. The variational method then provides expressions for the constants involved in these profiles. Already for these relatively simple forms the analytical equations for the constants become cumbersome.

The results for isobaric counterdiffusion of Ar and He, and for Ar and O_2 show reasonable agreement with Graham's law "in the transition" region, assuming a flat profile. However, to approach the Kramers–Kistemaker effect, parabolic velocity profiles are needed. For more complex situations Shendalman foresees "perhaps monumental arithmetic problems."

Zhdanov and Roldughin reported studies on the gas mixture transport in capillaries, mostly for binary systems, and on the nonequilibrium thermodynamics of such systems, recently published in two review papers.[51,59] Their method consists of formulating equations for the "core" of the capillary, supplemented by equations for the "Knudsen layers" at the wall. The importance of both regions of course varies with the Knudsen number $N_{Kn} = \Lambda/r_p$, with Λ the mean free path. For intermediate and low Knudsen numbers, in their term the "hydrodynamical region," they take as a starting point the ZKS momentum balance, which is identical to Eq. 61. In the absence of external forces this leads again to a zero mass-averaged velocity for isothermal isobaric diffusion. They do not discuss this consequence, but instead also eliminate the divergence from the momentum balance, as discussed before. They do present a formal solution for the cross-section–averaged value of the mass-averaged velocity, $\langle u_{c,x} \rangle$

$$\langle u_{c,x} \rangle = -\frac{r_p^2}{8\eta}\nabla p + u_x^{as}(r_p) + \frac{1}{\rho}j_m \qquad (150)$$

The asymptotic velocity $u_x^{as}(r_p)$ is also equal to zero for isobaric, isothermal diffusion, whereas for the term j_m, which is identified as "diffusive slip phenomena," a complicated expression is given that depends on Burnett second-order approximations (Zhdanov and Roldughin[51]; their Eq. 5.21 and text below). In the other paper[59] they present the Burnett correction function in their Eq. 57. What is clear from the equations is that they consist of higher-order and mixed derivatives. We do not see how the method can be handled to provide the component fluxes for a given problem, such as the Remick–Geankoplis experiments. Also it seems highly unlikely that the motion would be caused only by diffusive slip. The already quoted feeling of "intimidation" by the nonequilibrium thermodynamics becomes worse for us by the appearance of "non-physical fluxes"[59] (their pp. 139-140).

Plasma physics

Plasmas are a special kind of multicomponent systems. The ions are balanced in charge by much smaller electrons, and in general it is of interest to formulate laws of motion involving electrical and magnetic forces. As discussed by Bhatnagar et al.,[58] the solution of the Boltzmann equation is very complex, involving higher-order approximations. Therefore often limiting cases of very low or high density have been considered. At low density there are insufficient collisions to approach local equilibrium, and so different temperatures for electrons and ions (and neutral molecules) have to be assumed. At higher densities so-called hydrodynamic theories have been developed, which are related to the transport equations as we know them in chemical engineering. Examples of recent papers on multicomponent diffusion in multitemperature gas mixtures are those of Ramshaw and Chang[60,61]; a book by Zhdanov on

transport processes in multicomponent plasma has recently been published.[62] Ramshaw considers systems in which "viscosity has been neglected." The starting point is the momentum balance for a component i

$$\rho_i \frac{d_i \bar{\mathbf{v}}_i}{dt} = \rho_i\left(\frac{\partial \bar{\mathbf{v}}_i}{\partial t} + \bar{\mathbf{v}}_i \cdot \nabla \bar{\mathbf{v}}_i\right) = -\nabla p_i + \rho_i \mathbf{F}_i^m + \sum_j \mathbf{F}_{ji} \quad (151)$$

For a component i his derivations include a Maxwellian velocity distribution function that is centered around the average velocity of i. In his derivations he also substitutes the mixture momentum balance into that of the species, and he makes the assumption that the component velocities will be close to the mass-averaged velocity, and then replaces the substantial derivative by

$$\rho_i \frac{d_i \bar{\mathbf{v}}_i}{dt} = \rho_i\left(\frac{\partial \bar{\mathbf{v}}_i}{\partial t} + \bar{\mathbf{v}}_i \cdot \nabla \bar{\mathbf{v}}_i\right) = \rho_i\left(\frac{\partial \mathbf{u}_c}{\partial t} + \mathbf{u}_c \cdot \nabla \mathbf{u}_c\right) \quad (152)$$

Zhdanov also includes shear terms in the species momentum balance. For a multitemperature, multifluid plasma, he also uses the Maxwellian distribution around the component-averaged velocity, with a corresponding temperature definition (his Eqs. 2.4.4 and 2.4.5)

$$f_i^{[0]} = n_i\left(\frac{m_i}{2\pi k T_i}\right)^{3/2}\exp\left(-\frac{m_i(\mathbf{v}_i - \mathbf{v}_{i0})^2}{2kT_i^*}\right) \quad (153)$$

$$\frac{3}{2}n_i k T_i^* = \frac{1}{2}m_i\int f_i(\mathbf{v}_i - \mathbf{v}_{i0})^2 d\mathbf{v}_i \quad (154)$$

He provides relationships between variables defined within this frame of reference and those related of the mass-averaged velocity, including the stress tensor. However, in his Chapter 5 on multicomponent gas mixtures the expression for the viscous-stress tensor is again defined in terms of the gradients in the mass-averaged velocity. In Chapter 4 he shows the derivations of the 13-moment method, but there only the Maxwellian around the mass-averaged velocity is considered. Thus the expression for the shear in the momentum balance is identical to Eq. 65, as found from the earlier theory of ZKS.

Toward a New Diffusion Equation

In a previous section we found that the species momentum balance, obtained by considering transport phenomena as perturbations around the motion of a mixture with the mass-averaged velocity, leads to problems, even for simple situations. In the subsequent section we showed that within the general species momentum balance a molecular shear term is clearly present. This was included explicitly in the ZKS equations, but was obscured in the CE and HCB equations by substitution of the momentum balance of the mixture into that of the species. After this we cited the concept to take as a starting point the velocity distribution around the average component velocity. As far as we know, only Snell et al. pursued the derivation in their modified Bearman–Kirkwood theory for liquids. We thought it worthwhile to attempt a derivation for

dilute monatomic gases, which in many respects is similar to the Chapman–Enskog derivation. However, we do not assume as a zero-order approximation the local equilibrium moving with the mass-average velocity; here we start with a trial function centered around the individual component average velocity. Also we work within a fixed spatial coordinate system. Thus our approach starts with a nonequibrium trial function. Fortunately much of the mathematics is the same as that in the classic derivations; for details we refer to CC, HCB, and Ferziger and Kaper.[53]

A new solution to the Boltzmann equation for dilute monatomic gases

The starting point is again the Boltzmann equation:

$$\frac{\partial f_i}{\partial t} + (\mathbf{v}_i \cdot \nabla f_i) + \frac{1}{m_i}\left(\mathbf{X}_i \cdot \frac{\partial f_i}{\partial \mathbf{v}_i}\right)$$
$$= \sum_j \int \int \int (f_i'f_j' - f_if_j)\, g_{ij}b\,db\,d\varepsilon\,d\mathbf{v}_j \quad (70)$$

The Component-Centered Velocity Distribution. Similar to the Chapman–Enskog development, we approach the problem by assuming a trial function for the velocity distribution, and subsequently try to refine this. As a first trial function we take

$$h_i^{[0]} = n_i\left(\frac{m_i}{2\pi kT_i}\right)^{3/2}\exp\left(-\frac{m_i(\mathbf{v}_i - \mathbf{v}_{i0})^2}{2kT_i}\right) \quad (155)$$

which characterizes a Maxwellian distribution, but taken around the average velocity $\mathbf{v}_{i0}$ of species i. In principle we take into account here that each species may have its own temperature. We use here the notation h_i to make a clear distinction with the classic distribution function f_i, of which the first approximation is

$$f_i^{[0]} = n_i\left(\frac{m_i}{2\pi kT}\right)^{3/2}\exp\left(-\frac{m_i(\mathbf{v}_i - \mathbf{u}_c)^2}{2kT}\right) \quad (88)$$

where $\mathbf{u}_c$ is the mass-averaged velocity.
The following averages are obtained with the distribution (Eq. 155)

$$\int h_i^{[0]}d\mathbf{v}_i = n_i \quad (156)$$

$$n_im_i\overline{\mathbf{v}}_i = \int m_i\mathbf{v}_ih_i^{[0]}d\mathbf{v}_i = n_im_i\mathbf{v}_{i0} \quad (157)$$

$$\int \frac{1}{2}m_iv_i^2h_i^{[0]}d\mathbf{v}_i = \frac{1}{2}n_im_i\overline{u_i^2} + \frac{1}{2}n_im_iv_{i0}^2 = \frac{3}{2}n_ikT_i + \frac{1}{2}n_im_iv_{i0}^2$$
$$(158)$$

In Eq. 157 we see that, for the averaging already by the first trial function, $\mathbf{v}_{i0}$ is the average velocity of i. So in terms of our approximation we write

$$\mathscr{D}^{[0]}h = \frac{\partial h_i^{[0]}}{\partial t} + (\mathbf{v}_i \cdot \nabla h_i^{[0]}) + \frac{1}{m_i}\left(\mathbf{X}_i \cdot \frac{\partial h_i^{[0]}}{\partial \mathbf{v}_i}\right)$$
$$= \sum_j \int \int \int (h_i'^{[0]}h_j'^{[0]} - h_i^{[0]}h_j^{[0]})\, g_{ij}b\,db\,d\varepsilon\,d\mathbf{v}_j$$
$$= \sum_j J(h_i, h_j) \quad (159)$$

First we develop the differential part in the first approximation. We will also use the relative velocity

$$\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}_{i0} \quad (160)$$

We find

$$\frac{\partial \ln h_i^{[0]}}{\partial t} = \frac{\partial \ln n_i}{\partial t} - \left(\frac{3}{2} - \frac{m_iu_i^2}{2kT_i}\right)\frac{\partial \ln T_i}{\partial t} + \frac{m_i}{kT_i}\left(\frac{\partial \mathbf{v}_{i0}}{\partial t} \cdot \mathbf{u}_i\right) \quad (161)$$

$$\nabla \ln h_i^{[0]} = \nabla \ln n_i - \left(\frac{3}{2} - \frac{m_iu_i^2}{2kT_i}\right)\nabla \ln T_i + \frac{m_i}{kT_i}(\nabla\mathbf{v}_{i0}) \cdot \mathbf{u}_i \quad (162)$$

$$\frac{\partial \ln h_i^{[0]}}{\partial \mathbf{v}_i} = -\frac{m_i}{kT_i}\mathbf{u}_i \quad (163)$$

We develop the equations of change in a manner similar to that in HCB (pp. 461–463). For the species equation of continuity we have

$$\frac{\partial n_i}{\partial t} + (\nabla \cdot n_i\mathbf{v}_{i0}) = 0 \quad (164)$$

The species momentum balance reads

$$\frac{\partial(n_im_i\overline{\mathbf{v}}_i)}{\partial t} = -[\nabla \cdot n_im_i\overline{\mathbf{v}_i\mathbf{v}_i}] + n_i\mathbf{X}_i + \sum_j \mathbf{F}_{ji} \quad (165)$$

Here $\mathbf{F}_{ji}$ represents the force exerted on i through collisions with species j. This includes collisions of molecules i with the other molecules i; where needed we denote the latter with the subscript $i1$.

$$\mathbf{F}_{ji} = m_i \int \int \int \int \mathbf{v}_i(h_i'h_j' - h_ih_j)\, g_{ij}b\,db\,d\varepsilon\,d\mathbf{v}_i\,d\mathbf{v}_j \quad (166)$$

Using the equation of continuity and some rearrangement leads to the following alternative formulation

$$n_im_i\frac{\partial \mathbf{v}_{i0}}{\partial t} = -(\nabla \cdot \mathbf{\Pi}_i) + n_i\mathbf{X}_i - n_im_i\mathbf{v}_{i0} \cdot \nabla\mathbf{v}_{i0} + \sum_j \mathbf{F}_{ji} \quad (167)$$

Here we define $\mathbf{\Pi}_i$ as the species molecular stress tensor

$$\mathbf{\Pi}_i = n_i m_i \overline{\mathbf{u}_i \mathbf{u}_i} \qquad (168)$$

For the equation of energy we have

$$\frac{\partial}{\partial t}\left(\frac{1}{2} n_i m_i \overline{\nu_i^2}\right) = -\left(\nabla \cdot \frac{1}{2} n_i m_i \overline{\nu_i^2 \mathbf{v}_i}\right) + n_i(\overline{\mathbf{v}}_i \cdot \mathbf{X}_i) + \sum_j Q_{ij} \qquad (169)$$

Here Q_{ij} is the energy obtained by i, resulting from collisions with other molecules

$$Q_{ij} = \frac{1}{2} m_i \int \int \int \int \nu_i^2(h_i' h_j' - h_i h_j) \, g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i \, d\mathbf{v}_j \qquad (170)$$

Substitution of the equation of continuity and the momentum balance, after some rearrangement, leads to

$$\frac{3}{2} n_i k \frac{\partial T_i}{\partial t} = -(\mathbf{\Pi}_i : \nabla \mathbf{v}_{i0}) - (\nabla \cdot \mathbf{q}_{i,m}) - \frac{3}{2} n_i k(\mathbf{v}_{i0} \cdot \nabla T_i)$$
$$+ \sum_j Q_{ij} - \mathbf{v}_{i0} \cdot \sum_j \mathbf{F}_{ji} \qquad (171)$$

Here we define the species molecular heat flux as

$$\mathbf{q}_{i,m} = \frac{1}{2} n_i m_i \overline{u_i^2 \mathbf{u}_i} \qquad (172)$$

The next step is to insert the time derivatives into the first part of the first-order trial solution. Corresponding with the Chapman–Enskog method we first simplify by taking the first-order approximation into several variables in the equations of change:

$$\mathbf{q}_{i,m}^{[0]} = \frac{1}{2} \int m_i u_i^2 \mathbf{u}_i h_i^{[0]} d\mathbf{v}_i = \frac{1}{2} n_i m_i \overline{u_i^2 \mathbf{u}_i}^{[0]} = 0 \qquad (173)$$

$$\mathbf{\Pi}_i^{[0]} = m_i \int \mathbf{u}_i \mathbf{u}_i h_i^{[0]} d\mathbf{v}_i = \frac{1}{3} n_i m_i \overline{u_i^{2[0]}} \mathbf{I} = n_i k T_i \mathbf{I} = p_i \mathbf{I} \qquad (174)$$

The evaluation of $\mathbf{F}_{ji}^{[0]}$ and $Q_{ji}^{[0]}$ needs special attention for the chosen trial function.

$$h_i'^{[0]} h_j'^{[0]} = n_i n_j \left(\frac{m_i}{2\pi k T_i}\right)^{3/2} \left(\frac{m_j}{2\pi k T_j}\right)^{3/2}$$
$$\times exp\left[-\frac{m_i}{2kT_i}(\mathbf{v}_i' - \mathbf{v}_{i0})^2 - \frac{m_j}{2kT_j}(\mathbf{v}_j' - \mathbf{v}_{j0})^2\right] \qquad (175)$$

From here we proceed with a single temperature, so we assume $T_i \approx T_j \approx T$.

Conservation of momentum on collision leads to

$$m_i(\mathbf{v}_i' - \mathbf{v}_i) = -m_j(\mathbf{v}_j' - \mathbf{v}_j) \qquad (176)$$

and conservation of kinetic energy to

$$\frac{1}{2} m_i \nu_i'^2 + \frac{1}{2} m_j \nu_j'^2 = \frac{1}{2} m_i \nu_i^2 + \frac{1}{2} m_j \nu_j^2 \qquad (177)$$

This has as a consequence:

$$\frac{1}{2} m_i(\mathbf{v}_i' - \mathbf{v}_{i0})^2 + \frac{1}{2} m_j(\mathbf{v}_j' - \mathbf{v}_{j0})^2$$
$$= \frac{1}{2} m_i(\mathbf{v}_i - \mathbf{v}_{i0})^2 + \frac{1}{2} m_j(\mathbf{v}_j - \mathbf{v}_{j0})^2$$
$$- m_i(\mathbf{v}_i' - \mathbf{v}_i) \cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \qquad (178)$$

and so we obtain

$$h_i'^{[0]} h_j'^{[0]} - h_i^{[0]} h_j^{[0]}$$
$$= h_i^{[0]} h_j^{[0]}\left[1 - \exp\left(-\frac{m_i}{kT}(\mathbf{v}_i' - \mathbf{v}_i) \cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0})\right)\right] \qquad (179)$$

Alternatively we may write

$$h_i'^{[0]} h_j'^{[0]} - h_i^{[0]} h_j^{[0]} = h_i^{[0]} h_j^{[0]}\left[1 - \exp\left(-\frac{2\mu_{ij}}{kT}(\mathbf{v}_j - \mathbf{v}_i)\right.\right.$$
$$\left.\left.\cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0})\cos \theta_m\right)\right] \qquad (180)$$

in which μ_{ij} is the reduced mass and θ_m is the maximum angle of deflection. A large absolute value of $\mathbf{v}_j - \mathbf{v}_i$ will have a low value of the distribution functions. Thus upon performing the integration of a function F it is reasonable to approach the following:

$$\int \int \int \int F h_i^{[0]} h_j^{[0]}\left[1 - \exp\left(-\frac{m_i}{kT}(\mathbf{v}_i' - \mathbf{v}_i) \cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0})\right)\right]$$
$$\times g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i \, d\mathbf{v}_j \approx \int \int \int \int F h_i^{[0]} h_j^{[0]} \frac{m_i}{kT}(\mathbf{v}_i' - \mathbf{v}_i)$$
$$\cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0}) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i \, d\mathbf{v}_j \qquad (181)$$

This step resembles the derivation of the binary diffusion equation by Present[63] (p. 147, his Eq. 8-75) and the original derivation of Stefan[64] (p. 359).

For the evaluation of $\mathbf{F}_{ji}^{[0]}$ we find

$$\mathbf{F}_{ji}^{[0]} = \int \int \int \int m_i \mathbf{v}_i h_i^{[0]} h_j^{[0]} \frac{m_i}{kT}(\mathbf{v}_i' - \mathbf{v}_i)$$
$$\cdot (\mathbf{v}_{i0} - \mathbf{v}_{j0}) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i \, d\mathbf{v}_j$$

$$= (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \int \int \int \int h_i^{[0]} h_j^{[0]} \frac{m_i}{kT} m_i \mathbf{v}_i$$

$$\cdot (\mathbf{v}_i' - \mathbf{v}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \frac{1}{3kT} m_i^2 (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{v}_i$$

$$\cdot (\mathbf{v}_i' - \mathbf{v}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \frac{1}{3kT} m_i^2 (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{u}_i$$

$$\cdot (\mathbf{u}_i' - \mathbf{u}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j \quad (182)$$

The last step is justified, given that the integration

$$\int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{v}_{i0} \cdot (\mathbf{u}_i' - \mathbf{u}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \mathbf{v}_{i0} \int \int \int \int h_i^{[0]} h_j^{[0]} (\mathbf{u}_i' - \mathbf{u}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j = 0 \quad (183)$$

because of the uneven power of $\mathbf{u}$ within the integral.

Changing variables to $\mathbf{w}_i$ gives

$$\mathbf{F}_{ji}^{[0]} = \frac{1}{3} m_i (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{w}_i$$

$$\cdot (\mathbf{w}_i' - \mathbf{w}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= -\frac{1}{3} m_i n_i n_j (\mathbf{v}_{i0} - \mathbf{v}_{j0}) [\mathbf{w}_i; \mathbf{w}_i]_{ij} \quad (184)$$

in which $[\mathbf{G}; \mathbf{H}]_{ij}$ is the bracket integral as defined in HCB (p. 473). In Appendix B the equivalence between the bracket integrals with the h-functions and the f-functions is shown.

The bracket integral is equal to (HCB, p. 512)

$$[\mathbf{w}_i; \mathbf{w}_i]_{ij} = 8 \frac{m_j}{(m_i + m_j)} \Omega_{ij}^{(1,1)} \quad (185)$$

and so we find

$$\mathbf{F}_{ji}^{[0]} = -(\mathbf{v}_{i0} - \mathbf{v}_{j0}) n_i m_i n_j m_j \frac{16}{3(m_i + m_j)} \Omega_{ij}^{(1,1)} \quad (186)$$

The classical first approximation of the binary diffusion coefficient is

$$\mathscr{D}_{ij}(1) = \frac{3(m_i + m_j)}{16 n m_i m_j} \frac{kT}{\Omega_{ij}^{(1,1)}} \quad (187)$$

We will leave out the notation (1) for this treatment, and so we have

$$F_{ji}^{[0]} = -(\mathbf{v}_{i0} - \mathbf{v}_{j0}) \frac{n_i n_j kT}{n \mathscr{D}_{ij}} = -(\mathbf{v}_{i0} - \mathbf{v}_{j0}) \frac{p_i p_j}{p \mathscr{D}_{ij}} \quad (188)$$

This is the Maxwell–Stefan diffusion term.

For the integration of $Q_{ji}^{[0]}$ we obtain, using the following approximation (Eq. 181):

$$Q_{ij}^{[0]} = \frac{1}{2} m_i \int \int \int \int v_i^2 (h_i'^{[0]} h_j'^{[0]} - h_i^{[0]} h_j^{[0]}) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$\approx \frac{1}{2} m_i \frac{m_i}{kT} (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \cdot \int \int \int \int h_i^{[0]} h_j^{[0]} v_i^2$$

$$\times (\mathbf{v}_i' - \mathbf{v}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j \quad (189)$$

Switching to $\mathbf{u}$ as variable, and discarding uneven powers of $\mathbf{u}$ in the integrand, gives

$$Q_{ij}^{[0]} = m_i \frac{m_i}{kT} (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \cdot \mathbf{v}_{i0} \frac{1}{3} \int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{v}_i$$

$$\cdot (\mathbf{v}_i' - \mathbf{v}_i) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j = -\frac{2}{3} n_i n_j m_i (\mathbf{v}_{i0} - \mathbf{v}_{j0})$$

$$\cdot \mathbf{v}_{i0} [\mathbf{w}_i; \mathbf{w}_i]_{ij} = -\frac{n_i n_j kT}{n \mathscr{D}_{ij}} (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \cdot \mathbf{v}_{i0} \quad (190)$$

Substitution of the time derivatives, after rearrangement, gives

$$\frac{1}{h_i^{[0]}} \mathscr{D}^{[0]} h_i = \left(w_i^2 - \frac{5}{2} \right) \mathbf{u}_i \cdot \nabla \ln T$$

$$+ 2 \left[\mathbf{w}_i \mathbf{w}_i - \frac{1}{3} w_i^2 \mathbf{I} \right] : [\nabla \mathbf{v}_{i0}] + \frac{1}{n_i kT} \mathbf{u}_i \cdot \sum_j \mathbf{F}_{ji} \quad (191)$$

Here

$$\mathbf{w}_i = \mathbf{u}_i \sqrt{\frac{m_i}{2kT}} \quad (192)$$

Use has been made here of the relation

$$\sum_j Q_{ij}^{[0]} - \mathbf{v}_{i0} \cdot \sum_j \mathbf{F}_{ji}^{[0]} = 0 \quad (193)$$

First-Order Solution. We now have to solve

$$\mathscr{D}^{[0]} h_i = \frac{\partial h_i^{[0]}}{\partial t} + (\mathbf{v}_i \cdot \nabla h_i^{[0]}) + \frac{1}{m_i} \left(X_i \cdot \frac{\partial h_i^{[0]}}{\partial \mathbf{v}_i} \right)$$

$$= \sum_j \int \int \int (h_i' h_j' - h_i h_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (194)$$

As was done in the earlier methods, we put

$$h_i = h_i^{[0]}(1 + \phi_i) \qquad (195)$$

We will leave out the superscript [1] on the functions ϕ_i. Because the first trial function produces the desired averages of number density, component velocity, and energy, as shown in Eq. 156, we have the auxiliary equations

$$\int h_i^{[0]} \phi_i \Psi_i d\mathbf{v}_i = 0 \qquad (196)$$

with $\Psi_i = 1$, $m_i\mathbf{u}_i$, $1/2(m_i u_i^2)$.

Application of Eq. 195, and neglecting products $\phi_i\phi_j$, yields

$$h_i' h_j' - h_i h_j = h_i^{\prime[0]} h_j^{\prime[0]} - h_i^{[0]} h_j^{[0]} + h_i^{\prime[0]} h_j^{\prime[0]}(\phi_i' + \phi_j')$$
$$- h_i^{[0]} h_j^{[0]}(\phi_i + \phi_j) \quad (197)$$

Similar to the neglect of the products $\phi_i\phi_j$ we assume that we can take

$$h_i^{\prime[0]} h_j^{\prime[0]}(\phi_i' + \phi_j') = (h_i^{\prime[0]} h_j^{\prime[0]} - h_i^{[0]} h_j^{[0]})(\phi_i' + \phi_j')$$
$$+ h_i^{[0]} h_j^{[0]}(\phi_i' + \phi_j') \approx h_i^{[0]} h_j^{[0]}(\phi_i' + \phi_j')$$
$$h_i' h_j' - h_i h_j \approx h_i^{\prime[0]} h_j^{\prime[0]} - h_i^{[0]} h_j^{[0]} + h_i^{[0]} h_j^{[0]}(\phi_i' + \phi_j' - \phi_i - \phi_j)$$
$$(198)$$

and so we try to find a solution for

$$\mathscr{D}^{[0]} h_i = \sum_j \int\int\int (h_i^{\prime[0]} h_j^{\prime[0]} - h_i^{[0]} h_j^{[0]}) g_{ij} b db d\varepsilon d\mathbf{v}_j$$
$$+ \sum_j \int\int\int h_i^{[0]} h_j^{[0]}(\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (199)$$

With the approximations made above, we find the equation for ϕ_i:

$$h_i^{[0]} \left\{ \left(w_i^2 - \frac{5}{2} \right) \mathbf{u}_i \cdot \nabla \ln T + 2 \left[\mathbf{w}_i \mathbf{w}_i - \frac{1}{3} w_i^2 \mathbf{I} \right] : [\nabla \mathbf{v}_{i0}] \right.$$
$$\left. + \frac{1}{n_i kT} \mathbf{u}_i \cdot \sum_j \mathbf{F}_{ji} \right\} = \sum_j \int\int\int (h_i^{\prime[0]} h_j^{\prime[0]}$$
$$- h_i^{[0]} h_j^{[0]}) g_{ij} b db d\varepsilon d\mathbf{v}_j + \sum_j \int\int\int h_i^{[0]} h_j^{[0]}$$
$$\times (\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (200)$$

Let us start with the first integral

$$\int\int\int (h_i^{\prime[0]} h_j^{\prime[0]} - h_i^{[0]} h_j^{[0]}) g_{ij} b db d\varepsilon d\mathbf{v}_j$$

$$= (\mathbf{v}_{i0} - \mathbf{v}_{j0}) \cdot \int\int\int h_i^{[0]} h_j^{[0]} \frac{m_i}{kT} (\mathbf{v}_i' - \mathbf{v}_i) g_{ij} b db d\varepsilon d\mathbf{v}_j$$
$$= -(\mathbf{v}_{i0} - \mathbf{v}_{j0}) \cdot \int\int\int h_i^{[0]} h_j^{[0]} \frac{m_j}{kT} (\mathbf{v}_j' - \mathbf{v}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j = 0$$
$$(201)$$

because of the uneven power of $\mathbf{v}$.

Following HCB (p. 469), we then find that the following expression must hold

$$\phi_i = -\mathbf{C}_i \cdot \nabla \ln T - \mathbf{B}_i : \nabla \mathbf{v}_{i0} - \mathbf{A}_i \cdot \mathbf{F}_{ji} \qquad (202)$$

For the coefficients the following expressions must hold

$$h_i^{[0]} \left(w_i^2 - \frac{5}{2} \right) \mathbf{u}_i = -\sum_j \int\int\int h_i^{[0]} h_j^{[0]}$$
$$\times (\mathbf{C}_i' + \mathbf{C}_j' - \mathbf{C}_i - \mathbf{C}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (203)$$

$$2 h_i^{[0]} \mathbf{b}_i = -\sum_j \int\int\int h_i^{[0]} h_j^{[0]}(\mathbf{B}_i' + \mathbf{B}_j' - \mathbf{B}_i - \mathbf{B}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j$$
$$(204)$$

with

$$\mathbf{b}_i = \left(\mathbf{w}_i \mathbf{w}_i - \frac{1}{3} w_i^2 \mathbf{I} \right) \qquad (205)$$

$$h_i^{[0]} \frac{1}{n_i kT} \mathbf{u}_i = -\int\int\int h_i^{[0]} h_j^{[0]}(\mathbf{A}_i' + \mathbf{A}_j' - \mathbf{A}_i - \mathbf{A}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j$$
$$(206)$$

Note that Eq. 206 does not contain the sum.

As follows from CC and HCB, the vector functions can be written as

$$\mathbf{C}_i = \mathbf{w}_i C_i(w_i) \qquad (207)$$

$$\mathbf{B}_i = \left(\mathbf{w}_i \mathbf{w}_i - \frac{1}{3} w_i^2 \mathbf{I} \right) B_i(w_i) = \mathbf{b}_i B_i(w_i) \qquad (208)$$

$$\mathbf{A}_i = \mathbf{w}_i A_i(w_i) \qquad (209)$$

Development of the A_i. We develop the A_i in a series of Sonine polynomials (HCB, p. 475):

$$A_i = \sum_{k=0}^{r} a_i^{(k)} S_{3/2}^{(k)}(w_i^2) \qquad (210)$$

We multiply Eq. 206 on both sides with $S_{3/2}^{(k)}(w_i^2)\mathbf{u}_i$ and integrate over $\mathbf{v}_i$. For the left-hand side we obtain

$$\frac{1}{n_i kT} \int h_i^{[0]} \mathbf{u}_i \mathbf{u}_i S_{3/2}^{(k)}(w_i^2) d\mathbf{v}_i = \frac{1}{n_i kT} \frac{1}{3} \int h_i^{[0]} u_i^2 S_{3/2}^{(k)}(w_i^2) d\mathbf{v}_i$$

$$= \frac{1}{n_i kT} \frac{2kT}{m_i} \int h_i^{[0]} S_{3/2}^{(0)}(w_i^2) S_{3/2}^{(k)}(w_i^2) d\mathbf{v}_i$$

$$= \frac{1}{n_i kT} \begin{pmatrix} \frac{3n_i kT}{m_i} & k=0 \\ 0 & k>0 \end{pmatrix} \quad (211)$$

So, by limiting the expansion to $k = 0$, we have

$$A_i = a_i^{(0)} S_{3/2}^{(0)}(w_i^2) = a_i^{(0)} \quad (212)$$

We now have

$$\frac{3}{m_i} = -\int \int \int \int h_i^{[0]} h_j^{[0]} a_i^{(0)} \mathbf{u}_i (\mathbf{w}_i' + \mathbf{w}_j' - \mathbf{w}_i - \mathbf{w}_j)$$

$$\cdot g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j - \frac{1}{3} a_i^{(0)} \sqrt{\frac{2kT}{m_i}} \int \int \int \int h_i^{[0]} h_j^{[0]} \mathbf{w}_i$$

$$\cdot (\mathbf{w}_i' + \mathbf{w}_j' - \mathbf{w}_i - \mathbf{w}_j) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \frac{1}{3} a_i^{(0)} \sqrt{\frac{2kT}{m_i}} n_i n_j ([\mathbf{w}_i; \mathbf{w}_i]_{ij} + [\mathbf{w}_i; \mathbf{w}_j]_{ij}) \quad (213)$$

For the distribution function in the first approach we can write

$$h_i \approx h_i^{[0]} + h_i^{[1]} = h_i^{[0]}(1 + \phi_{i,A} + \phi_{i,B} + \phi_{i,C}) \quad (214)$$

For the interspecies friction force $\mathbf{F}_{ji}$ we now have

$$\mathbf{F}_{ji} = \mathbf{F}_{ji}^{[0]} + \mathbf{F}_{ji,A}^{[1]} + \mathbf{F}_{ji,C}^{[1]} \quad (215)$$

There is no contribution from the integral containing the **B**-part because this results in a value of 0. Here we consider the contribution of the **A**-part:

$$\mathbf{F}_{ji,A}^{[1]} = \int \int \int \int h_i^{[0]} h_j^{[0]} m_i \mathbf{v}_i (\phi_{i,A}' + \phi_{j,A}' - \phi_{i,A} - \phi_{j,A})$$

$$\times g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \mathbf{F}_{ji}^{[0]} \int \int \int \int h_i^{[0]} h_j^{[0]} m_i \mathbf{v}_i (a_i^{(0)}(\mathbf{w}_i' - \mathbf{w}_i)$$

$$+ a_j^{(0)}(\mathbf{w}_j' - \mathbf{w}_j)) g_{ij} b db d\varepsilon d\mathbf{v}_i d\mathbf{v}_j$$

$$= \mathbf{F}_{ji}^{[0]} \sqrt{2kTm_i} \, n_i n_j \{-a_i^{(0)}[\mathbf{w}_i; \mathbf{w}_i]_{ij} - a_j^{(0)}[\mathbf{w}_i; \mathbf{w}_j]_{ij}\} \quad (216)$$

From Eq. 213 we find

$$a_i^{(0)} \sqrt{2kTm_i} \, n_i n_j [\mathbf{w}_i; \mathbf{w}_i]_{ij} = \frac{9}{1 + [\mathbf{w}_i; \mathbf{w}_j]_{ij}/[\mathbf{w}_i; \mathbf{w}_i]_{ij}}$$

$$= \frac{9}{1 - \sqrt{m_j/m_i}} \quad (217)$$

and in a similar manner

$$a_j^{(0)} \sqrt{2kTm_i} \, n_i n_j [\mathbf{w}_i; \mathbf{w}_j]_{ij} = -\frac{9}{1 - \sqrt{m_j/m_i}} \quad (218)$$

and so we find that in the present approximation

$$\mathbf{F}_{ji,A}^{[1]} = \mathbf{0} \quad (219)$$

Development of the B_i. The starting point is Eq. 204

$$2h_i^{[0]} \mathbf{b}_i = -\sum_j \int \int \int h_i^{[0]} h_j^{[0]} (\mathbf{B}_i' + \mathbf{B}_j' - \mathbf{B}_i - \mathbf{B}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (204)$$

Now we approach by means of a series of Sonine polynomials:

$$B_i = \sum_{k=0}^{\infty} b_i^{(k)} S_{5/2}^{(k)}(w_i^2) \quad (220)$$

and so we obtain

$$2h_i^{[0]} \mathbf{b}_i = -\sum_j \int \int \int h_i^{[0]} h_j^{[0]}$$

$$\times \begin{bmatrix} \sum_{k=0}^{\infty} b_i^{(k)} (S_{5/2}^{(k)}(w_i'^2) \mathbf{b}_i' - S_{5/2}^{(k)}(w_i^2) \mathbf{b}_i) + \\ \sum_{k=0}^{\infty} b_j^{(k)} (S_{5/2}^{(k)}(w_j'^2) \mathbf{b}_j' - S_{5/2}^{(k)}(w_j^2) \mathbf{b}_j) \end{bmatrix} g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (221)$$

We double-dot both sides of Eq. 221 with $\mathbf{b}_i S_{5/2}^{(k)}(w_i^2)$ and integrate over $\mathbf{v}_i$.

We now have

$$(\mathbf{b}_i : \mathbf{b}_i) = \frac{2}{3} w_i^4 \quad (222)$$

For the lefthand side we obtain

$$2 \int h_i^{[0]} (\mathbf{b}_i : \mathbf{b}_i) S_{5/2}^{(k)}(w_i^2) d\mathbf{v}_i = \frac{4}{3} \pi^{-3/2} n_i \int e^{-w_i^2} w_i^4 S_{5/2}^{(k)}(w_i^2) d\mathbf{w}_i$$

$$= \begin{pmatrix} 5n_i & k=0 \\ 0 & k>0 \end{pmatrix} \quad (223)$$

2This means that the set of equations, which is obtained by carrying out the integration of the right-hand side, will lead to $b_i^{(k)} = 0$, for $k > 0$. So we can suffice with the development for $k = 0$. Using $S_m^{(0)} = 1$, we obtain

$$5n_i = -b_i^{(0)} \int \int \int \int h_i^{[0]} h_{i1}^{[0]} (\mathbf{b}_i' - \mathbf{b}_i + \mathbf{b}_{i1}' - \mathbf{b}_{i1}) :$$

$$\mathbf{b}_i g_{i,i1} b db d\varepsilon d\mathbf{v}_{i1} d\mathbf{v}_i - \sum_{\substack{j \\ j \neq i}} \int \int \int h_i^{[0]} h_j^{[0]} (b_i^{(0)} (\mathbf{b}_i' - \mathbf{b}_i) :$$

$$\mathbf{b}_i + b_j^{(0)} (\mathbf{b}_j' - \mathbf{b}_j) : \mathbf{b}_i) g_{ij} b db d\varepsilon d\mathbf{v}_j d\mathbf{v}_i \quad (224)$$

Here we have split up the integral in collisions between molecules of the same kind, indicated by i and $i1$, and molecules of i and j. In terms of bracket integrals this can be written as

$$n_i b_i^{(0)} [\mathbf{b}_i; \mathbf{b}_i]_{i,i1} + \sum_{\substack{j \\ j \neq i}} (n_j b_i^{(0)} [\mathbf{b}_i; \mathbf{b}_i]_{ij} + n_j b_j^{(0)} [\mathbf{b}_i; \mathbf{b}_j]_{ij}) = 5 \quad (225)$$

In matrix form this can be expressed as

$$[N](b^{(0)}) = (r) \quad (226)$$

then we have

$$N_{ii} = n_i [\mathbf{b}_i; \mathbf{b}_i]_{i,i1} + \sum_{\substack{j \\ j \neq i}} n_j [\mathbf{b}_i; \mathbf{b}_i]_{ij} \quad (227a)$$

$$N_{ij} = n_j \lfloor \mathbf{b}_i; \mathbf{b}_j \rfloor_{ij} \quad (227b)$$

$$r_i = 5 \quad (228)$$

With the expression in terms of Ω-integrals:

$$[\mathbf{b}_i; \mathbf{b}_i]_{i,i1} = 4\Omega_i^{(2,2)} \quad (229a)$$

$$[\mathbf{b}_i; \mathbf{b}_i]_{ij} = \frac{16}{3} \frac{m_j}{(m_i + m_j)^2} \left(5m_i \Omega_{ij}^{(1,1)} + \frac{3}{2} m_j \Omega_{ij}^{(2,2)}\right) \quad (229b)$$

$$[\mathbf{b}_i; \mathbf{b}_j]_{ij} = -\frac{16}{3} \frac{m_i m_j}{(m_i + m_j)^2} \left(5\Omega_{ij}^{(1,1)} - \frac{3}{2} \Omega_{ij}^{(2,2)}\right) \quad (229c)$$

the elements of the N-matrix can be calculated, and Eq. 226 can be solved for $b_i^{(0)}$. Later in this section, we will work this out further for the determination of the partial viscosities.

Development of the C_i. Here we start with Eqs. 203 and 207:

$$h_i^{[0]} \left(w_i^2 - \frac{5}{2}\right) \mathbf{u}_i = -\sum_j \int \int \int h_i^{[0]} h_j^{[0]}$$

$$\times (\mathbf{C}_i' + \mathbf{C}_j' - \mathbf{C}_i - \mathbf{C}_j) g_{ij} b db d\varepsilon d\mathbf{v}_j \quad (230)$$

$$\mathbf{C}_i = \mathbf{w}_i C_i(w_i) \quad (207)$$

We develop the C_i as a series of Sonine polynomials:

$$C_i = \sum_{k=0}^{r} c_i^{(k)} S_{3/2}^{(k)}(w_i^2) \quad (231)$$

First we apply the third of the auxiliary Eqs. 196 for the C-coefficients (see HCB, p. 475, Eq. 7.3-59):

$$\sum_{k=0}^{r} c_i^{(k)} \int h_i^{[0]} S_{3/2}^{(k)}(w_i^2) u_i^2 d\mathbf{v}_i = c_i^{(0)} \frac{3n_i kT}{m_i} = 0 \quad (232)$$

and so

$$c_i^{(0)} = 0 \quad (233)$$

and we can start the series with $k = 1$.

We now multiply both sides of Eq. 203 with $S_{3/2}^{(k)}(w_i^2) \mathbf{u}_i$ and integrate over $\mathbf{v}_i$:

$$-\int h_i^{[0]} S_{3/2}^{(1)}(w_i^2) S_{3/2}^{(k)}(w_i^2) \mathbf{u}_i \mathbf{u}_i d\mathbf{v}_i = -\sum_j \int \int \int \int h_i^{[0]} h_j^{[0]}$$

$$\times \begin{bmatrix} \sum_{k=1}^{r} c_i^{(k)} (S_{3/2}^{(k)}(w_i'^2) \mathbf{w}_i' - S_{3/2}^{(k)}(w_i^2) \mathbf{w}_i) + \\ \sum_{k=1}^{r} c_j^{(k)} (S_{3/2}^{(k)}(w_j'^2) \mathbf{w}_j' - S_{3/2}^{(k)}(w_j^2) \mathbf{w}_j) \end{bmatrix}$$

$$* S_{3/2}^{(1)}(w_i^2) \mathbf{u}_i g_{ij} b db d\varepsilon d\mathbf{v}_j d\mathbf{v}_i \quad (234)$$

The left-hand side of the equation is equal to

$$-\int h_i^{[0]} S_{3/2}^{(1)}(w_i^2) S_{3/2}^{(k)}(w_i^2) \mathbf{u}_i \mathbf{u}_i d\mathbf{v}_i = -\frac{1}{3} \int h_i^{[0]} S_{3/2}^{(1)}(w_i^2)$$

$$\times S_{3/2}^{(k)}(w_i^2) u_i^2 d\mathbf{v}_i = -\frac{2}{3} \pi^{-1/2} n_i \left(\frac{2kT}{m_i}\right) \int_0^{\infty} e^{-w_i^2} w_i^3 S_{3/2}^{(1)}(w_i^2)$$

$$\times S_{3/2}^{(k)}(w_i^2) dw_i^2 = \begin{pmatrix} -\frac{5}{2} \frac{n_i kT}{m_i} & k = 1 \\ 0 & k > 1 \end{pmatrix} \quad (235)$$

So within this approach, the single expansion $k = 1$ is sufficient.

For the integral part we have

$$-\sum_j \int \int \int \int h_i^{[0]} h_j^{[0]} \begin{bmatrix} c_i^{(1)} (S_{3/2}^{(1)}(w_i'^2) \mathbf{w}_i' - S_{3/2}^{(1)}(w_i^2) \mathbf{w}_i) + \\ c_j^{(1)} (S_{3/2}^{(1)}(w_j'^2) \mathbf{w}_j' - S_{3/2}^{(1)}(w_j^2) \mathbf{w}_j) \end{bmatrix}$$

$$* S_{3/2}^{(1)}(w_i^2) \mathbf{u}_i g_{ij} b db d\varepsilon d\mathbf{v}_j d\mathbf{v}_i$$

$$= -\frac{1}{3} \sqrt{\frac{2kT}{m_i}} \sum_j \int \int \int \int h_i^{[0]} h_j^{[0]}$$

$$\cdot \begin{bmatrix} c_i^{(1)}(S_{3/2}^{(1)}(w_i'^2)\mathbf{w}_i' - S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i) + \\ c_j^{(1)}(S_{3/2}^{(1)}(w_j'^2)\mathbf{w}_j' - S_{3/2}^{(1)}(w_j^2)\mathbf{w}_j) \end{bmatrix}$$

$$\cdot S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i g_{ij} b db d\varepsilon d\mathbf{v}_j d\mathbf{v}_i$$

Again we split the integration between i–i and i–j collisions, and so we obtain after some reordering in terms of bracket integrals:

$$\frac{15}{2} n_i \sqrt{\frac{kT}{2m_i}} = -c_i^{(1)} n_i^2 [S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i]_{i,i1} - \sum_{\substack{j \\ j \neq i}} n_i n_j$$

$$\times (c_i^{(1)}[S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i]_{ij} + c_j^{(1)}[S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_j^2)\mathbf{w}_j]_{ij})$$

$$(237)$$

Formally, we can write

$$[L][c^{(1)}] = (e) \tag{238}$$

with

$$L_{ii} = -n_i^2 \lfloor S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i \rfloor_{i,i1}$$

$$- \sum_{\substack{j \\ j \neq i}} n_i n_j (\lfloor S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i \rfloor_{ij}) \tag{239a}$$

$$L_{ij} = -n_i n_j ([S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i; S_{3/2}^{(1)}(w_j^2)\mathbf{w}_j]_{ij}) \tag{239b}$$

$$e_i = \frac{15}{2} n_i \sqrt{\frac{kT}{2m_i}} \tag{240}$$

In terms of the Ω-integrals this reads

$$L_{ii} = -n_i^2 4\Omega_i^{(2,2)} - \sum_{\substack{j \\ j \neq i}} n_i n_j 8 \frac{m_j}{(m_i + m_j)^3} \left(\frac{5}{4} (6m_i^2 + 5m_j^2)\Omega_{ij}^{(1,1)} \right.$$

$$\left. - 5m_j^2 \Omega_{ij}^{(1,2)} + m_j^2 \Omega_{ij}^{(1,3)} + 2m_i m_j \Omega_{ij}^{(2,2)} \right) \quad (241a)$$

$$L_{ij} = n_i n_j 8 \frac{(m_i m_j)^{3/2}}{(m_i + m_j)^3} \left(\frac{55}{4} \Omega_{ij}^{(1,1)} - 5\Omega_{ij}^{(1,2)} + \Omega_{ij}^{(1,3)} - 2\Omega_{ij}^{(2,2)} \right)$$

$$(241b)$$

Evaluation of the Momentum Balance. We already determined the zero-order interspecies friction force $\mathbf{F}_{ji}^{[0]}$, as given in Eq. 188. We found that the **A**-part of the perturbation function did not contribute to further refinement in this equation, as shown in Eq. 221. Therefore we consider here the other elements of the perturbation function

$$\phi_{i,C} + \phi_{i,B} = -(c_i^{(1)} S_{3/2}^{(1)}(w_i^2)\mathbf{w}_i) \cdot \nabla \ln T$$

$$- (b_i^{(0)} S_{5/2}^{(0)}(w_i^2)) \left[\mathbf{w}_i \mathbf{w}_i - \frac{1}{3} w_i^2 \mathbf{I} \right] : \nabla \mathbf{v}_{i0} \quad (242)$$

First we will consider the contribution of the **B**-part. We can write the following for the molecular stress tensor of i

$$\mathbf{\Pi}_i = \mathbf{\Pi}_i^{[0]} + \mathbf{\Pi}_i^{[1]} = m_i \int \mathbf{u}_i \mathbf{u}_i h_i^{[0]} d\mathbf{v}_i + m_i \int \mathbf{u}_i \mathbf{u}_i h_i^{[0]} \phi_{i,B}^{[1]} d\mathbf{v}_i$$

$$(243)$$

because the integration with the **C**-part delivers 0.

Already we had

$$\mathbf{\Pi}_i^{[0]} = p_i \mathbf{I} \tag{174}$$

and for the second term we find

$$\mathbf{\Pi}_i^{[1]} = -m_i b_i^{(0)} \int \mathbf{u}_i \mathbf{u}_i \left[\mathbf{u}_i \mathbf{u}_i - \frac{1}{3} u_i^2 \mathbf{I} \right] : \nabla \mathbf{v}_{i0} h_i^{[0]} d\mathbf{v}_i \quad (244)$$

According to the work of CC and HCB this leads to

$$\mathbf{\Pi}_i^{[1]} = -\left(\frac{1}{15} \frac{m_i^2}{kT} b_i^{(0)} \int u_i^4 h_i^{[0]} d\mathbf{v}_i \right) \mathbf{S}_i \tag{245}$$

with

$$\mathbf{S}_i = \frac{1}{2} \left[\nabla \mathbf{v}_{i0} + \nabla^T \mathbf{v}_{i0} - \frac{2}{3} (\nabla \mathbf{v}_{i0} : \mathbf{I})\mathbf{I} \right] \tag{246}$$

Here we define the partial viscosity by

$$\mathbf{\Pi}_i^{(1)} = -2\eta_i \mathbf{S}_i \tag{247}$$

and so we find for the partial viscosity in this approximation:

$$\eta_i = \frac{m_i^2}{30kT} b_i^{(0)} \int u_i^4 h_i^{(0)} d\nu_i = \frac{1}{2} kT n_i b_i^{(0)} \tag{248}$$

and for the total stress tensor for component i

$$\mathbf{\Pi}_i = p_i \mathbf{I} - 2\eta_i \mathbf{S}_i \tag{249}$$

The total stress tensor for the mixture becomes

$$\mathbf{\Pi}_{mix} = \mathbf{\Pi}_i = p\mathbf{I} - 2 \sum_i \eta_i \mathbf{S}_i \tag{250}$$

Only when all components have the same gradients in average velocity does this becomes equal to the classical expression. Under this limit condition we have

$$\eta_{\text{limit}} = \sum_i \eta_i \tag{251}$$

When velocity differences between components are considerable with respect to each other, the concept of mixture viscosity loses its meaning.

For a pure component the following expressions hold

$$b_{i,pure}^{(0)} = \frac{5}{4 n_i \Omega_i^{(2,2)}} \tag{252}$$

$$\eta_{i,pure} = \frac{5}{8} \frac{kT}{\Omega_i^{(2,2)}} \tag{253}$$

which is equal to the classical result.

Now let us consider the contribution of ϕ_{iC}. We have

$$F_{ji,C}^{[1]} = \int \int \int \int m_i \mathbf{v}_i h_i^{[0]} h_j^{[0]} (\phi_{iC}'^{[1]} + \phi_{jC}'^{[1]} - \phi_{iC}^{[1]}$$
$$- \phi_{jC}^{[1]}) g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i d\mathbf{v}_j \tag{254}$$

$$F_{ji,C}^{[1]} = -\int \int \int \int m_i \mathbf{v}_i h_i^{[0]} h_j^{[0]} \{(C_i' \mathbf{w}_i' - C_i \mathbf{w}_i + C_j' \mathbf{w}_j'$$
$$- C_j \mathbf{w}_j) \cdot \nabla \ln T\} g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i d\mathbf{v}_j$$
$$= -\nabla \ln T \frac{1}{3} \int \int \int \int m_i \mathbf{v}_i \cdot h_i^{[0]} h_j^{[0]} \{(C_i' \mathbf{w}_i' - C_i \mathbf{w}_i + C_j' \mathbf{w}_j'$$
$$- C_j \mathbf{w}_j)\} g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i d\mathbf{v}_j \tag{255}$$

This is equivalent to

$$\mathbf{F}_{ji,C}^{[1]} = -\nabla \ln T \frac{1}{3} \int \int \int \int m_i \mathbf{u}_i \cdot h_i^{[0]} h_j^{[0]} \{(C_i' \mathbf{w}_i' - C_i \mathbf{w}_i + C_j' \mathbf{w}_j'$$
$$- C_j \mathbf{w}_j)\} g_{ij} b \, db \, d\varepsilon \, d\mathbf{v}_i d\mathbf{v}_j \tag{256}$$

given that the integral with $\mathbf{v}_{i0}$ will vanish.

Splitting the integral again in i–i and i–j parts, leads to the bracket expressions

$$F_{ji,C}^{[1]} = \nabla \ln T \frac{1}{3} \sqrt{2 m_i kT} \, n_i n_j (c_i^{(1)} [\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2) \mathbf{w}_i]_{ij}$$
$$+ c_j^{(1)} [\mathbf{w}_i; S_{3/2}^{(1)}(w_j^2) \mathbf{w}_j]_{ij}) \tag{257}$$

The bracket integrals are

$$[\mathbf{w}_i; S_{3/2}^{(1)}(w_i^2) \mathbf{w}_i]_{ij} = -8 \frac{m_j^2}{(m_i + m_j)^2} \left(\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)} \right) \tag{258a}$$

$$[\mathbf{w}_i; S_{3/2}^{(1)}(w_j^2) \mathbf{w}_j]_{ij} = 8 \frac{m_i \sqrt{m_i m_j}}{(m_i + m_j)^2} \left(\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)} \right) \tag{258b}$$

and so

$$\mathbf{F}_{ji,C}^{[1]} = \frac{8}{3} n_i n_j \sqrt{2 m_i kT} \left(-\frac{m_j^2}{(m_i + m_j)^2} c_i^{(1)} + \frac{m_i \sqrt{m_i m_j}}{(m_i + m_j)^2} c_j^{(1)} \right)$$
$$\times \left(\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)} \right) \nabla \ln T$$
$$= \frac{8}{3} n_i n_j \sqrt{2kT} \left(-\frac{m_j^2 \sqrt{m_i}}{(m_i + m_j)^2} c_i^{(1)} + \frac{m_i^2 \sqrt{m_j}}{(m_i + m_j)^2} c_j^{(1)} \right)$$
$$\times \left(\Omega_{ij}^{(1,2)} - \frac{5}{2} \Omega_{ij}^{(1,1)} \right) \nabla \ln T \tag{259}$$

Substituting Eq. 187 for the binary diffusion coefficient, after some rearrangement, gives

$$\mathbf{F}_{ji,C}^{[1]} = -p \frac{x_i x_j}{\mathscr{D}_{ij}} \frac{1}{2} \frac{\sqrt{2kT}}{(m_i + m_j)} \left(c_i^{(1)} \frac{m_j}{\sqrt{m_i}} - c_j^{(1)} \frac{m_i}{\sqrt{m_j}} \right)$$
$$\times \left(\frac{5}{2} - \frac{\Omega_{ij}^{(1,2)}}{\Omega_{ij}^{(1,1)}} \right) \nabla \ln T \tag{260}$$

This can also be written as

$$\mathbf{F}_{ji,C}^{[1]} = -p \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} \left(\frac{D_{ij}^T}{n_i m_i} - \frac{D_{ji}^T}{n_j m_j} \right) \nabla \ln T \tag{261}$$

and so

$$D_{ij}^T = \frac{1}{2} \frac{\sqrt{2kT}}{(m_i + m_j)} c_i^{(1)} n_i m_j \sqrt{m_i} \left(\frac{5}{2} - \frac{\Omega_{ij}^{(1,2)}}{\Omega_{ij}^{(1,1)}} \right) \tag{262}$$

Alternatively, we can use the *thermal diffusion ratio*:

$$F_{ji,C} = -p k_{T,ij} \nabla \ln T \tag{263}$$

$$k_{T,ij} = \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} \left(\frac{D_{ij}^T}{n_i m_i} - \frac{D_{ji}^T}{n_j m_j} \right) \tag{264}$$

With this we find the expression for the momentum balance:

$$\frac{\partial \mathbf{v}_{i0}}{\partial t} = -\frac{1}{n_i m_i} \nabla p_i + \frac{2}{n_i m_i} \nabla \cdot (\eta_i \mathbf{S}_i) + \frac{\mathbf{X}_i}{m_i} - \mathbf{v}_{i0} \cdot \nabla \mathbf{v}_{i0}$$
$$+ \frac{1}{n_i m_i} \sum_j \left[-\frac{p_i p_j}{p \mathscr{D}_{ij}} (\mathbf{v}_{i0} - \mathbf{v}_{j0}) - p \frac{n_i n_j}{n^2 \mathscr{D}_{ij}} \left(\frac{D_{ij}^T}{n_i m_i} - \frac{D_{ji}^T}{n_j m_j} \right) \nabla \ln T \right] \tag{265}$$

or, in slightly different form, replacing the notation $\mathbf{v}_{i0}$ by $\overline{\mathbf{v}}_i$:

$$\rho_i \frac{\partial \overline{\mathbf{v}}_i}{\partial t} = -\nabla p_i + 2 \nabla \cdot (\eta_i \mathbf{S}_i) + \rho_i \hat{\mathbf{F}}_i - \rho_i \overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i$$
$$- p \left[\sum_j \frac{x_i x_j}{\mathscr{D}_{ij}} (\overline{\mathbf{v}}_i - \overline{\mathbf{v}}_j) + \sum_j \frac{x_i x_j}{\mathscr{D}_{ij}} \left(\frac{D_{ij}^T}{\rho_i} - \frac{D_{ji}^T}{\rho_j} \right) \nabla \ln T \right] \tag{266}$$

which can be considered as a new diffusion equation for dilute monatomic gases. The difference lies in the individual shear stress term, and also in the way the physical properties of mixtures are evaluated. Here $\mathbf{S}_i$ is defined in Eq. 246. Summing over all components i leads to the momentum balance for the mixture as a whole

$$\sum_i \rho_i \frac{\partial \overline{\mathbf{v}}_i}{\partial t} = -\sum_i \rho_i\{\overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i\} - \nabla p + \sum_i \rho_i \hat{\mathbf{F}}_i + 2\nabla \cdot \sum_i [\eta_i \mathbf{S}_i]$$

(267)

Let us consider Eq. 266 in terms of physical forces, and let it be applied to a small-volume element of the mixture. On the left-hand side we have the acceleration force on a species i, expressed as the force on i per unit of volume. The first term on the right-hand side is the partial pressure gradient. The second term is the shear force, which is caused by the exchange between molecules i inside and outside of the volume element, having different molecular average velocities because of the velocity gradients. The third term represents the external forces on i. In the fourth term the change in momentum carried by the convective flow of i is represented. The fifth term stands for the interspecies friction between i and the other components arising from their velocity differences. The sixth term represents the momentum transferred because of the gradient in temperature over the element, which causes a gradient in the molecular velocity distributions. Both the fifth and the sixth terms can be ascribed to interspecies collisions. Within the volume element the collisions between i and i do not influence the average momentum of i. Molecules j, moving in and out of the volume element, do not influence the convective momentum of i. Because of their velocity gradients, they produce a shearing force on species j, but this is felt by i only through the collisions inside the element, as already accounted for in the two last terms of the equation. In the classic equations the shear term in the i-momentum balance comes out as proportional to the change in gradients in the mass-averaged velocity; this would imply that it is the result of the differences in average velocity of all species entering and leaving the element. However, the other species can affect the momentum of i only through the collision terms, which already have been accounted for separately. In the classic equations the change in convected momentum of i is represented as $\rho_i \mathbf{u}_c \cdot \nabla \mathbf{u}_c$. However, the flow of i is equal to $\rho_i \overline{\mathbf{v}}_i$, and if there are considerable differences between $\mathbf{v}_i$ and $\mathbf{u}_c$ there is already a difference in flow of i; furthermore, the magnitude and direction of $\overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i$ may then differ considerably from $\mathbf{u}_c \cdot \nabla \mathbf{u}_c$. Thus we feel that the shape of the present equation is a more accurate representation of the physical phenomena within a volume element than that of the classic equations.

In the next paragraph we will consider the physical properties according to the new scheme. Following this, we will present generalized equations for polyatomic molecules and dense media, and after that we will comment on the discrepancy between the sums of the individual stress tensors and the usual definition of the stress tensor for a mixture. Finally, we will show the importance of the individual shear stress for the description of practical problems.

The Equation of Energy and the Molecular Heat Flux. The starting point here is the equation of energy in the form of Eq. 173:

$$\frac{3}{2} n_i k \frac{\partial T}{\partial t} = -(\mathbf{\Pi}_i : \nabla \overline{\mathbf{v}}_i) - (\nabla \cdot \mathbf{q}_{i,m})$$
$$- \frac{3}{2} n_i k (\overline{\mathbf{v}}_i \cdot \nabla T) + \sum_j Q_{ij} - \left(\overline{\mathbf{v}}_i \cdot \sum_j \mathbf{F}_{ji}\right) \quad (173)$$

Addition over all components gives

$$\frac{3}{2} nk \frac{\partial T}{\partial t} = -\sum_i (\mathbf{\Pi}_i : \nabla \overline{\mathbf{v}}_i) - \sum_i (\nabla \cdot \mathbf{q}_{i,m})$$
$$- \frac{3}{2} k \sum_i n_i (\overline{\mathbf{v}}_i \cdot \nabla T) - \sum_i \left(\overline{\mathbf{v}}_i \cdot \sum_j \mathbf{F}_{ji}\right) \quad (268)$$

For the molecular heat flux of i we find

$$\mathbf{q}_{i,m} = \frac{1}{2} m_i \int h_i^{[0]}(1 + \phi_i^{[1]}) u_i^2 \mathbf{u}_i d\mathbf{v}_i = \frac{1}{2} m_i \int h_i^{[0]} \phi_i^{[1]} u_i^2 \mathbf{u}_i d\mathbf{v}_i$$

$$= -\frac{1}{2} m_i (\nabla \ln T) c_i^{(1)} \int h_i^{[0]} S_{3/2}^{(1)}(w_i^2) \mathbf{w}_i u_i^2 \mathbf{u}_i d\mathbf{v}_i$$

$$= -\frac{1}{6} m_i (\nabla \ln T) c_i^{(1)} \int h_i^{[0]} S_{3/2}^{(1)}(w_i^2) u_i^4 d\mathbf{v}_i$$

$$= \frac{5}{4} \sqrt{2} n_i m_i \left(\frac{kT}{m_i}\right)^{3/2} c_i^{(1)} \nabla \ln T \quad (269)$$

and so we can define a partial thermal conductivity by

$$\mathbf{q}_{i,m} = \lambda_i \nabla T \quad (270)$$

with

$$\lambda_i = -\frac{5\sqrt{2}}{4} k^{3/2} T^{1/2} n_i (m_i)^{-1/2} c_i^{(1)} \quad (271)$$

For the total molecular heat flux we have

$$\mathbf{q}_m = \sum_i \mathbf{q}_{i,m} = -\lambda_{mix} \nabla T \quad (272)$$

and so we obtain for the thermal conductivity of the mixture

$$\lambda_{mix} = -\frac{5\sqrt{2}}{4} k^{3/2} T^{1/2} \sum_i n_i (m_i)^{-1/2} c_i^{(1)} \quad (273)$$

The energy balance for the mixture can be written in other terms as

$$\frac{3}{2} c_t R \frac{\partial T}{\partial t} = -\sum_i ([p_i \mathbf{I} - 2\eta_i \mathbf{S}_i] : \nabla \overline{\mathbf{v}}_i) + \nabla \cdot [\lambda_{mix} \nabla T]$$

$$-\frac{3}{2} R \sum_i c_i \overline{\mathbf{v}}_i \cdot \nabla T + p \sum_i \frac{x_i x_j}{\mathcal{D}_{ij}} \overline{\mathbf{v}}_i$$

$$\times \left(\sum_j \left[(\overline{\mathbf{v}}_i - \overline{\mathbf{v}}_j) + \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j} \right) \nabla \ln T \right] \right) \quad (274)$$

For a single gas it follows that

$$\lambda_{i,pure} = \frac{75}{32} \frac{k^2 T}{m_i \Omega_i^{(2,2)}} \quad (275)$$

which is the classical result.

Transport coefficients for dilute monatomic gases according to the new solution

Comparison of the equations for physical transport properties of Chapman–Enskog[12] (CC), Hirschfelder et al.[13] (HCB), and Ferziger and Kaper[53] on one hand and those of our present approach shows that there are differences for mixture properties. The equations for pure components are identical because the model approaches also become identical. It is thus of interest to compare some of the present results for mixtures with those obtained from previous methods. Because our derivations were for dilute monatomic gases, we will limit ourselves here to properties of such gases.

For the binary diffusion coefficient we also directly obtained the same first-order Eq. 187 as follows from the classic treatment. However, in our methodology it followed directly from the momentum balance, whereas in the classic approach multicomponent Fickian equations with subsequent complicated

inversions were necessary. This is the consequence of the elimination of the $\mathbf{F}_{ij}$-terms by taking the summed momentum balance (Eq. 119) in the classic treatment. We limited ourselves to first-order approximation, and found a second-order effect to be equal to zero; however, a refinement of the assumptions in Eq. 192 might be interesting to study.

For the other transport properties we derived expressions in terms of $b_i^{(0)}$ and $c_i^{(1)}$, and provided the principal methods to calculate them in terms of the Ω-integrals. Through some mathematical rearrangement the equations for the transport properties can be streamlined somewhat, with the following results.

For the partial viscosities we obtain

$$[P](\eta) = (r_\eta) \quad (276)$$

$$P_{ii} = \frac{2}{kT} \left[\frac{4}{5} \Omega_i^{(2,2)} + \sum_{\substack{j \\ j \neq i}} \frac{x_j}{x_i} \frac{16}{15} \frac{m_j}{(m_i + m_j)^2} \right.$$

$$\left. \times \left(5m_i \Omega_{ij}^{(1,1)} + \frac{3}{2} m_j \Omega_{ij}^{(2,2)} \right) \right] \quad (277a)$$

$$P_{ij} = -\frac{2}{kT} \left[\frac{16}{15} \frac{m_i m_j}{(m_i + m_j)^2} \left(5\Omega_{ij}^{(1,1)} - \frac{3}{2} \Omega_{ij}^{(2,2)} \right) \right] \quad (277b)$$

$$r_{\eta,i} = 1 \quad (278)$$

From this set we can calculate the η_i directly, and by addition we find the mixture dynamic viscosity.

For the partial thermal conductivities can be found

$$[M](\lambda) = (r_\lambda) \quad (279)$$

with

$$M_{ii} = \frac{32}{75} \frac{m_i}{k^2 T} \left[\Omega_i^{(2,2)} + 2 \sum_{\substack{j \\ j \neq i}} \frac{x_j}{x_i} \frac{m_j}{(m_i + m_j)^3} \left(\frac{5}{4} (6m_i^2 + 5m_j^2) \Omega_{ij}^{(1,1)} - 5m_j^2 \Omega_{ij}^{(1,2)} + m_j^2 \Omega_{ij}^{(1,3)} + 2m_i m_j \Omega_{ij}^{(2,2)} \right) \right] \quad (280a)$$

$$M_{ij} = -\frac{64}{75} \frac{1}{k^2 T} \frac{(m_i m_j)^2}{(m_i + m_j)^3}$$

$$\times \left(\frac{55}{4} \Omega_{ij}^{(1,1)} - 5\Omega_{ij}^{(1,2)} + \Omega_{ij}^{(1,3)} - 2\Omega_{ij}^{(2,2)} \right) \quad (280b)$$

$$r_{\lambda,i} = 1 \quad (281)$$

Again the partial thermal conductivities can be calculated from Eq. 280, and the thermal conductivity of the mixture follows by simple addition.

For the multicomponent thermal diffusion coefficients, as defined in Eq. 262, the following expression can also be found

$$D_{ij}^T = \frac{m_i m_j}{(m_i + m_j)} \frac{\lambda_i}{k} \left(\frac{2}{5} \frac{\Omega_{ij}^{(1,2)}}{\Omega_{ij}^{(1,1)}} - 1 \right) \quad (282)$$

and for the thermal diffusion ratio

$$k_{T,ij} = \frac{T}{p\mathcal{D}_{ij}(m_i + m_j)} (x_j m_j \lambda_i - x_i m_i \lambda_j) \left(\frac{2}{5} \frac{\Omega_{ij}^{(1,2)}}{\Omega_{ij}^{(1,1)}} - 1 \right) \quad (283)$$

In the following we compare our results with those of CC and HCB, as based on the Lennard–Jones 12-6 potential function

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (284)$$

The Lennard–Jones constants σ and ε/k were taken from Table I-A in HCB (pp. 1110–1111); they are given here in Appendix C, Table C1. For mixtures we used the usual mixing rules

Table 1. Comparison between Experimental and Calculated Values for the Viscosity of a Mixture of Ar and Ne*

T (K)	% Ar	0.000	26.800	60.910	74.210	100.000
293.16	Exptl.	3.092	2.808	2.504	2.401	2.213
	Calc, HCB	3.070	2.795	2.493	2.390	2.208
	Calc, this work	3.110	2.819	2.504	2.397	2.211
373.16	Exptl.	3.623	3.313	2.990	2.885	2.693
	Calc, HCB	3.566	3.281	2.963	2.853	2.660
	Calc, this work	3.640	3.330	2.997	2.883	2.686
473.16	Exptl.	4.220	3.890	3.529	3.413	3.222
	Calc, HCB	4.170	3.847	3.495	3.375	3.164
	Calc, this work	4.245	3.905	3.541	3.417	3.202

*Dynamic viscosity η in 10^{-5} Pa · s. Experimental (Exptl.) and calculated (calc), HCB from Hirschfelder et al.,[13] Table 8.4-5, p. 568. Calculated values from this work are according to Eqs. 276–278.

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \qquad \varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \qquad (285)$$

In our calculations we evaluated the Ω-integrals through

$$\Omega^{(l,s)} = \Omega*^{(l,s)} \Omega_{rs}^{(l,s)} \qquad (286)$$

in which

$$[Q^{(l)}]_{rs} = \left[1 - \frac{1}{2} \frac{1 + (-1)^l}{1 + l} \right] \pi \sigma^2 \qquad (287)$$

$$[\Omega^{(l,s)}]_{rs} = \sqrt{\frac{kT}{2\pi\mu}} \frac{(s + 1)!}{2} [Q^{(l)}]_{rs} \qquad (288)$$

are the equations for rigid spheres (HCB, p. 525).

HCB provide in Table I-M (pp. 1126–1127) tabulated values of $\Omega*^{(l,s)}$ for different values of l and s, in dependency on $T* = Tk/\varepsilon$. Rather than trying to calculate such values ourselves, we fitted the data with a Neufeld-type equation, as cited by Poling et al.[65]

$$\Omega* = a(T*)^{-b} + c \exp(-dT*) \qquad (289)$$

Fitting constants are given in Table C2 in Appendix C.

In Table 1 we compare our results for the viscosity of a mixture of Ar and Ne at three temperature levels, with experimental data, and with calculated data by the classical methods, of HCB. In Table 2 we compare the results of the present theory for a ternary mixture of Ne, Ar, and He, with experimental data and data obtained by the classical methods. We

have an excellent agreement between our new calculation and experiments, even a little bit better than the classical data. To illustrate the dependency of partial viscosities on concentration, we present in Figure 6 the results for a mixture of Ar and He, at 273.16 K, from CC. We see that the present theory describes the mixture viscosity very well, comparably to the classic calculations, including the maximum in the viscosity–composition curve. It is clear that the partial viscosities are nonlinear functions of composition.

In Figure 7 we present the comparison for the thermal conductivity for mixtures of He and Ar at 273.16 K, again with experimental data and calculations by CC. The agreement is again very good. The partial thermal conductivities are again nonlinear functions of composition.

In Table 3, we compare the present calculations with experimental and classic calculations for the thermal diffusion ratio k_T for a mixture of He and Ar, and in Table 4 for mixtures of Ne and Ar. The effect of temperature at a given composition and the effect of composition at given temperature are both better than or equal to values of the experimental data within 5%. The deviations for the present and the HCB calculations are of the same order.

Although it is of interest to compare more data for monatomic dilute gases, we conclude from the limited comparison made here that the calculations according to the new theory are of the same precision as those obtained by the classic equations. In our opinion they are also a bit simpler than calculations derived according to the classic schemes. Here we developed the momentum balance and transport equations for each species separately, and we did not place restrictions on the summed momentum and energy balances. Mathematically this

Table 2. Dynamic Viscosity of Ternary Mixtures of Ne, Ar, and He, at Different Temperatures*

T (K)	% Ne	% Ar	% He	Exptl.	HCB, Calc	This Work
293	55.76	26.70	17.54	2.740	2.718	2.736
293	31.93	32.13	35.94	2.569	2.562	2.575
293	21.66	58.51	19.83	2.411	2.429	2.432
293	21.89	23.82	54.29	2.504	2.500	2.512
373	55.76	26.70	17.54	3.237	3.205	3.233
373	31.93	32.13	35.94	3.044	3.025	3.050
373	21.66	58.51	19.83	2.886	2.895	2.910
373	21.89	23.82	54.29	2.957	2.938	2.965
473	55.76	26.70	17.54	3.790	3.752	3.792
473	31.93	32.13	35.94	3.574	3.551	3.582
473	21.66	58.51	19.83	3.415	3.425	3.439
473	21.89	23.82	54.29	3.470	3.449	3.476

*Dynamic viscosity η in 10^{-5} Pa · s. Experimental (Exptl.) and calculated (calc), HCB from Hirschfelder et al.,[13] Table 8.4-6, p. 570. Calculated values from this work are according to Eqs. 276–278. First temperature corrected from 193 (HCB) to 293 K.
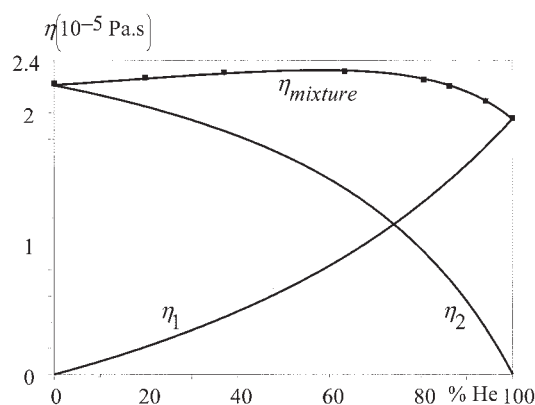
Figure 6. Partial and mixture viscosities of a mixture of He and Ar, at 273.16 K.

Lines: according to present theory; symbols: experimental data (Chapman and Cowling,[12] Table 19, p. 241), virtually coinciding with classic calculated data.

produced straightforward equations for the partial mixture quantities and of their sums for the whole of the mixture.

Proposed extension to dense gases and liquids

Generalization of the equation derived for monatomic gases by replacing the partial pressure gradient by the gradient of the chemical potential, and introduction of the coefficient of bulk viscosity, leads to the following momentum balance equation for dense gases and liquids

$$\rho_i \frac{\partial \overline{\mathbf{v}}_i}{\partial t} = -\rho_i\{\overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i\} - c_i \nabla_{T,p} \mu_i - c_i \bar{V}_i \nabla p + \rho_i \hat{\mathbf{F}}_i$$

$$- c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j}\right) \nabla \ln T + c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathscr{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i)$$

$$+ \nabla \cdot \{2\eta_i \mathbf{S}_i + \varphi_i (\nabla \cdot \overline{\mathbf{v}}_i)\mathbf{I}\} \quad (290)$$
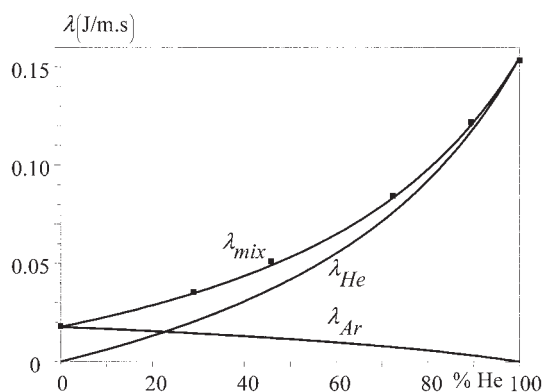

Figure 7. Partial and mixture thermal conductivities of a mixture of He and Ar.

Lines: according to present theory; symbols: experimental data (Chapman and Cowling,[12] Table 21, p. 254), virtually coinciding with classic calculated data.

Table 3. Dimensionless Thermal Diffusion Ratio k_T for a Mixture of He and Ar*

T (K)	% He	Exptl.	Calc, HCB	Calc, This Work
179	51.2	0.0910	0.0944	0.0891
205	51.2	0.0920	0.0957	0.0925
365	51.2	0.0956	0.0961	0.0987
330	10.0	0.0250	0.0259	0.0256
330	20.0	0.0476	0.0494	0.0488
330	30.0	0.0660	0.0698	0.0690
330	40.0	0.0810	0.0893	0.0855
330	50.0	0.0931	0.0979	0.0972

*Experimental (Exptl.) and calculated (calc), HCB from Hirschfelder et al.,[13] Table 8.4-14, p. 568. Calculated values from this work are according to Eqs. 279–283.

with $\mathbf{S}_i$ given in Eq. 246. The equations given in Appendix A for $\mathbf{S}$ can be used for $\mathbf{S}_i$ by substituting $\overline{\mathbf{v}}_i$ for the velocity. For the mixture as a whole, addition over all species i gives

$$\sum_i \rho_i \frac{\partial \overline{\mathbf{v}}_i}{\partial t} = -\sum_i \rho_i\{\overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i\} - \nabla p + \sum_i \rho_i \hat{\mathbf{F}}_i$$

$$+ \nabla \cdot \sum_i \{2\eta_i \mathbf{S}_i + \varphi_i (\nabla \cdot \overline{\mathbf{v}}_i)\mathbf{I}\} \quad (291)$$

For the energy equation we propose the following generalization

$$c_t \overline{C}_v \frac{\partial T}{\partial t} = -\sum_i ([p_i \mathbf{I} - 2\eta_i \mathbf{S}_i] : \nabla \overline{\mathbf{v}}_i) + \nabla \cdot [\lambda_{mix} \nabla T]$$

$$- \sum_i c_i \overline{\mathbf{v}}_i C_{vi} \cdot \nabla T + c_t RT \sum_i \frac{x_i x_j}{\mathscr{D}_{ij}} \overline{\mathbf{v}}_i$$

$$\cdot \left(\sum_j \left[(\overline{\mathbf{v}}_i - \overline{\mathbf{v}}_j) + \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j}\right) \nabla \ln T\right]\right) \quad (292)$$

In general for dense, polyatomic media, the physical transport properties have a different dependency on temperature, composition, and molecular mass. However, as shown in many previous studies the mathematical shape of the transport equations remains the same as that for monatomic gases. Moreover, in view of our discussion in earlier sections, we are also confident that for dense media and polyatomic molecules, derivations similar to our new approach and that of Snell at al.

Table 4. Dimensionless Thermal Diffusion Ratio k_T for a Mixture of Ne and Ar*

T (K)	% Ne	Exptl.	Calc, HCB	Calc, This Work
179	51.2	0.0350	0.0347	0.0343
205	51.2	0.0380	0.0385	0.0374
261	51.2	0.0415	0.0425	0.0425
406	51.2	0.0477	0.0490	0.0489
324	20	0.0233	0.0257	0.0255
324	30	0.0339	0.0353	0.0350
324	40	0.0407	0.0424	0.0420
324	50	0.0457	0.0463	0.0460
324	60	0.0467	0.0468	0.0465

*Experimental (Exptl.) and calculated (calc), HCB from Hirschfelder et al.,[13] Table 8.4-14, p. 568. Calculated values from this work are according to Eqs. 279–283.

will provide equations of the forms proposed above. This will be an interesting field of research. As we will show further on, the present equations allow the accurate description of problems such as the isobaric counterdiffusion of gases, Fick's experiment, as well as liquid ultrafiltration and nonisobaric diffusion of gases in porous media. To apply the equations we need physical data, such as thermodynamic data and transport coefficients, such as diffusion coefficients, thermal conductivity, all in dependency on composition and temperature. In addition we see that we will also need the partial viscosities, also in dependency on composition and temperature. For many properties we can rely on a large amount of very well-documented methods, such as described in the work by Poling et al.[65] As we have shown elsewhere, the partial viscosities of gases can be estimated from Wilke's equation.[25] In our study of the modeling of liquid ultrafiltration we fitted suitable equations to the measured mixture viscosity data for aqueous solutions of biopolymers. Here we used fractional viscosity coefficients defined by[25]

$$\kappa_i = \frac{\eta_i}{c_t RT \phi_i} \qquad (293)$$

Because the partial viscosity of a component goes to zero when the fraction of this component approaches zero, the κ_i are less concentration dependent.

Some remarks about the stress tensor and the energy flux for the mixture

In our current approach we have mainly focused on the momentum balance for each single species in a mixture. In many texts the concept of an overall molecular stress tensor is used, also in combination with partial stress tensors.[47] In our view, the momentum balance for the whole of the mixture is nothing more than the sum of the species balances, and as a consequence we have the opinion that the concept of a molecular stress tensor for the mixture as a whole makes sense only in the situation that all species move with virtually the same velocity, and under the same gradients.

Within the momentum balance a distinction is made between molecular and convective flow of momentum. For the first, in the classic approach, is written

$$\boldsymbol{\pi}_m = \sum_i \boldsymbol{\pi}_i = \sum_i n_i m_i \overline{\mathbf{V}_i \mathbf{V}_i} = \sum_i n_i m_i \overline{(\mathbf{v}_i - \mathbf{u}_c)(\mathbf{v}_i - \mathbf{u}_c)}$$

$$(107)$$

For the convective flow of momentum of the "mixture as a whole" one would tend to consider

$$\boldsymbol{\pi}_{con} = \rho \mathbf{u}_c \mathbf{u}_c \qquad (294)$$

However, for the total momentum flow with respect to fixed coordinates one would have

$$\boldsymbol{\pi}_t = \sum_i n_i m_i \overline{\mathbf{v}_i \mathbf{v}_i} \qquad (295)$$

and this is not equal to the sum of the molecular and convective momentum flow defined above. It is this addition problem that causes a "stress" in the mathematical treatment.

A similar problem lies in the splitting of kinetic energy into a thermal part and a part attributed to the kinetic energy of the overall flow. Here we find

$$\sum_i \frac{1}{2} n_i m_i \overline{\nu_i^2 \mathbf{v}_i} \neq \sum_i \frac{1}{2} n_i m_i \overline{(\nu_i - u_c)^2 (\mathbf{v}_i - \mathbf{u}_c)} + \frac{1}{2} \rho u_c^2 \mathbf{u}_c \quad (296)$$

Although the differences are often probably small, the discrepancy between required single mixture stress and thermal energy, and the sum of the parts, causes considerable confusion. Here we propose again that the total molecular stress is just the sum of the species molecular stresses, and the total thermal energy is the sum of the species thermal energies. In the special situation of equal species velocities, the sums reduce to the classic equations, as will be discussed in the next section.

Some Properties of the New Equations

Limit expressions

In the following we will treat a few limit situations. A special case is the transport of a binary mixture in long channels and pores; this will be considered separately in the next paragraphs, where the Remick and Geankoplis experiment and the Fick experiment are reconsidered.

We start with the proposed general momentum balance, Eq. 290.

Single Component. For a single component one obtains

$$\rho \frac{\partial \mathbf{u}}{\partial t} = -\rho \{\mathbf{u} \cdot \nabla \mathbf{u}\} - \nabla p + \rho \hat{\mathbf{F}} + \nabla \cdot \{2\eta \mathbf{S} + \varphi (\nabla \cdot \mathbf{u}) \mathbf{I}\} \quad (297)$$

the Navier–Stokes Equation, with $\mathbf{S}$ given by Eq. 19.

For a monatomic single gas, or an incompressible single liquid, one can neglect the bulk viscosity or $(\nabla \cdot \mathbf{u})$, respectively, resulting in

$$\rho \frac{\partial \mathbf{u}}{\partial t} = -\rho \{\mathbf{u} \cdot \nabla \mathbf{u}\} - \nabla p + \rho \hat{\mathbf{F}} + \nabla \cdot \{2\eta \mathbf{S}\} \qquad (298)$$

Isothermal (Quasi-) Steady Transport for Mixtures in the Absence of Shear and External Forces. If we can neglect acceleration, bulk viscosity, and convected momentum, and we have no external forces, for the sum of Eq. 1 over all species is obtained

$$-\nabla p + \nabla \cdot \sum_i \{2\eta_i \mathbf{S}_i\} = 0 \qquad (299)$$

This means that when shear and external forces are absent, the process is also isobaric. For the single species transport we then have

$$-c_i \nabla_{T,p} \mu_i + c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i) = 0 \qquad (300)$$

the isothermal, isobaric Maxwell–Stefan equation for an unconstrained medium. For an ideal gas this is expressed as

$$-\nabla x_i + \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i) = 0 \quad (301)$$

Shear Force Small Compared to Interspecies Friction. Depending on the circumstances, velocity gradients may be small or large, and as a consequence shear forces may be small or large compared to other terms in the momentum balance. When the shear force is relatively small, it means that in a volume element the interspecies friction dominates, which tends to "homogenize" the velocities of the different species, and so the differences $\mathbf{v}_{i0} - \mathbf{u}_c$ become very small. Thus the velocity gradients of different species also tend to be closely together. For a binary system in a long cylindrical capillary or flat channel we developed a criterion within the framework of the velocity profile model (VPM-1)[25]

$$\varphi = \frac{\mathcal{D}_{12}}{c_t RT x_1 x_2} \frac{\eta_1 \eta_2}{\eta B_0} \quad (302)$$

in which

$$B_0 = \begin{cases} r_p^2/8 & \text{cylinder} \\ r_p^2/3 & \text{flat channel} \end{cases} \quad (303)$$

This modulus is a measure of the ratio between shear and diffusive friction. For low values of φ the interspecies diffusive friction dominates. We do not yet have such a criterion for multicomponent systems; however, one could make an estimate by considering two "key" components of a mixture. Under low-shear conditions the equation for the whole of the mixture can than be approximated by

$$\rho \frac{\partial \mathbf{u}_c}{\partial t} = -\rho\{\mathbf{u}_c \cdot \nabla \mathbf{u}_c\} - \nabla p + \sum_i \rho_i \hat{\mathbf{F}}_i$$
$$- \nabla \cdot \{2\eta\mathbf{S} + \eta_b(\nabla \cdot \mathbf{u}_c)\mathbf{I}\} \quad (304)$$

so in the summation where the diffusive terms cancel out, the shear is still present, and we have the Navier–Stokes equation for the whole of the fluid. In the species equation we obtain

$$\rho_i \frac{\partial \overline{\mathbf{v}}_i}{\partial t} = -\rho_i\{\overline{\mathbf{v}}_i \cdot \nabla \overline{\mathbf{v}}_i\} - c_i \nabla_{T,p}\mu_i - c_i \bar{V}_i \nabla p + \rho_i \hat{\mathbf{F}}_i$$
$$- c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j}\right)\nabla \ln T + c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i)$$
$$(305)$$

which for many problems can also be approached by

$$-c_i \nabla_{T,p}\mu_i - c_i \bar{V}_i \nabla p + \rho_i \hat{\mathbf{F}}_i - c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} \left(\frac{D_i^T}{\rho_i} - \frac{D_j^T}{\rho_j}\right)\nabla \ln T$$
$$+ c_t RT \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\overline{\mathbf{v}}_j - \overline{\mathbf{v}}_i) = 0 \quad (306)$$

Thus, under these conditions the motion of the fluid as a whole and the motion of the individual species become coupled only through the temperature and pressure gradients, and the dependency of physical properties on composition, and the equations become identical to those of the Chapman–Enskog and HCB theory.

Isothermal Trace Diffusion of Component 1 in Nearly Pure 2. We assume that we have a trace of component 1, and so $x_2 \to 1$. Let us also neglect the effect of bulk viscosity. For component 2 we have the Navier–Stokes Eq. 297. We write $\rho_2 = \rho$, and so forth. For component 1 we have

$$0 = -\rho_1\{\overline{\mathbf{v}}_1 \cdot \nabla \overline{\mathbf{v}}_1\} - c_1 \nabla_{T,p}\mu_1 - c_1 \bar{V}_1 \nabla p + \rho_1 \hat{\mathbf{F}}_1$$
$$+ c_t RT \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1) - \nabla \cdot \{2\eta_1 \mathbf{S}_1\} \quad (307)$$

If we also neglect the convected 1-momentum, and assume no external force, then it follows that

$$0 = -c_1 \nabla_{T,p}\mu_1 - c_1 \bar{V}_1 \nabla p + c_t RT \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1) - \nabla \cdot \{2\eta_1 \mathbf{S}_1\}$$
$$(308)$$

If the shear term is much smaller than the other terms, the last term disappears too, and we keep

$$0 = -c_1 \nabla_{T,p}\mu_1 - c_1 \bar{V}_1 \nabla p + c_t RT \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1) \quad (309)$$

which is the boundary-free Maxwell–Stefan equation.

For a gas mixture we have

$$\nabla p_1 + p \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{\mathbf{v}}_2 - \overline{\mathbf{v}}_1) = 0 \quad (310)$$

This can simply be converted to

$$\mathbf{N}_1 = \mathbf{u}c_1 - \mathcal{D}_{12}\nabla c_1 \quad (311)$$

For a liquid we have similarly

$$\mathbf{N}_1 = \mathbf{u}c_1 - \mathcal{D}_{12}\left(c_t\Gamma_1\nabla x_1 - \frac{\phi_1}{RT}\nabla p\right) \approx \mathbf{u}c_1 - \mathcal{D}_{12}c_t\Gamma_1\nabla x_1$$
$$(312)$$

This means that for a trace component under the above conditions, the flow problem is solved for the solvent, and subsequently the diffusion problem is solved separately for compo-

nent 2. This is, among other factors, essentially the basis for the Taylor-dispersion treatment.

Isothermal gas diffusion in long channels: the Remick and Geankoplis experiments reconsidered

For the description of the binary Remick and Geankoplis experiments, we assume the following: steady flow, negligible momentum convection, isothermal operation, negligible bulk viscosity effects, no radial flow, no radial partial pressure gradients, and cylindrical symmetry.

Under these assumptions, the general transport equation goes over in the basic equation for the velocity profile model (VPM-1)[25]

$$\frac{dp_i}{dx} - \eta_i \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \overline{v_{i,x}}}{\partial r} \right) + p \sum_{j=1}^{n} \frac{x_i x_j}{\mathcal{D}_{ij}} (\overline{v_{i,x}} - \overline{v_{j,x}}) = 0 \quad (313)$$

For a binary system we obtain

$$B_1 = \frac{dp_1}{dx} = \eta_1 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \overline{v_{1,x}}}{\partial r} \right) - p \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{v_{1,x}} - \overline{v_{2,x}}) \quad (314a)$$

$$B_2 = \frac{dp_2}{dx} = \eta_2 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \overline{v_{2,x}}}{\partial r} \right) + p \frac{x_1 x_2}{\mathcal{D}_{12}} (\overline{v_{1,x}} - \overline{v_{2,x}}) \quad (314b)$$

We solved this problem earlier with the Maxwell-slip boundary condition[25]

$$r = r_p \qquad v_{i,x,s} = -G_i \frac{\partial \overline{v_{i,x}}}{\partial r} \quad (315)$$

in which the slip modulus ("Gleitmodulus") is given by

$$G_i = \frac{2 \eta_i D_i^K}{p_i r_p} \quad (316)$$

and D_i^K is the effective Knudsen coefficient[24]

$$D_i^K = 0.89 D_i^{K0}, \qquad D_i^{K0} = \frac{2}{3} r_p \left(\frac{8RT}{\pi M_i} \right)^{1/2} \quad (317)$$

The solution for the velocity profiles is expressed in the following system of equations

$$\overline{v_{1,x}} = v_{1,x,s} - \frac{\eta_2}{\eta_t} (v_{1,x,s} - v_{2,x,s}) f(\lambda \xi)$$
$$+ \frac{-B_1 \eta_2 \eta_t + B_t \eta_1 \eta_2}{A \eta_t^2} f(\lambda \xi) - \frac{r_p^2}{4} \frac{B_t}{\eta_t} (1 - \xi^2) \quad (318a)$$

$$\overline{v_{x,2}} = v_{2,x,s} - \frac{\eta_1}{\eta_t} (v_{2,x,s} - v_{1,x,s}) f(\lambda \xi)$$
$$+ \frac{-B_2 \eta_1 \eta_t + B_t \eta_1 \eta_2}{A \eta_t^2} f(\lambda \xi) - \frac{r_p^2}{4} \frac{B_t}{\eta_t} (1 - \xi^2) \quad (318b)$$

Here

$$\xi = r/r_p \quad (319)$$

The pore-averaged velocities are expressed as

$$\langle \overline{v_{1,x}} \rangle = v_{1,x,s} - \frac{\eta_2}{\eta_t} (v_{1,x,s} - v_{2,x,s}) h(\lambda r_p)$$
$$+ \frac{-B_1 \eta_2 \eta_t + B_t \eta_1 \eta_2}{A \eta_t^2} h(\lambda r_p) - \frac{r_p^2}{8} \frac{B_t}{\eta_t} \quad (320a)$$

$$\langle \overline{v_{2,x}} \rangle = v_{2,x,s} - \frac{\eta_1}{\eta_t} (v_{2,x,s} - v_{1,x,s}) h(\lambda r_p)$$
$$+ \frac{-B_2 \eta_1 \eta_t + B_t \eta_1 \eta_2}{A \eta_t^2} h(\lambda r_p) - \frac{r_p^2}{8} \frac{B_t}{\eta_t} \quad (320b)$$

The slip velocities are given by

$$v_{1,x,s} = -\frac{1}{F} (K_{11} B_1 + K_{12} B_2) \quad (321a)$$

$$v_{2,x,s} = -\frac{1}{F} (K_{21} B_1 + K_{22} B_2) \quad (321b)$$

with

$$K_{11} = \frac{D_1^K}{p_1} \left[\frac{\eta_1}{\eta_t} h + (1 - h) \right] + \frac{D_1^K D_2^K (1 - h)}{p \mathcal{D}_{12}} \quad (322a)$$

$$K_{12} = \frac{D_1^K}{p_1} h + \frac{D_1^K D_2^K (1 - h)}{p \mathcal{D}_{12}} \quad (322b)$$

$$K_{21} = \frac{D_2^K}{p_2} h + \frac{D_1^K D_2^K (1 - h)}{p \mathcal{D}_{12}} \quad (322c)$$

$$K_{22} = \frac{D_2^K}{p_2} \left[\frac{\eta_2}{\eta_t} h + (1 - h) \right] + \frac{D_1^K D_2^K (1 - h)}{p \mathcal{D}_{12}} \quad (322d)$$

$$F = 1 + (1 - h) \frac{x_2 D_1^K + x_1 D_2^K}{\mathcal{D}_{12}} \quad (322e)$$

$$A = p \frac{x_1 x_2}{\mathcal{D}_{12}} \quad (323)$$
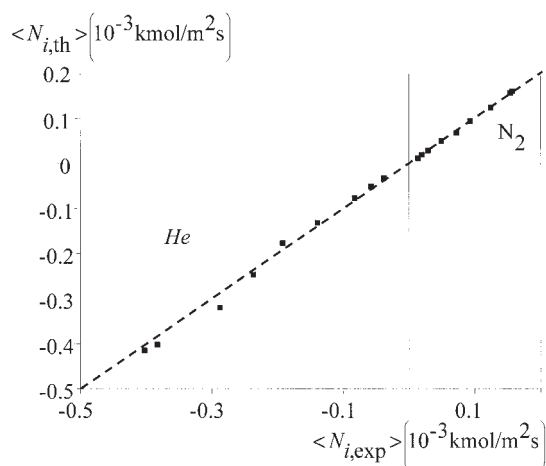
In the above we have

Figure 8. Fluxes of He and Ar in counterdiffusion experiment of Remick and Geankoplis.[38]

Comparison between results from velocity profile model (VPM-1) and experimental values.

$$f(\lambda\xi) = 1 - \frac{I_0(\lambda r_p\xi)}{I_0(\lambda r_p)} \qquad (324)$$

$$h = 1 - \frac{2}{\lambda r_p}\frac{I_1(\lambda r_p)}{I_0(\lambda r_p)} \qquad (325)$$

$$\lambda r_p = \sqrt{\frac{3}{\varphi}} \qquad (326)$$

$$\varphi = \frac{\mathscr{D}_{12}}{px_1x_2}\frac{\eta_1\eta_2}{\eta_t B_0} \qquad (327)$$

For the isobaric counterdiffusion $B_t = dp/dx = 0$, and so

$$\langle\overline{\nu_{1,x}}\rangle = \nu_{1,x,s} - \frac{\eta_2}{\eta_t}(\nu_{1,x,s} - \nu_{2,x,s})h(\lambda r_p) - \frac{B_1\eta_1\eta_2}{A\eta_t^2}h(\lambda r_p) \qquad (328a)$$

$$\langle\overline{\nu_{2,x}}\rangle = \nu_{2,x,s} - \frac{\eta_1}{\eta_2}(\nu_{2,x,s} - \nu_{1,x,s})h(\lambda r_p) - \frac{B_2\eta_1\eta_2}{A\eta_t^2}h(\lambda r_p) \qquad (328b)$$

For the steady state the averaged fluxes are constant

$$\langle N_{i,x}\rangle = \langle\overline{\nu_{i,x}}\rangle\frac{p_i}{RT} = \text{constant} \neq f(x) \qquad (329)$$

Formally, we can write

$$(\langle N_{i,x}\rangle) = [E]\left(\frac{dp_i}{dx}\right) \qquad (330)$$

and the complementary equation

$$\left(\frac{dp_i}{dx}\right) = [E]^{-1}(\langle N_{i,x}\rangle) \qquad (331)$$

In the case of an infinite medium, with only diffusive friction, the velocity of component i is given by

$$\nu_{1,MS,\infty} = -\frac{\mathscr{D}_{12}}{p_1x_1x_2}\frac{dp_1}{dx} \qquad (332)$$

We solved Eq. 331 iteratively according to the methods described earlier.[24] In Figure 8 the fluxes are plotted, comparing the simulated and the experimental values, where very good agreement is observed. In Figure 9 the velocity profiles of the two components are shown for the Remick and Geankoplis experiments, at a mole fraction $x = 0.5$, for different values of the total pressure. For low pressure effectively flat velocity profiles are found, corresponding to Knudsen diffusion. For intermediate pressure the profiles are more curved, whereas at high pressure a flat core with a velocity gradient near the wall is found. The values of the core velocity approach those of the situation for diffusion in a channel of infinite dimensions.

By elimination of the total pressure gradient one can write the transport equations in the form of the binary friction model[24,25]

$$\frac{dp_1}{dx} = -g_D\frac{px_1x_2}{\mathscr{D}_{12}}(\langle\overline{\nu_{1,x}}\rangle - \langle\overline{\nu_{2,x}}\rangle) - f_{1m}\langle\overline{\nu_{1,x}}\rangle p_1 \qquad (333a)$$

$$\frac{dp_2}{dx} = -g_D\frac{px_1x_2}{\mathscr{D}_{12}}(\langle\overline{\nu_{2,x}}\rangle - \langle\overline{\nu_{1,x}}\rangle) - f_{2m}\langle\overline{\nu_{2,x}}\rangle p_2 \qquad (333b)$$

The equation resembles the Maxwell–Stefan equation, but in the diffusion term the diffusion averaging factor g_D occurs, which accounts for the fact that using the difference in averaged velocities is not equal to the average of the velocity differences.

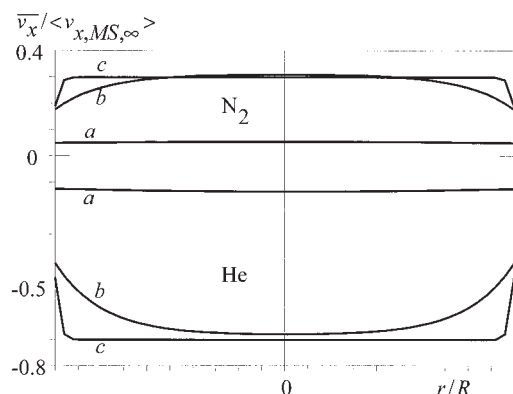For the diffusion averaging factor for gases we have

Figure 9. Calculated relative species velocity profiles for capillaries as used by Remick and Geankoplis.[38]

Reference velocity is the velocity difference for an infinite medium (Eq. 332). Parameter is the total pressure: (a) 0.15 kPa, (b) 3 kPa, (c) 40 kPa.
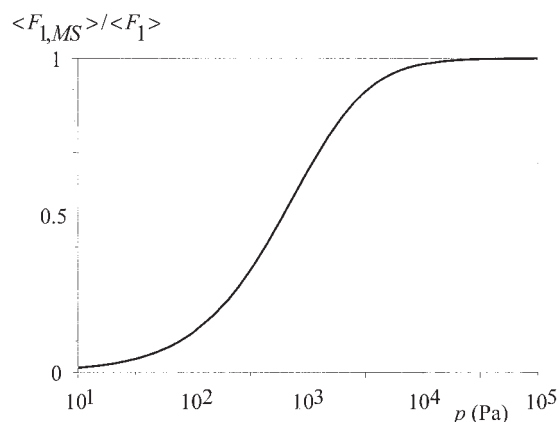
Figure 10. Ratio of cross-section–averaged interspecies friction force and partial pressure difference, for component 1 (N₂), in dependency on total pressure.

Conditions as in Figure 2.

$$g_D = \frac{[1 + (1 - h)\zeta_{12}]Q_{12}}{d_1 d_2 + (d_1 + d_2)Q_{12}} \qquad (334)$$

and for the wall-friction factors:

$$f_{1m} = \frac{x_2}{\mathcal{D}_{12}} d_2 \frac{1 + (1 - h)\zeta_{12}}{d_1 d_2 + (d_1 + d_2)Q_{12}} \qquad (335a)$$

$$f_{2m} = \frac{x_1}{\mathcal{D}_{12}} d_1 \frac{1 + (1 - h)\zeta_{12}}{d_1 d_2 + (d_1 + d_2)Q_{12}} \qquad (335b)$$

with the following symbols:

$$d_1 = h \frac{\eta_2}{\eta_t} + (1 - h) x_2 \zeta_1 \qquad (336a)$$

$$d_2 = h \frac{\eta_1}{\eta_t} + (1 - h) x_1 \zeta_2 \qquad (336b)$$

$$\zeta_i = \frac{D_i^K}{\mathcal{D}_{12}} \qquad (336c)$$

$$\zeta_{12} = \frac{D_{12}^K}{\mathcal{D}_{12}} \qquad (336d)$$

$$D_{12}^K = x_2 D_1^K + x_1 D_2^K \qquad (336e)$$

It is remarkable that the wall-friction coefficients are numerically very close to those estimated in the BFM:

$$f_{i,m} \approx \left(D_i^K + \frac{B_0}{\kappa_i} \right)^{-1} = \left(D_i^K + \frac{B_0 x_i p}{\eta_i} \right)^{-1} \qquad (337)$$

With Eq. 333 it is possible to calculate the contribution of the various cross-section–averaged force terms. In Figure 10

the interspecies, or Maxwell–Stefan, force for component 1, N₂, is presented as a fraction of the total force on 1, here its partial pressure gradient. For low absolute pressures, the interspecies force is very low, so wall friction is the dominant force. With increasing pressure the interspecies friction force gradually increases, and at high pressures this fully dominates. This means that physically "simple" diffusion is approached.

Fick's experiment reconsidered

To keep the problem within bounds, we assume that we may describe the salt as one component; otherwise, we might redo the experiment with sugar.

It is clear that no fluxes go through the walls, and we make the reasonable assumption that there is no radial transport of water (2) and salt (1). From the generalized diffusion equation we obtain for this case the VPM-1 equations[25]:

$$B_1 - \eta_1 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \overline{v_{1,x}}}{\partial r} \right) = -A(\overline{v_{1,x}} - \overline{v_{2,x}}) \qquad (338a)$$

$$B_2 - \eta_2 \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \overline{v_{2,x}}}{\partial r} \right) = A(\overline{v_{1,x}} - \overline{v_{2,x}}) \qquad (338b)$$

with the shorthand notation B_i for the driving force for i transport, and

$$A = c_t RT \frac{x_1 x_2}{\mathcal{D}_{12}} \qquad (339)$$

For the driving force we have

$$B_i = c_i \left(\frac{d\mu_i}{dx} \right)_{T,p} + c_i \bar{V}_i \frac{dp}{dx} - \rho_i g \qquad (340)$$

Addition over the two components gives

$$B_t = B_1 + B_2 = \frac{dp}{dx} - \rho g \qquad (341)$$

We start the analysis with the integrated form of the VPM-1, in the Maxwell–Stefan form:

$$B_1 = -c_t RT g_D \frac{x_1 x_2}{\mathcal{D}_{12}} (\langle \overline{v_{1,x}} \rangle - \langle \overline{v_{2,x}} \rangle) - \frac{\eta_1}{B_0} \langle \overline{v_{1,x}} \rangle \qquad (342a)$$

$$B_2 = c_t RT g_D \frac{x_1 x_2}{\mathcal{D}_{12}} (\langle \overline{v_{1,x}} \rangle - \langle \overline{v_{2,x}} \rangle) - \frac{\eta_2}{B_0} \langle \overline{v_{2,x}} \rangle \qquad (342b)$$

Addition gives

$$B_t = \frac{dp}{dx} - \rho g = -\frac{1}{B_0}(\eta_1\langle\overline{\nu_{1,x}}\rangle + \eta_2\langle\overline{\nu_{2,x}}\rangle) \qquad (343)$$

Here g_D is the diffusion averaging factor, which for liquids, without wall-slip, is equivalent to

$$g_D = \frac{1}{h} - \varphi \qquad (344)$$

and we have the modulus φ, which represents the ratio between shear and diffusive friction, given by Eq. 302. Let us first make an order-of-magnitude estimate of φ. Very roughly we take

$$\mathscr{D}_{12} \approx 10^{-9}\ \mathrm{m^2/s},\ c_t \approx 50\ \mathrm{kmol/m^3},$$

$$x_1 = 0.05,\ x_2 = 0.95,\ T = 298\ \mathrm{K},$$

$$\eta_1 \approx 5.10^{-5}\ \mathrm{Pa\cdot s},\ \eta_2 \approx 95.10^{-5}\ \mathrm{Pa\cdot s},\ r_p = 0.02\ \mathrm{m}$$

which leads to $\varphi \approx 1.6 \times 10^{-16}$, which is a very low value. This means that the shear friction is negligible compared to the diffusive friction. For this low value of φ, the value of g_D is virtually equal to 1.

There are now several ways to approach the problem. We take here the assumption that there is no molecular volume contraction, and so the net volumetric flow is equal to 0

$$\langle N_{1,x}\rangle\bar{V}_1 + \langle N_{2,x}\rangle\bar{V}_2 = 0 \qquad (30)$$

Also by definition

$$c_1\bar{V}_1 + c_2\bar{V}_2 = 1 \qquad (31)$$

With the relation

$$\mathbf{N}_i = c_i\bar{\mathbf{v}}_i \qquad (345)$$

we find

$$\langle\overline{\nu_{2,x}}\rangle = -\langle\overline{\nu_{1,x}}\rangle\frac{\phi_1}{\phi_2} \qquad (346)$$

$$\langle\overline{\nu_{1,x}}\rangle - \langle\overline{\nu_{2,x}}\rangle = \langle\overline{\nu_{1,x}}\rangle\frac{1}{\phi_2} \qquad (347)$$

and so we have

$$B_1 = -\left[c_t R_g T g_D \frac{x_1 x_2}{\mathscr{D}_{12}}\frac{1}{\phi_2} + \frac{\eta_1}{B_0}\right]\langle\overline{\nu_{1,x}}\rangle \qquad (348)$$

From density data we estimate the specific volume of salt in solution as $\hat{V}_1 = 3.56 \times 10^{-4}\ \mathrm{m^3/kg}$, $\bar{V}_1 = 2.08 \times 10^{-2}$ $\mathrm{m^3/kmol}$. At the average salt fraction $\omega_1 = 0.05$ we then find $\phi_1 \approx 0.018$. For the first term between brackets we find a value of approximately 5.9×10^{15}, for the second 0.38. The exact

values are not so important, but we see that the second term may be neglected for engineering purposes.

If we choose to neglect it, we also find that in good approximation

$$B_t \approx 0 \qquad (349)$$

$$\frac{dp}{dx} = \rho g \qquad (350)$$

This means that we can write

$$B_i = c_i\left(\frac{d\mu_i}{dx}\right)_{T,p} + (\phi_i - \omega_i)\rho g \qquad (351)$$

We introduce the thermodynamic factor as in Eq. 42:

$$\Gamma_1 = \frac{\partial \ln a_1}{\partial \ln x_1} \qquad (352)$$

and can write

$$B_1 = c_t RT\Gamma_1\frac{dx_1}{dx} + (\phi_1 - \omega_1)\rho g \qquad (353)$$

Substitution in Eq. 342, and some rearrangement, gives

$$\langle N_{1,x}\rangle = \langle N_{t,x}\rangle x_1 - \mathscr{D}_{12}\left[c_t\Gamma_1\frac{dx_1}{dx} + \frac{1}{RT}(\phi_1 - \omega_1)\rho g\right] \qquad (354)$$

The average density of the solution is approximately 1033 $\mathrm{kg/m^3}$. For the second term between brackets we then find

$$\frac{1}{RT}(\phi_1 - \omega_1)\rho g \approx -1.3\cdot 10^{-4}\ \mathrm{N/m^3}.$$

For the first term we have

$$c_t\Gamma_1\frac{dx_1}{dx} \approx 1780\Gamma_1\ \mathrm{N/m^3}$$

For an ideal solution $\Gamma_1 = 1$, and so even in large ranges of nonideality we see that the gravity term is negligible.

This means that we may simplify Eq. 354 to

$$\langle N_{1,x}\rangle = \langle N_{t,x}\rangle x_1 - \mathscr{D}_{12}c_t\Gamma_1\frac{dx_1}{dx} = \langle N_{t,x}\rangle x_1 - \mathscr{D}_{12}c_t\frac{dx_1}{dx} \qquad (355)$$

As derived in Eq. 32 this leads to Fick's first law:

$$\langle N_{1,x}\rangle = -\mathscr{D}_{12}\frac{dc_1}{dx} \qquad (29)$$

For the average velocity of component 1 (salt), assuming negligible wall friction, we neglect the second term in Eq. 348,
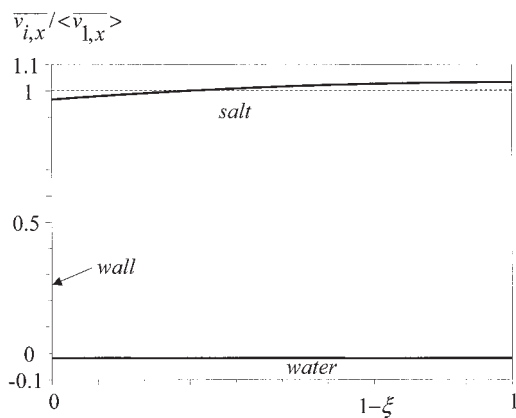
Figure 11. Calculated velocity profiles of salt and water for Fick's diffusion experiment in vertical cylinder, with relative radius ξ considered over whole cylinder radius.

and because of the small value of φ, the value of $g_D \approx 1$. This leads to

$$\langle \overline{\nu_{1,x}} \rangle_{MS} = - \frac{\mathcal{D}_{12}\phi_2}{c_t RT x_1 x_2} B_1 \quad (356)$$

It might be interesting, at least for educational purposes, to observe more precisely the velocity profiles of both components. Should we neglect wall friction, then the velocity profiles are flat, with that for salt equal to the average velocity given by Eq. 356, and that for water follows from Eq. 346.

Taking into account the full momentum balance, and the no-slip condition at the wall, we have[25]

$$\overline{\nu_{1,x}} = -B_1 \frac{B_0}{\eta_1} \varphi f(\lambda \xi) + B_t \frac{B_0}{\eta_t} [\varphi f(\lambda \xi) - 2(1 - \xi^2)] \quad (357a)$$

$$\overline{\nu_{2,x}} = -B_2 \frac{B_0}{\eta_2} \varphi f(\lambda \xi) + B_t \frac{B_0}{\eta_t} [\varphi f(\lambda \xi) - 2(1 - \xi^2)] \quad (357b)$$

We find the total driving force from Eqs. 343 and 346

$$B_t = \frac{dp}{dx} - \rho g = - \frac{\langle \overline{\nu_{1,x}} \rangle}{B_0} \left(\eta_1 - \eta_2 \frac{\phi_1}{\phi_2} \right)$$

$$= - \frac{\langle \overline{\nu_{1,x}} \rangle}{B_0} \frac{1}{\phi_2} (\eta_1 \phi_2 - \eta_2 \phi_1) \quad (358)$$

Substitution of Eq. 348 gives

$$B_t = \frac{B_1}{\phi_2} \frac{(\eta_1 \phi_2 - \eta_2 \phi_1)}{\eta_1 \left(\frac{g_D}{\phi_2} \frac{1}{\varphi} \frac{\eta_2}{\eta_t} + 1 \right)} = q B_1 \quad (359)$$

For the velocity profile of the salt this gives

$$\overline{\nu_{1,x}} = -B_1 B_0 \left[\varphi f(\lambda \xi) \left(\frac{1}{\eta_1} - \frac{q}{\eta_t} \right) + \frac{q}{\eta_t} 2(1 - \xi^2) \right] \quad (360)$$

The averaged velocity of the salt is found to be

$$\langle \overline{\nu_{1,x}} \rangle = - \frac{B_1 B_0}{\frac{1}{\varphi} g_D \frac{\eta_1 \eta_2}{\eta_t \phi_2} + \eta_1} \quad (361)$$

With Eqs. 360 and 361 we can compare the local salt velocity with the average value

$$\frac{\overline{\nu_{1,x}}}{\langle \overline{\nu_{1,x}} \rangle} = \left[\varphi f(\lambda \xi) \left(\frac{1}{\eta_1} - \frac{q}{\eta_t} \right) + 2 \frac{q}{\eta_t} (1 - \xi^2) \right]$$
$$\times \left[\frac{1}{\varphi} g_D \frac{\eta_1 \eta_2}{\eta_t \phi_2} + \eta_1 \right] \quad (362)$$

For very small values of φ we have the following in good approximation

$$\frac{q}{\eta_t} \approx \frac{1}{\phi_2 \eta_t} \frac{(\phi_2 \eta_1 - \phi_1 \eta_2)}{\frac{\eta_1 \eta_2}{\eta_t} \frac{g_D}{\phi_2}} \varphi = \frac{(\phi_2 \eta_1 - \phi_1 \eta_2)}{\eta_1 \eta_2} \varphi \quad (363)$$

Similarly we find that for very small φ the average salt velocity is virtually equal to that without wall friction:

$$\langle \overline{\nu_{1,x}} \rangle \approx \langle \overline{\nu_{1,x}} \rangle_{MS} = - \frac{\mathcal{D}_{12}\phi_2}{c_t RT x_1 x_2} B_1 \quad (364)$$

In Figures 11 and 12 the reduced velocity profiles of salt (1) and water (2) are shown, calculated for the set of conditions used above. When looking over the whole radius of the glass vessel, as in Figure 11, the salt velocity profile looks a little bit curved, and that of water flat. If we enlarge the picture to very close to the wall, as in Figure 12, we see that a very steep velocity gradient is present, over a very short distance from the wall, and a zero velocity for both components at the wall. Over the rest of the vessel, the deviation of the salt velocity is within a few % of the
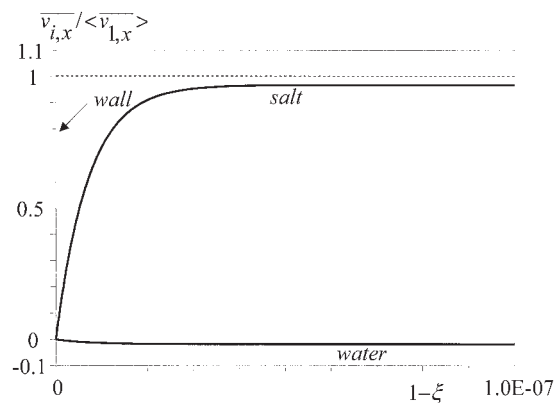

Figure 12. Calculated velocity profiles of salt and water for Fick's diffusion experiment in vertical cylinder, with relative radius ξ considered in small region near the cylinder wall.

average velocity, wich in turn is very close to that corresponding to the Fickian transport relation.

We have shown that the VPM-1, which rests on the general 3D new diffusion equation, provides a description of the salt and water velocity, which is consistent in momentum transfer and the no-slip condition. Also the detailed result shows that for the Fick experiment the usual approximation through a flat uniform velocity is very close to that when wall friction is taken into account. Thus, to obtain Fick's equation as a limit we have to make the following assumptions: no radial velocity or concentration gradients, negligible shear, and negligible influence of gravity.

Perspectives

Fundamentals

We think it of great interest to investigate the possibility of extending the approximate solution method that we presented here for dilute, monatomic gases, to polyatomic molecules and dense media. Possible other extensions could also be made in the description of polymer diffusion and for transport in plasmas.

It is of interest to analyze our equations in the framework of irreversible thermodynamics.

Mathematical solutions

For unidirectional transport such as in capillaries and pores, it would be interesting to obtain analytical solutions for the velocity profiles of multicomponent systems, analogous to those for a binary system.

More-dimensional systems

Even for highly idealized systems, such as a cylindrical pore with a catalytic or adsorbing wall, the transport of the various species is essentially at least two-dimensional. The present theory makes it possible to calculate velocity and concentration profiles for each species in both axial and radial directions. The results can be translated in averaged fluxes and concentrations, and averaged kinetics and effectiveness. It will be very interesting to compare such results with simpler one-dimensional approximations.

A major aspect of solving such equations is the formulation of the boundary conditions. For inert walls without temperature gradients we have used Maxwell-slip boundary conditions for gases, and no-slip boundary conditions for liquids. In the presence of temperature gradients along the wall, for gases the slip condition can be extended possibly by means of the second slip term derived by Maxwell.[39] Formulations for reactive or adsorbing walls will require detailed study.

In principle the equations can also be solved for 3-D systems of any geometry. This requires the development of multicomponent computational fluid dynamics (MCCFD). This will also increase precision in design and analysis in membrane technology, and in micro- and nanotechnologies, in which large gradients in velocity may be expected.

Discussion of physical processes in terms of forces

For the Remick–Geankoplis experiment, we evaluated the importance of interspecies friction and wall-friction forces.
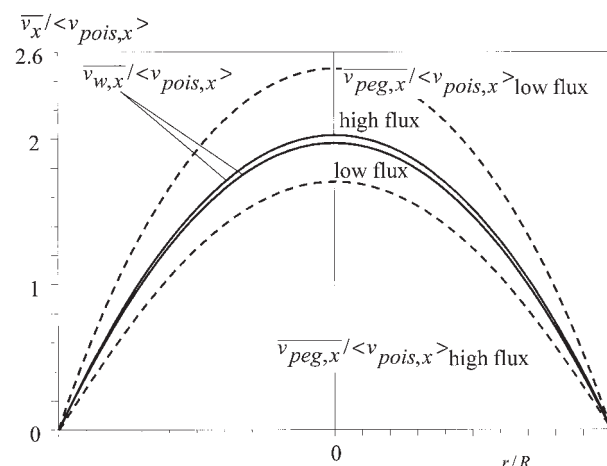
Figure 13. Relative velocity profiles for transport through a pore during liquid ultrafiltration of polyethylene glycol (PEG-3400) solutions, as calculated with the VPM-1 theory.

Physical properties as in Kerkhof[24] and Kerkhof et al.[25] Tubular membrane, circulation velocity 1.95 m/s. Low flux: 10^{-5} m/s; high flux: 5×10^{-5} m/s. Dotted lines: PEG velocity profile; drawn lines: water velocity profiles.

Earlier we gave a similar analysis for the importance of the wall-friction force in the counterdiffusion of gases through porous graphite plugs.[24] Here we present an additional example from liquid ultrafiltration. In the foregoing we have shown that the present general theory fully supports the earlier velocity profile model (VPM-1).[25] In its integrated form this in turn supports the binary friction model (BFM),[24] in which equations for the cross-section–averaged fluxes are given. In this previous work we have shown that the model developed for liquid-phase transport accurately describes the experimental data in ultrafiltration. In Figure 13 the modeled velocity profiles inside a membrane for the solute, poly(ethylene glycol) (PEG) 3400, and for the solvent, water, are presented, for low and high fluxes through the membrane. Here the situation is somewhat more complex because concentration polarization occurs in the boundary layer near the membrane, and so the inlet concentration in the pore depends on the flux. At low flux the solute moves faster than the water, at high fluxes it is slower. In Figure 14 the forces on the solute are shown, as experienced over the whole membrane pore, with increasing transmembrane pressure, corrected for osmotic pressure differences. At low pressure the PEG is held back by the slower water; at higher pressures it is dragged along. The shear force is seen to be the largest in magnitude. The difference in chemical potential stemming from the concentration gradient is larger than that attributed to the pressure gradient. The sum of the "hydrodynamic" forces is equal to that of the "thermodynamic" forces.

Such evaluations not only may help our understanding of transport processes, but also may be helpful in education.

Conclusions

We have presented in detail some examples that show that the classic formulation of molecular transport—as based on the
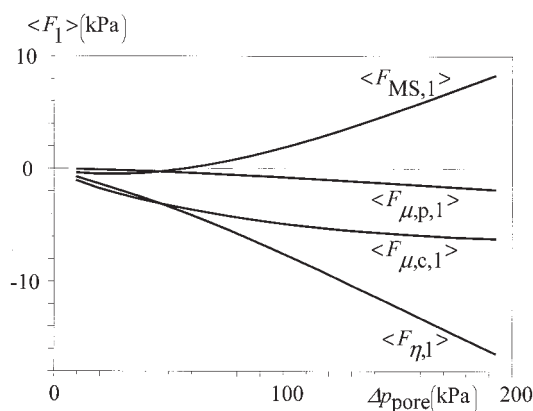
Figure 14. Calculated forces on PEG-3400 in aqueous solution upon transport through a pore in an ultrafiltration membrane, in dependency on net pressure difference across the membrane.

Forces have been integrated both over the pore cross section and pore length, and are expressed per m^2 of cross-sectional area. Δp_{pore} is the pressure drop along the pore caused by friction only, and thus the difference is between total pressure drop and osmotic pressure difference. The interspecies friction force $\langle F_{MS,1} \rangle = c_t RT \int_0^L (x_1 x_2 / \mathscr{D}_{12}) g_D (\langle v_2 \rangle - \langle v_1 \rangle) dx$ shows that at low pressures the PEG (1) moves faster than water (2), and at higher pressures, slower. The difference in chemical potential results in a force $\langle F_{\mu,[\text{infi}]c,1} \rangle = \int_0^L c_1 (\partial \mu_1 / \partial x)_{T,p} dx$, attributed to a concentration difference, and one attributed to the pressure difference, $\langle F_{\mu,[\text{infi}]p,1} \rangle = \int_0^L c_1 \bar{V}_1 (dp/dx) dx$. The shear force is given by $\langle F_{\eta,1} \rangle = -(1/B_0) \int_0^L \eta_1 \langle v_1 \rangle dx$. The total chemical potential force is balanced by the sum of the interspecies and shear forces: $\langle F_{\mu,[\text{infi}]c,1} \rangle + \langle F_{\mu,[\text{infi}]p,1} \rangle = \langle F_{MS,1} \rangle + \langle F_{\eta,1} \rangle$.

statistical-mechanics theories of Chapman–Enskog, Hirschfelder et al., Zhdanov et al., and Bearman and Kirkwood—leads to contradictions. One example is the isobaric counterdiffusion of two gases through capillaries, as studied experimentally by Remick and Geankoplis. Another example is the salt diffusion experiment of Fick in a glass cylinder. We have presented arguments that reveal that the approaches of Hirschfelder et al. and of Lightfoot, based on irreversible thermodynamics, do not provide an adequate framework for the description of the molecular transport in constrained geometries. We have examined in detail the derivations of the equations from statistical mechanics, and shown that the limitations of the final equations are caused by the assumption that the molecular transport phenomena are the result of small velocity fluctuations around the mass-averaged velocity. Mathematically this has been laid down in the choice of velocity or momentum probability distributions centered on the mass-averaged velocity, which finally has as a consequence that the shear in the momentum balance is described in terms of gradients of this velocity. In the process we have made clear that in the species momentum balance the viscous shear is present, but may be hidden in the classical equations through the substitution of the total pressure gradient. This leads to the rather complex formulations of the various forces for diffusion, as in Eq. 56. We have also analyzed in greater detail the dusty gas model of Mason and coinvestigators, and shown additional internal contradictions. It becomes clear that they started with a formulation of the momentum balance, which could not lead

to the description of counterdiffusion phenomena, and they tried to remedy this by the confusing statement about the additivity of viscous and diffusive fluxes, where mathematically they inserted extra terms in the momentum balance, and finally gave a viscous drag force the name of a Knudsen coefficient.

We have presented an alternative approximate solution of the Boltzmann equation for dilute monatomic gases, starting from nonequilibrium trial functions. The final result shows in the species momentum balance an individual species stress tensor, which describes the viscous shear by means of a partial viscosity and the gradients of the species velocity. The Maxwell–Stefan diffusion term arises naturally during the derivation, and so the cumbersome mathematics of formulating Fickian diffusion coefficients and subsequent inversion in the classic treatments are avoided. The new theory provides equations for the partial viscosities and partial thermal conductivities of mixtures, which by addition lead to the overall mixture viscosity and thermal conductivity. The numerical values for these quantities, as well as for the thermal diffusion ratio, have been compared to experimental values and classic results. The comparison shows that the new calculation schemes are in very good agreement.

We have presented generalized versions of the transport theory, for dense media and polyatomic molecules, and derived a number of practical limit theories from those. We have shown that for transport in one direction the new generalized transport equations reduce to the earlier developed velocity profile model (VPM-1), and we have demonstrated that this can successfully be applied to describe the diffusion experiments of both Remick and Geankoplis and of Fick. With our present approach we have made it possible to extend the rigorous mathematical modeling to areas where this was not possible before, such as in the transport in small pores. Also it presents a framework with which the complete calculation of transport in the Stefan tube becomes possible. In the use of the presented theory, the partial viscosities appear as important physical parameters, in addition to others known from earlier theory on transport phenomena. For dilute gases we have previously presented expressions based on the Wilke equation. It will be of interest to study experimentally and theoretically the partial viscosities in dense media and liquid mixtures, and set up equations and parameters in databank format.

In a clear way the presented theory shows the effect of various physical phenomena in the momentum balance, and has no need of the earlier very confusing artificial concepts such as diffusion velocity, viscous, segregative and nonsegregative fluxes, and the like.

We see perspectives for many applications in descriptions of reactors, catalyst and adsorbent particles, membrane transport, and transport in micro- and nanodevices.

Acknowledgments

Notation

A = see Eq. 323 [m^{-2} Pa·s

$\mathbf{A}_i$ = function, Eqs. 115 and 202

A_i = function, Eqs. 122 and 209

a = thermodynamic activity

$a_i^{(k)}$ = coefficient in Sonine polynomial development, *

B_0 = permeability of channel, Eq. 303, m^2

$\mathbf{B}_i$ = function, Eqs. 115 and 202

B_i = function, Eqs. 123 and 208

B_1 = driving force for motion of species 1, N m^{-3}

B_{i0} = constant, Eq. 53, s m^{-2}

b = impact parameter, m

$\mathbf{b}_i$ = function, Eq. 113

$b_i^{(k)}$ = coefficient in Sonine polynomial development, *

$\mathbf{C}_i$ = function, Eqs. 115 and Eq. 202

C_i = function, Eqs. 124 and Eq. 207

$C_i^{(j)}$ = function, Eq. 124

C_v = molar specific heat, J kmol^{-1} K^{-1}

c = molar concentration, kmol m^{-3}

c_1 = constant, Eq. 21, m s^{-1}

$c_i^{(k)}$ = coefficient in Sonine polynomial development, *

D = Fickian diffusion coefficient, m^2 s^{-1}

D^K = Knudsen coefficient, m^2 s^{-1}

D_i^T = thermal diffusion coefficient, kg m^{-1} s^{-1}

$\mathcal{D}_{ij}$ = Maxwell–Stefan diffusion coefficient, m^2 s^{-1}

$\mathscr{D}$ = Boltzmann operator, Eq. 73

$\mathbf{d}_i$ = driving force, Eq. 52, m^{-1}

d_1 = see Eq. 336a

$[E]$ = matrix, Eq. 330, kmol mN^{-1} s^{-1}

(e) = vector, Eq. 238, molecules m^{-2} s^{-1}

F = function, *

$\mathbf{F}_i$ = force per kmol i, N kmol^{-1}

$\hat{\mathbf{F}}_i$ = force per kg i, N kg^{-1}

$\mathbf{F}_{ji}$ = collision force of j on i, Eq. 166, N m^{-3}

f = molecular velocity distribution function, molecules m^{-6} s^3

$f(\lambda\xi)$ = function; see Eq. 324

f_{im} = wall-friction coefficient, Eq. 333, m^{-2} s

G_i = slip modulus, m

g = gravitational acceleration, m s^{-2}

g_D = diffusion averaging factor

$g_{i,S}$ = perturbation function in Shendalman[57] theory, Eq. 149

$\mathbf{g}_{ij}, g_{ij}$ = difference in molecular speed, m s^{-1}

$\mathbf{H}$ = shear force in Snell et al.,[55] Eq. 145, N

h = function; see Eq. 325

h_i = velocity distribution function in present theory, molecules m^{-6} s^3

$h_{i,S}$ = perturbation function in Shendalman[57] theory, Eq. 148, m^{-3} s^3

$\mathbf{I}$ = diagonal unit tensor

J = integral operator, Eq. 75

J = molecular flux, molecules m^{-2} s^{-1}

$\mathbf{j}, j$ = mass flux, kg m^{-2} s^{-1}

j_m = Zhdanov and Roldughin,[51] Roldughin and Zhdanov[59] diffusive slip mass flux, Eq. 150, kg m^{-2} s^{-1}

K = permeability, m^2

K_{kl} = coefficient, Eq. 322, m^4 N^{-1} s^{-1}

k = Boltzmann's constant, J K^{-1}

k_T = thermal diffusion ratio, Eq. 264

L = length, m

$[L]$ = matrix, Eq. 238, molecules^2 m^{-3} s^{-1}

$[M]$ = matrix, Eq. 279, J^{-1} m s K

M = molar mass, kg kmol^{-1}

m = molecular mass, kg molecule^{-1}

$\mathbf{N}, N$ = molar flux with respect to fixed coordinates, kmol m^{-2} s^{-1}

$[N]$ = matrix, Eq. 226, molecules^2

n = molecular density, molecules m^{-3}

n = number of components

NKn = Knudsen number, Λ/r_p

$[P]$ = matrix, Eq. 276, Pa^{-1} s^{-1}

p = pressure, Pa

$\mathbf{p}$ = momentum, kg m s^{-1}

Q^* = enthalpy, Eq. 33b, J kg^{-1}

Q_{ij} = energy transfer rate between j and i, Eq. 170, J m^{-3} s^{-1}

$\mathbf{q}$ = heat flux, J m^2 s^{-1}

q = see Eq. 359

R = gas constant, J kmol^{-1} K^{-1}

R_{ij} = Bearman–Kirkwood constant, Eq. 33a, m^3 kg^{-1} s^{-1}

R_{vi} = production rate of i, kmol m^{-3} s^{-1}

$\mathbf{r}, r$ = coordinate, radius, m

(r) = vector, Eqs. 226, 276, 279

$\mathbf{S}$ = rate of deformation tensor, s^{-1}

$\hat{S}$ = entropy per unit mass, J kg^{-1} K^{-1}

$S_p^q(x)$ = Sonine polynomial (HCB), *

T = temperature, K

T_i^* = Zhdanov[62] species temperature, Eq. 153, K

t = time, s

$\mathbf{u}, u$ = velocity, m s^{-1}

$\mathbf{u}_i$ = relative velocity, Eq. 160, m s^{-1}

$\mathbf{V}$ = relative velocity, Eq. 97, m s^{-1}

$\bar{V}$ = specific volume, m^3 kmol^{-1}

$\mathbf{v}, v$ = velocity, m s^{-1}

$\mathbf{W}, W$ = dimensionless velocity, Eq. 114

$\mathbf{w}$ = dimensionless velocity, Eq. 192

$\mathbf{X}$ = force per molecule, N molecule^{-1}

x = mole fraction

x = Cartesian coordinate, m

y = Cartesian coordinate, m

z = Cartesian coordinate, m

Mathematical notation

$\langle\rangle$ = area-averaged

$\overline{a_i}$ = quantity $\bar{a}$, averaged over velocity distribution of i, *

$[N]$ = matrix

(b) = vector

$[\mathbf{G}; \mathbf{H}]_{ij}$ = bracket integral, Appendix B, *

Greek letters

α = constant, Eq. 80, *

α_{ij} = modified thermal diffusion ratio, below Eq. 63, N m^{-2}

δ_{ij} = Kronecker delta

ε = angle, in Eq. 70

ε_{kl} = element of rate of deformation tensor, Eq. 63, s^{-1}

ϕ = perturbation function

ϕ_i = volume fraction

Γ = thermodynamic factor, Eq. 42

γ = activity coefficient

φ = bulk viscosity, Pa·s

φ = modulus, Eq. 302

$\varphi(r)$ = potential function, Eq. 284, J

η = dynamic viscosity, Pa·s

η_i = partial dynamic viscosity, Pa·s

η_t = mixture dynamic viscosity, Pa·s

κ_i = fractional viscosity coefficient, s

$\boldsymbol{\kappa}_i^0$ = force in Snell et al.,[55] Eq. 145, N

Λ = mean free path, m

$\boldsymbol{\Lambda}_i$ = driving force, Eq. 48, N kg^{-1}

λ = thermal conductivity, J m^{-1} s^{-1} K^{-1}

λ = see Eq. 326

μ = chemical potential, J kmol^{-1}

μ_{ij} = reduced mass, $[(1/m_i) + (1/m_j)]^{-1}$, kg

ν = number of components

$\boldsymbol{\pi}$ = stress tensor, Eq. 14, Pa

θ_m = maximum angle of deflection upon collision

ρ = concentration, density, kg m^{-3}

$\boldsymbol{\sigma}$ = Bearman–Kirkwood stress tensor, N m^{-3}

σ = molecular diameter, m

ξ = dimensionless coordinate

Ψ = property, above Eq. 89, *

ζ_1 = see Eq. 336

$\Omega^{(l,s)}$ = omega integral, m$_3$ s^{-1}

$\Omega^{*(l,s)}$ = dimensionless omega integral

ω = mass fraction

$\omega^{(1,0)}$ = singlet distribution function, kmol kg-3 m^{-6} s^3

* = dimension dependent on context

Subscripts

0 = averaged (velocity), Eq. 157
$1, 2$ = position
$1, 2$ = species 1 and 2, respectively
A = refers to A-term, Eq. 214
a = air, species a
B = refers to B-term, Eq. 214
b = species b
C = refers to C-term, Eq. 214
c = mass-averaged
c = classic
d = dust
$limit$ = in limit of equal velocities, Eq. 251
ln = logarithmic average
m = molecular
mix = mixture
p = pore, capillary
p = constant pressure
$pure$ = for pure component
rs = rigid sphere
ref = reference
S = Shendalman
s = slip
T = constant temperature
t = total
w = water
x, y, z = in x-, y-, and z-direction, respectively
η = dynamic viscosity
λ = thermal conductivity

Superscripts

0 = equilibrium
$[0]$ = zero-order approximation
$[1]$ = first-order approximation
as = asymptotic
D = diffusive
T = transpose

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Appendix

A. Expressions of S and $(\nabla \cdot \mathbf{v})$ in different coordinate systems

We have

$$\mathbf{S} = \frac{1}{2}\left(\nabla\mathbf{v} + (\nabla\mathbf{v})^T - \frac{2}{3}(\nabla \cdot \mathbf{v})\mathbf{I}\right) \tag{A1}$$

Cartesian Coordinates

$$(\nabla \cdot \mathbf{v}) = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{\partial v_z}{\partial z} \tag{A2}$$

$$S_{xx} = 2\frac{\partial v_x}{\partial x} - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A3}$$

$$S_{yy} = 2\frac{\partial v_y}{\partial y} - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A4}$$

$$S_{zz} = 2\frac{\partial v_z}{\partial z} - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A5}$$

$$S_{xy} = S_{yx} = \frac{\partial v_y}{\partial x} + \frac{\partial v_x}{\partial y} \tag{A6}$$

$$S_{yz} = S_{zy} = \frac{\partial v_z}{\partial y} + \frac{\partial v_y}{\partial z} \tag{A7}$$

$$S_{xz} = S_{zx} = \frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \tag{A8}$$

Cylindrical Coordinates

$$(\nabla \cdot \mathbf{v}) = \frac{1}{r}\frac{\partial}{\partial r}(rv_r) + \frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z} \tag{A9}$$

$$S_{rr} = 2\frac{\partial v_r}{\partial r} - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A10}$$

$$S_{\theta\theta} = 2\left(\frac{1}{r}\frac{\partial v_\theta}{\partial \theta} + \frac{v_r}{r}\right) - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A11}$$

$$S_{zz} = 2\frac{\partial v_z}{\partial z} - \frac{2}{3}(\nabla \cdot \mathbf{v}) \tag{A12}$$

$$S_{r\theta} = S_{\theta r} = r\frac{\partial}{\partial r}\left(\frac{v_\theta}{r}\right) + \frac{1}{r}\frac{\partial v_r}{\partial \theta} \tag{A13}$$

$$S_{\theta z} = S_{z\theta} = \frac{1}{r}\frac{\partial v_z}{\partial \theta} + \frac{\partial v_\theta}{\partial z} \tag{A14}$$

$$S_{zr} = S_{rz} = \frac{\partial v_r}{\partial z} + \frac{\partial v_z}{\partial r} \qquad (A15)$$

B. Comparison of "old" and "new" bracket integrals

We consider the bracket integral in the notation of HCB:

$$\Lambda_1 = [F; G]_{ij} = \frac{1}{n_i n_j} \int \int \int \int f_i^{[0]} f_j^{[0]}$$
$$\times F(G - G') g_{ij} b db d\varepsilon dv_i dv_j \quad (B1)$$

Let it be assumed here that F is a function of $\mathbf{W}_i$ only, and G is a function either of $\mathbf{W}_i$ or $\mathbf{W}_j$ only. F and G may be scalar, vector, or tensor functions, but are of the same order. The product FG is understood to be the appropriate scalar product (such as fg, $\mathbf{f} \cdot \mathbf{g}$, $\mathbf{F} : \mathbf{G}$). It should be noted that here the index j is also meant to cover the identical molecules of i, indicated in this text by $i1$. Here

$$\mathbf{W}_i = \mathbf{V}_i \sqrt{\frac{m_i}{2kT_i}} \qquad \mathbf{V}_i = \mathbf{v}_i - \mathbf{u}_c \qquad (B2)$$

Also we have

$$f_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_i V_i^2}{2kT_i}\right) \qquad (B3)$$

and so

$$f_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp(-W_i^2) \qquad (B4)$$

and

$$f_i^{[0]} d\mathbf{v}_i = f_i^{[0]} dv_{xi} dv_{yi} dv_{zi} = \left(\frac{2kT}{m_i}\right)^{3/2} f_i^{[0]} dW_{xi} dW_{yi} dW_{zi}$$
$$= n_i \pi^{-3/2} \exp(-W_i^2) d\mathbf{W}_i \qquad (B5)$$

With this we obtain

$$\Lambda_1 = \pi^{-3} \int \int \int \int e^{-W_i^2} e^{-W_j^2} F(G - G') d\mathbf{w}_i d\mathbf{w}_j \quad (B6)$$

Now let us look at the corresponding integral with the new distribution function:

$$M_1 = [K; L]_{ij} = \frac{1}{n_i n_j} \int \int \int \int h_i^{[0]} h_j^{[0]}$$
$$\times K(L - L') g_{ij} b db d\varepsilon dv_i dv_j \quad (B7)$$

with

$$\mathbf{w}_i = \mathbf{u}_i \sqrt{\frac{m_i}{2kT_i}} \qquad \mathbf{u}_i = \mathbf{v}_i - \mathbf{v}_{i0} \qquad (B8)$$

Here we have

$$h_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_i u_i^2}{2kT_i}\right) \qquad (B9)$$

and so

$$h_i^{[0]} = n_i \left(\frac{m_i}{2\pi kT}\right)^{3/2} \exp(-w_i^2) \qquad (B10)$$

and

$$h_i^{[0]} d\mathbf{v}_i = h_i^{[0]} dv_{xi} dv_{yi} dv_{zi} = \left(\frac{2kT}{m_i}\right)^{3/2} h_i^{[0]} dw_{xi} dw_{yi} dw_{zi}$$
$$= n_i \pi^{-3/2} \exp(-w_i^2) d\mathbf{w}_i \qquad (B11)$$

With this we obtain

$$M_1 = \pi^{-3} \int \int \int \int e^{-w_i^2} e^{-w_j^2} K(L - L') d\mathbf{w}_i d\mathbf{w}_j \quad (B12)$$

From Eqs. B6 and B12 it can be seen that for equivalent functions $F(\mathbf{W}_i)$, $G(\mathbf{W}_j)$ and $K(\mathbf{w}_i)$, $L(\mathbf{w}_j)$ the same integration result is obtained.

So, if we have bracketed expressions in terms of the "new" $\mathbf{w}_i$ and $\mathbf{w}_j$, they lead to the identical expressions in terms of Ω integrals as the corresponding ones expressed in terms of $\mathbf{W}_i$ and $\mathbf{W}_j$.

C. Parameter values and fitting constants

Table C1. Parameter Values of Monatomic Gases Used in Calculations of Physical Properties*

Gas	M	$\sigma \times 10^{-10}$ (m)	ε/k_B (K)
He	4.0026	2.576	10.22
Ne	20.183	2.789	35.70
Ar	39.948	3.418	124.00

*Lennard–Jones constants from Hirschfelder et al.,[13] Table I-A, p. 1111.

Table C2. Fitting Constants for Dimensionless $\Omega_{ij}^{*(k,l)}$ as a Function of T^* for Lennard–Jones Potential*

	Region					
Variable	1 $\Omega^{*(1,1)}$	2 $\Omega^{*(1,1)}$	1 $\Omega^{*(1,2)}$	2 $\Omega^{*(1,2)}$	1 $\Omega^{*(1,3)}$	2 $\Omega^{*(1,3)}$
a	1.340794	1.066993	1.741422	1.003297	1.545882	0.962972
b	0.326244	0.157384	0.464673	0.155509	0.486775	0.155179
c	1.546648	0.424013	−0.919037	0.242573	−1.030862	0.166330
d	2.768179	0.698873	0.539680	0.861931	0.782950	1.069524
	$\Omega^{*(2,2)}$	$\Omega^{*(2,2)}$	$\Omega^{*(2,3)}$	$\Omega^{*(2,3)}$	$\Omega^{*(2,4)}$	$\Omega^{*(2,4)}$
a	26.425725	1.151508	3.330643	1.108727	1.952370	1.075110
b	0.045563	0.145812	0.289203	0.145671	0.438902	0.145389
c	−25.232304	0.437374	−2.260093	0.335694	−1.106327	0.251811
d	0.016075	0.670219	0.155237	0.845834	0.472274	0.981188
	$\Omega^{*(2,5)}$	$\Omega^{*(2,5)}$	$\Omega^{*(2,6)}$	$\Omega^{*(2,6)}$	$\Omega^{*(4,4)}$	$\Omega^{*(4,4)}$
a	1.130542	1.047606	1.088304	1.025857	1.268624	1.105170
b	0.218753	0.145060	0.207307	0.145043	0.252000	0.140801
c	2.298589	0.153173	2.369669	0.134687	2.028933	0.324439
d	4.064280	1.000631	4.642174	1.162116	2.945438	0.842279

*Fitting equation: $\Omega^* = a(T^*)^{-b} + c\exp(-dT^*)$. Fitting was performed on data on Hirschfelder et al.,[13] Table I-M, pp. 1126–1127. Region 1: $0.3 \leq T^* < 2.5$; region 2: $2.5 \leq T^* \leq 400$.